Treatment of Airborne Radioactive Wastes

Proceedings of a Symposium
New York, 26–30 August 1968
TREATMENT OF AIRBORNE RADIOACTIVE WASTES
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The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world".

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TREATMENT OF AIRBORNE RADIOACTIVE WASTES

PROCEEDINGS OF A SYMPOSIUM ON OPERATING AND DEVELOPMENTAL EXPERIENCE IN THE TREATMENT OF AIRBORNE RADIOACTIVE WASTES HELD BY THE INTERNATIONAL ATOMIC ENERGY AGENCY IN NEW YORK, 26-30 AUGUST 1968
TREATMENT OF AIRBORNE RADIOACTIVE WASTES
(Proceedings Series)

ABSTRACT Proceedings of a Symposium convened by the IAEA in cooperation with the USAEC and Harvard University and held in New York 26-30 August 1968. The meeting was attended by 150 participants and 80 observers from 17 countries and five international organizations.

Contents
Monitoring air contaminants (3 papers)
Characteristics of air contaminants from nuclear reactors (8 papers)
Filtration design, development cost (7 papers)
Testing high efficiency filters (4 papers)
Removal of noble gases (3 papers)
Special problems related to heat and moisture (6 papers)
Developments in the removal of iodine and its compounds (4 papers)
Recent developments in spray technology (5 papers)
Airborne wastes from incineration (4 papers)
Operational experience in the treatment of airborne wastes (8 papers)
Panel discussions
Author index

Each paper is in its original language (44 English, 7 French, and 1 Spanish) and is preceded by an abstract in English with one in the original language if this is not English. Discussions are in English.

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TREATMENT OF AIRBORNE RADIOACTIVE WASTES
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Among the many industries whose gaseous emissions require treatment before release, the atomic energy industry has an unequalled record in the scope of its efforts and in its success in preventing contamination of the environment. Though the industry has grown rapidly, research and development of means for treating airborne wastes have kept pace, and internationally established standards for air quality with respect to radionuclide concentrations are normally maintained or exceeded.

Nuclear power is proving economical in many areas of the world and the rate of construction of power reactors is exceeding earlier forecasts. The liquid-metal-cooled fast-breeder reactor is entering the power program and fuel-reprocessing facilities are being constructed in parallel with these developments. Problems in the treatment of airborne wastes are increasing not only in size but also in scope. Much research is still devoted to the removal of iodine and its compounds, but the emphasis is shifting to new problems such as treatment for removal of the noble gases and investigations on the generation of aerosols in fast-breeder reactor accidents.

The Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes was convened by the Agency, in co-operation with the United States Atomic Energy Commission and Harvard University, at the United Nations Headquarters in New York. Approximately 150 participants and 80 observers from 17 Member States and five international organizations attended. After a representative of WHO had delivered a special address on world health considerations in the control of airborne radioactive wastes, 52 papers dealing mainly with current research were presented by scientists from 13 of the Member States. In addition, a panel met to suggest methods of action by the Agency to meet its international responsibilities in this matter.

The volume of proceedings includes the full texts of all the papers together with the discussions, and an edited summary of the panel meeting.

It is hoped that the book will be a valuable contribution to the international library of information on airborne radioactive wastes and will indicate the most profitable lines for future work.
EDITORIAL NOTE

The papers and discussions incorporated in the proceedings published by the International Atomic Energy Agency are edited by the Agency's editorial staff to the extent considered necessary for the reader's assistance. The views expressed and the general style adopted remain, however, the responsibility of the named authors or participants.

For the sake of speed of publication the present Proceedings have been printed by composition typing and photo-offset lithography. Within the limitations imposed by this method, every effort has been made to maintain a high editorial standard; in particular, the units and symbols employed are to the fullest practicable extent those standardized or recommended by the competent international scientific bodies.

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OPENING ADDRESS

WORLD HEALTH CONSIDERATIONS IN AIRBORNE POLLUTION WITH SPECIAL REFERENCE TO RADIOACTIVE WASTES

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REPRESENTATIVE OF THE WORLD HEALTH ORGANIZATION

The World Health Organization is concerned with the promotion of health and human well-being throughout the world. For this reason, it is as closely concerned with the problem of pollution as it is with other better defined problems such as malaria, plague, influenza, cancer, mental illness, and all other killing and debilitating diseases of man.

At this meeting we are concerned specifically with the cleaning of airborne radioactive waste and the operation and developmental experience acquired from the management of these wastes in the past. We can view the present and future with reasonable confidence, and this is justifiable since the experience of the past 20 years has been reassuring. Despite many residual uncertainties we probably know a great deal more of the risks of radiation exposure than we do of almost any other actual or potential atmospheric contaminants. The World Health Organization is also concerned with this problem, but I wish to emphasize that the question of radioactive waste is only part, and maybe a very small part, of the problem of pollution as a whole. Indeed, it is probably unwise, except in very exceptional circumstances, to treat and view radioactive waste, either airborne or waterborne, as a single series of contaminants posing a single problem in their own right.

Let us turn now to pollution in general, which is the major and real problem. I would suggest at the outset that it will be useful for you now, and in the future, to view your own work as part of a much larger whole; and it may well be as a part which should not be dealt with alone, as in the past. In the past, there has been a practice and tendency to regard each major type of pollution (radioactive, chemical, dust, etc.) as presenting a definable and soluble problem in its own right and in isolation. This view still persists, and a good example is that of some present proposals which are being implemented for new coal-fired power stations. In these brand new plants, the gaseous discharge, after being cleaned to remove gross chemical contamination and the larger particulate matter, is being discharged via high-stack velocity. The phrase of 'punching-up' the discharge through the lower levels of the atmosphere is used, this ensures widespread dissemination over an area of many miles from the point of discharge, depending of course on atmospheric conditions. The high-velocity discharge rate is achieved by high thermal efficiency so that an appreciable thermal contribution is also present in the discharge.

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This approach to the gaseous discharge problem, from the power plant operator's and designer's viewpoint, is apparently a satisfactory solution to their problem and, by ground monitoring, it will be virtually impossible to attribute any contamination to any specific plant operation. However, as is obvious, all that is being achieved is a wider dissemination and ultimate deposition of a particulate discharge. This may well be acceptable for totally remote plants away from urban conurbations where dilution is acceptable, but these are not the normal conditions of discharge for these plants. It is difficult to view with equanimity a philosophy and practice which discharges annually, from one plant into an already unclean environment, 5 - 10 000 tons of particulate matter and many more tens of thousands of tons of sulphurous oxides as SO_2 and SO_3. This 'normal' discharge is made into an atmosphere already polluted by other similar and different pollutants.

Air pollution arises from an almost infinite variety of sources and there is little point in removing, for example, sulphur compounds from your own discharge, if the remaining particulate discharge is immediately combined with someone else's sulphur discharge. This is particularly true if the two combined are then capable of a synergistic effect in the production of respiratory illness.

This example is illustrative - or can be used to illustrate - the fact that it is no longer a valid assumption for pollution to be treated as being composed of a number of separate and separable entities. It is essential when attempting to relate total pollution to the total effect on health, to define the total problem and then to compartmentalize if and only if necessary. It is too, I believe, long overdue for some unifying set of recommendations based on dose effect data to be promulgated by an internationally acceptable body. This latter view is a personal one and though WHO may be a suitable body, it is not necessarily the most appropriate, as has been shown by the International Commission on Radiological Protection, which is quite definitely not a child of WHO.

The environment of man can be and has already been changed in many ways - by man. These changes, in the vast majority of cases, have occurred as unforeseen, but not necessarily unforeseeable by-products of man's industry. Of course, not all the environmental changes produced have been a result of direct pollution in the sense that we now know it and certainly not of airborne pollution alone. However, I would emphasize that airborne pollution or airborne pollutants do not always remain airborne and, in fact, we know that airborne chemicals can and do produce some of the most dramatic 'blasted heath' and 'mountain of the moon' effects as is seen in many old mineral mining areas.

Man's potential for increasing the rate of environmental change is now widespread and much greater than at any time in the past. It is, therefore, the main responsibility of all concerned with pollution and all aspects of pollution control to seek methods of:

(a) Minimizing discharges
(b) Understanding the effects of such discharges and components of discharges as occur, both in the short- and long-term
(c) Relating the inter-relating effects of discharges from different sources.

While the World Health Organization is concerned with human health and well-being, pollution and pollution control is concerned with much
more than man alone. This concern must be with the biosphere as a whole, recognizing that the biosphere is composed of a very large number of interdependent biological systems set in a planetary environment. Not every biological system is totally dependent on every other system, but every biological system is dependent on some biological systems.

The extinction of animal species by man alone has already been demonstrated. Only some men and some other species have so far been affected by this destruction (the virtual extinction of the North American buffalo and the ensuing changes for the indigenous Indian peoples is only one but probably adequate example). However, each such extinction or major adjustment necessitates major adjustments in biological systems closely related to the ones primarily affected, with a ripple or chain effect on all more distantly-related systems.

The world is increasingly short of food, mainly as a result of increasing populations, and it could be that an inadvertent reduction in world food supplies, resulting from vegetation or insect damage - as from pesticides, might have a much greater effect on man than the action of a number of agents acting directly on man himself.

Since its inception, the record of the nuclear power and atomic energy industry as a whole, has been quite remarkably good. Indeed, any comparison of the safety record of the industry with the safety record of almost any other established industry, is invariably favourable to atomic energy. There are a number of reasons for this satisfactory state of affairs - which I will not explore here. The main reasons, however, are undoubtedly (a) the early recognition, before the establishment of the industry, of the main potential hazards involved, and (b) safety planning and implementation based on the hazard recognition, (a) above.

Our present basic exposure guidelines, which are virtually uniformly internationally accepted, are derived from the Recommendations of the International Commission on Radiological Protection. These recommendations are based primarily on available human and extrapolated animal dose-effect/data and incorporate a safety factor. The use of this type of data and a conservative approach to airborne contamination levels has permitted the industry to reach its present state of comparative security in the field of safety.

Thus, the nature and possible sequelae of radiation exposure are now reasonably well understood, and in certain areas, we are able with some confidence, to relate dose and effect in quantitative terms. There still remain, however, uncertainties and large areas of ignorance. Probably the greatest area of ignorance is in our ignorance of the basic mechanism(s) involved by which ionizing radiation produces mutagenic and cancerogenic effects. This ignorance exists despite intensive past and present radio-biological effort, and though a great deal has been learned, the basic mechanisms remain a subject for speculation of hypothesis.

It is known that the mechanisms of action of radiation are very similar to, if not identical with, a number of other agents, many of which may occur as airborne pollutants. In other words, it is by no means impossible and is in fact probable that the conditions produced by ionizing radiation, and by a variety of other physical and chemical agents, can be and frequently are common.

Good examples of multi-causal end-effects produced, or which may be initiated by different initiating agents, are leukaemia and lung cancer.
Lung cancer, as you all know, has been causatively associated with a number of factors which include mining (particularly uranium mining), cigarette smoking and residence in polluted urban conurbations with the highest incidence in such areas being to the windward side of the conurbation; the incidence being affected also by such factors as dust and hydrocarbon content in the atmosphere, as well as by previous exposure to causal and precipitating agents such as smoking and chronic respiratory diseases which may or may not arise from the same atmospheric causes.

As representatives of the atomic energy industry, you are all to be congratulated on having contributed in the past and in contributing now to the safety of your industry and I am very much looking forward to the forthcoming papers.

However, if I may end on a cautionary note. Your own record is good and other industries' present performances and past records are so relatively poor and this may consciously, or unconsciously, colour the view of the atomic energy industry. I respectfully suggest that if this view does exist it is a source of potential danger and can only hamper the proper approach to the hazard of pollution as a community and global problem. It is no longer good enough to consider one's own problem alone, whether arising from an industry, plant or laboratory installation. All potential and actual pollution must be viewed as a contribution to the whole ecological environmental picture. The potential and actual effect of pollution must be assessed as a whole and in terms of all agents which are acting on all or any polluted systems which may be involved directly or indirectly.

I have just suggested that there is a possibility that the good record of the atomic energy industry may mislead and I believe this to be possible. I think, however, it is much more likely that you will, in fact, make a disproportionate contribution to the pollution problem as a whole. The very fact that you come from, and operate in, an industry which has recognized that serious hazards exist, and which has planned to contain or limit these hazards, means that you operate from a position of strength.

Your future contributions must be in the area of combined action with others in the pollution field. This will lead to systematic planning and operation in such areas as cleaning, quantitative monitoring and ecological evaluation.

From an international viewpoint, pollution is now an urgent problem. Its own priority must be assessed and it should then be treated in an analogous way to radiation hazard management. The problem as a whole must be defined in quantitative terms of cause and effect and an attempt must then be made to balance potential (or actual) good against potential (or actual) damage. This assessment may be made in a number of ways, the simplest is probably entirely economic and the most desirable—and most difficult—is in terms of human happiness and suffering.

Finally, let me repeat—not every biological system is totally dependent on every other system, but every biological system is dependent on some biological systems.
MONITORING AIR CONTAMINANTS
(Session I)
Chairman: P. J BARRY
AN AUTOMATIC MONITOR FOR ALL FORMS OF AIRBORNE RADIOIODINE

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Abstract

AN AUTOMATIC MONITOR FOR ALL FORMS OF AIRBORNE RADIOIODINE. One of the main problems encountered in monitoring air near a reactor for radioiodine is that an appreciable, though variable, proportion of the activity is associated with organic forms of iodine such as methyl iodide. Charcoal-loaded filter papers, such as Whatman ACG/B, do not retain this form of iodine for any appreciable time, although their efficiency for iodine in the elemental form is very high; and therefore in the past they have not been considered suitable for many applications in health physics. We have discovered, however, that the addition of a few parts per million of elemental bromine to the incoming air stream overcomes this difficulty and enables the paper to extract both elemental iodine and methyl iodide from air with high efficiency. This has been established directly by laboratory experiments and indirectly on a prototype of the instrument under working conditions.

In our instrument ACG/B paper is used in the form of a roll so that the area of filter in use can be changed automatically at suitable intervals. The activity on the area in use is monitored continuously by a single-channel scintillometer, giving an output which is proportional to the cumulative exposure to radioiodine since the last change of paper. The output is displayed on a recorder with a linear scale which is switched automatically over six ranges. This is used in preference to a single logarithmic scale because the concentration of radioiodine in the air can more easily be estimated from the rate of increase of the count rate on a linear scale.

The detection limit depends on the background level, and to achieve the best performance as much shielding should be used as is practicable in a semi-portable instrument. Performance can also be improved by using some form of background subtraction. A background signal can be obtained by adding a second channel to the scintillometer, but the energy of this correction channel has to be chosen carefully to avoid misleading results.

INTRODUCTION

Monitoring for radioiodines, particularly for $^{131}$I, presents several special problems. The element is concentrated by the human body in the thyroid gland, and because of this the maximum permissible concentration in breathing air is very low - $9 \times 10^{-9}$ μCi/ml for a 40-hour week [1]. As a result special apparatus is required to distinguish $^{131}$I activity from other airborne radioactive materials.

Although the isotope is continuously produced in reactors by nuclear fission, it is not released in measurable quantities except accidentally. Therefore if air is monitored continuously for $^{131}$I most of the results will be blank, which represents a considerable waste of time, whereas if monitoring is only begun when the presence of iodine is suspected some releases may be missed completely and the first part of all releases will not be monitored.
A third problem is that most observers report that an appreciable, though highly variable, proportion of radioiodine is released in a chemically less reactive form, probably methyl iodide and higher alkyl iodides [2,3]. Methyl iodide is absorbed by the human lung almost as readily as is molecular iodine [4], but is poorly absorbed by many types of filter [5,6]. A comprehensive review of this problem containing many additional references has recently been published by Mishima [7], and I believe it will also be discussed in later sessions of this conference.

DETECTION OF RADIOIODINE

Having outlined the problems I shall now show how they are dealt with in our instrument. Firstly, there is the question of detecting a small amount of $^{131}$I in the presence of other, probably much higher, activities. The basic method here, which is used almost universally in some form or other, is to filter the air sample through an activated charcoal trap. In this way sufficient activity can be collected for counting without retention of other airborne isotopes such as the noble gases. In our instrument the filter material is Whatman type ACG/B charcoal-loaded glass-fibre filter paper, in roll form. Figure 1 shows how the portion being used is held between a cup-shaped clamp and a fixed base. The top clamp is connected to the air to be sampled, which is drawn through the paper by a pump connected to the base portion. The top of the base is grooved to improve the distribution of the air flow over the area of filter under the clamp. The presence of $^{131}$I is detected by the usual combination of an activated sodium iodide crystal and photomultiplier. The crystal fits inside the clamp support to be as close to the filter as possible, and the only material between it and the filter is polythene, which should give little absorption of $\gamma$-rays.

![Diagram showing the arrangement of the filter paper, clamp and radiation detector inside the iodine-in-air monitor.](image-url)
Shielding against background radiation is provided by ~4 cm of lead around the detector; the amount is limited by the weight that can be managed in a transportable equipment.

Energy discrimination is used in the electronics, but in high background areas additional discrimination against the background may be needed. This can be achieved, in the case of $^{131}$I at least, by using background subtraction. The main line in the $\gamma$-spectrum of $^{131}$I is at 364 keV, and it produces practically no $\gamma$-rays with energies above 700 keV. At these lower energies the shielding given by the lead is quite adequate, so that the observed background must be produced indirectly by high-energy $\gamma$-rays which are incompletely absorbed by the scintillator. A correction signal for background subtraction can be obtained by using a single discriminator set at some energy above 700 keV such that the number of pulses triggering it is equal to the number of pulses falling in the normal signal channel. This correction is only approximate, since it depends on the $\gamma$-spectrum of the background radiation, but I find that if the circuit is adjusted as described above using $^{60}$Co as a source of background radiation, there is very little difference in the effectiveness of the background subtraction when the external radiation is from $^{226}$Ra plus daughters, which has a completely different $\gamma$-spectrum. This suggests that once the adjustment is made it should be adequate for most likely sources of background radiation.

If large amounts of short-lived fission-product radioiodines are present, such as $^{133}$I and $^{136}$I, erroneous results may be obtained and the subtraction circuit should be switched off. However the most prominent line in the $\gamma$-spectrum of both $^{133}$I and $^{136}$I is at about 530 keV, which lies between the $^{131}$I signal channel and the background correction channel, so that moderate amounts of these two isotopes will be ignored by the instrument.

**AUTOMATION OF MONITORING**

The dilemma posed by the low frequency of measurable iodine releases can be avoided by designing the instrument to run automatically and keep a continuous record of all iodine releases, while requiring only occasional attention from an operator.

One operation which needs to be automated is the changing of the filter paper, which will be described with reference to Figure 2. This shows a general view of the apparatus on a bench. The roll of unused filter-paper is on the left of the lead castle while the take-up spool is inside the plastic box on the right. The portion of paper being used is inside the castle, as shown in Figure 1. The air inlet is behind the castle; the outlet, in front, goes through a flow-meter to a carbon-vane pump which has a maximum capacity of about 20 litres/min. The paper is moved on at fixed intervals, 8 hours in this case for reasons given
FIG 2. Photograph of the iodine-in-air monitor, bench set-up.

later, but a change can also be initiated manually by the operator, or automatically if full scale is exceeded on the highest range. The pump is switched off and the solenoid on top of the castle is activated, releasing the paper. A motor attached to the take-up spool then draws fresh paper into the castle for a distance determined by the circumference of the two rubber rollers on the left, which drive a cam operating a micro-switch. The spike on the right of the castle is also operated by the solenoid; it punches a small hole in the paper at a known distance from the clamp, so that the paper which has filtered the air can be located, cut out, and recounted if necessary.

The solenoid, motor and pump are each controlled by a triac triggered from a gated blocking-oscillator. In this way they can be switched on and off by low-level signals from the control circuit. If the instrument runs out of filter paper, or the operation is not completed for some other reason, a time delay in the control circuit operates to switch off the motor and solenoid, and flash a warning lamp. The control unit, which also contains the main amplifier, discriminators and count-rate circuit, is mounted with a pen recorder on a separate chassis, so that the mechanical part of the instrument, shown in Figure 2, can be placed as close to the sampling point as is practical, to minimize pipe lengths, without inconveniencing the operator.
The limited range of a pen recorder is a problem in an automatic instrument, but this can be overcome by providing for automatic range changing. Our instrument has a recorder with a 0-1 linear scale and 6 ranges from one to 100,000 counts/second full scale. Switching between the first two ranges is accomplished by changing the gain of the count-rate circuit; switching between higher ranges is accomplished by prescaling the input to the circuit. The switching is controlled by semiconductor logic circuits, the range being determined by the state of a 6-stage shift-register counter. The circuit switches up one range by advancing the counter one stage whenever full scale deflection of the output is reached, while it resets to the most sensitive range every time the filter paper is changed. Two event pens on the recorder are used to indicate the range. The first three ranges are indicated by the numbers 1 to 3 in binary code, binary "1" being represented for both pens by an outward deflection. For the other three ranges the coding is repeated using pulsed deflection of the pens, which gives a comb-like trace, for binary "1".

These features are illustrated in Figure 3, which shows part of the record of the release of $^{131}$I from a defective fuel rod, as monitored on the exhaust duct of a "hot cell". The time scale goes from right to left and the heavy vertical lines mark the hours. At the start of the record range 3 (binary 11, 100 counts/second full scale) was being used, then at 0045 hours on the time scale a regular automatic paper change occurred, which reset the instrument to range 1 (binary 01, 1 count/second full scale). After about ten minutes, full scale was exceeded on this range and an automatic switch to range 2 (binary 10, 10 counts/second full scale) occurred. One hour later full scale was reached again and the circuit switched up to range 3, the condition it was in at the beginning of this record.

**THE METHYL IODIDE PROBLEM**

This problem is disturbing because the proportion of methyl iodide in contaminated air is so variable. However, it seldom contributes more than 30% of the iodine, so the simplest solution to the problem is to admit that methyl iodide is not measured and to apply a safety factor of 50% to the recorded activity in estimating the hazard. Such a procedure might be satisfactory in some applications, but it is obviously better to include methyl iodide in the measurement if possible, and avoid arbitrary correction factors. This can be accomplished by chemically impregnating the paper to increase its efficiency, as has been done with charcoal filter beds for air cleaning [8].

I have found that elemental bromine is highly effective for this purpose, since it raises the efficiency of the ACG/B paper for methyl iodide from practically zero to better than 99% with freshly impregnated paper. Impregnation can be achieved by
FIG. 3. Record of the release of $^{31}$I from a defective fuel rod. For explanation of scales used, see text.
adding bromine vapour to the incoming air stream using the method shown in Figure 4. The venturi in the main air stream produces a small pressure drop which tends to direct part of the airflow through a flask containing liquid bromine. Normally this flow is blocked by an electrically controlled valve, but to impregnate the paper the valve is opened, allowing bromine-saturated air to enter the main air stream at a rate determined by the setting of a needle valve in series with the control valve. The long tube on the inlet to the bromine flask limits the escape of bromine caused by thermal expansion of the air in the flask or by diffusion. Any bromine that does escape is trapped in a tube of steel wool. About 30 mg of bromine is normally added in 10 seconds immediately after a change of filter paper. Frequent "topping-up" of the bromine on the paper is apparently necessary to maintain the highest efficiency for methyl iodide. This was provided for in the first model of the instrument by a slow leak around the control valve, but in the system shown here it is achieved by pulsing the valve open for one second in every thousand throughout the sampling period. A steel wool trap is also needed in the outlet from the castle to protect the pump from bromine, and additional protection is provided by a charcoal respirator canister. Since bromine is highly corrosive the materials that come into contact with it have to be chosen carefully, and in most places glass or Teflon is used. Fortunately these materials are also among the best for lack of retention of radioiodine [9].

I do not know for certain what the minimum effective addition of bromine would be, but an experiment on the retention of bromine by the paper, Figure 5, suggests that it is saturated with bromine with a loading of 12-14 mg. Bromine in excess of
this is quickly lost from the paper, but even passage of air overnight failed to reduce the loading below 11 mg. However, an experiment with methyl iodide labelled with $^{131}$I showed a definite falling off in the efficiency of the impregnated paper with passage of bromine-free air down to about 70% after four hours. The reason for this is uncertain, but the reimpregnation technique described above apparently avoids it.

![FIG. 5. Retention of bromine by ACG/B filter paper. Air flow 20 litre/min. Bromine added in 1 min or less. Paper analysed after 5 min by neutron activation. Horizontal scale assumes 2 mg bromine per ml of air passing through control valve. Dashed line - theoretical for 100% retention.]

**PERFORMANCE OF INSTRUMENT**

The volume of air sampled by the instrument must be sufficient to give a measurable amount of $^{131}$I, which implies a fairly long sampling period - that is a fairly long interval between changes of filter paper. This is also dictated by the need to run the instrument continuously with a minimum of attention, since one roll of filter paper only lasts for about 50 paper changes. When a long sampling period is used the output count-rate at any time is proportional to the total amount of activity collected since the last paper change, or to the time integral of the concentration in air. This method of collection can be used to advantage in health physics, since it corresponds to the process of uptake by a person breathing contaminated air. The maximum permissible concentration given earlier is the limit for continuous exposure on the basis of a 40-hour working week of five 8-hour shifts, but the exposure to a person working one hour a day in air containing 8 (MPC)$a$ will be no higher. In other words the limit of daily exposure is 8 (MPC)$a$-hours for the time integral of the concentration; variation of concentration with time is unimportant. If the sampling intervals of the instrument correspond to working
shifts this integration is carried out automatically, and a record is provided of the exposure in \((\text{MPC})_a\)-hours per shift. An alarm can be given if the exposure in one shift exceeds 8 \((\text{MPC})_a\)-hours (or some fraction of this).

Although the time integral of the concentration of radiiodine is more important than the concentration itself, the concentration can be obtained from a continuous record of the activity on the filter paper. In the simple case of a constant concentration of \(^{131}\text{I}\), the activity on the paper rises linearly with time, and the concentration can readily be found from the slope of the record, provided that a linear count-rate scale is used.

At a sampling rate of 20 litres/min, 9600 litres of air will pass through the filter in an 8-hour period. If this air contains \(^{131}\text{I}\) at 1 \((\text{MPC})_a\) \((9 \times 10^{-9} \mu \text{Ci/ml})\) then 0.0804 \(\mu \text{Ci}\) will be collected on the paper, assuming 100% filtration efficiency. The counter efficiency is about 7%, so that this will give an output of 224 counts/second on the recorder. Since smoothing time constants of up to 10 min can be used, statistical accuracy is easy to achieve and the limit of detection is determined by the background level. This will be about 2 counts/second in a 2½ mR/h gamma field, using background subtraction, or 120 counts/second without subtraction. Since a 2½ mR/h gamma field and air contaminated at a level of 1 \((\text{MPC})_a\) represent approximately equal hazards, this means that the instrument can measure potential exposures of people to \(^{131}\text{I}\) which are only a few per cent of the external \(\gamma\)-ray dose. At present whenever people are exposed to \(^{131}\text{I}\) expensive and time-consuming procedures, such as urine analysis and whole-body counting, have to be undertaken, although the results usually show that the equivalent dose received in rem was negligible in comparison with the external \(\gamma\)-ray dose.

With our instrument we should be able to predict the exposures more accurately, and only select for bioassay those cases in which the instrument shows that the \(^{131}\text{I}\) dose is likely to be of the order of 10% or more of the external \(\gamma\)-ray dose. It will also provide a record of the times of releases, which will allow more accurate calculation of exposures from bioassay data.

A prototype of the instrument was tried out as a stack monitor for about three months last summer, and several releases of \(^{131}\text{I}\) were observed (Figure 3). Engineering drawings are now being prepared, and we hope to bring the instrument into operational use in the not too distant future.

ACKNOWLEDGMENTS

Many people at Chalk River have aided in this project. Thanks are particularly due to G. Cowper, who initiated it, and to P.J. Bunge who was mainly responsible for the construction of the prototype instrument.
REFERENCES


DISCUSSION

C. PELLETIER: Does the addition of bromine affect the collection efficiency of the ACG/B filter for elemental iodine?

R. M. HOLFDOR: No.

C. PELLETIER: Our experience when using the ACG/B filter as an environmental monitor indicated that the efficiency for elemental iodine collection decreases markedly when sampling large volumes of air (about 10,000 ft³). In these cases, the filter has a diameter of 2 inches.

B. HEKKALA: What was the efficiency of the filter paper for elemental iodine before treating with bromine?

R. M. HOLFDOR: Better than 99%. I measured the efficiency by adding another filter - a tube of activated charcoal - in the pipe from the ACG/B filter to the pump. However, the amount of activity collected in this way was usually so low that it was difficult to measure accurately.

L. F. FRANZEN: Did you investigate (by bromine impregnation of the charcoal paper) the effect of relative humidity and temperature on the improved retention efficiency for methyl iodide?

R. M. HOLFDOR: No. The experiments were all carried out under normal laboratory conditions.
R. E. HOLMES: Are there any limitations on the use of your equipment for the measurement of higher concentrations of iodine than would normally be experienced in the measurement of laboratory air?

R. M. HOLFORD: The maximum count rate the instrument is designed to handle is 100,000 cps. If the concentration of iodine activity were so high that this figure would be exceeded before the end of an 8-hour sampling period, the period could be shortened. It would not be very difficult to modify the instrument to handle higher count rates.
MEASUREMENT OF ARGON-41 ACTIVITY DISCHARGED FROM THE SHIELD COOLING AIR OF MAGNOX REACTORS

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Abstract

MEASUREMENT OF ARGON-41 ACTIVITY DISCHARGED FROM THE SHIELD-COOLING AIR OF MAGNOX REACTORS. The early magnox reactors built in the United Kingdom utilized steel pressure vessels surrounded by concrete biological shields. Cooling of these shields is achieved by means of large volumes of atmospheric air. Argon in the air is activated by the $^{40}\text{Ar}(n,\gamma)^{41}\text{Ar}$ thermal neutron reaction. Low-cost portable equipment was designed to measure the specific activity of this shield-cooling air.

Calibration of the equipment was achieved by means of a 5-cm³ ampoule of argon activated in BEPO. The calibrated equipment was utilized to measure the specific activity of shield-cooling air discharged from Bradwell, Calder Hall, Hunterston, Trawsfynydd and Tokai Mura power stations.

1. INTRODUCTION

The majority of the Stage 1 nuclear power stations developed in the United Kingdom utilize steel pressure vessels to contain the reactor coolant. These vessels are surrounded by concrete biological shields which are protected from overheating by ventilation with atmospheric air. That fraction which passes between the pressure vessel and the biological shield is irradiated during its passage, producing $^{41}\text{Ar}$ from the $^{40}\text{Ar}(n,\gamma)$ reaction; $^{19}\text{O}$ from the $^{16}\text{O}(n,\gamma)$ reaction and $^{15}\text{N}$ from the $^{16}\text{O}(n,p)$ reaction. The short half lives of the latter (29.4 and 7.5 seconds respectively) result in the principal activity being due to $^{41}\text{Ar}$.

The $^{41}\text{Ar}$ production rate $P$ can be calculated to be

$$P \approx \frac{0.6023 \cdot f \cdot p \cdot \sigma}{3.7 \times 10^7 \cdot A} \cdot \int \phi dv \quad \text{mCi/sec}$$

where

- $a$ = abundance of argon 40 in natural argon (0.996)
- $f$ = fraction by weight of argon in air (0.0128)
- $p$ = density of air (gm cm$^{-3}$)
- $\sigma$ = thermal activation cross section of $^{40}\text{Ar}$ (barns) (0.64)
- $A = \text{atomic weight of } ^{40}\text{Ar}$
- $t = \text{average transit time of air through activating flux(sec)}$
- $\phi$ = thermal neutron flux (Westcott convention) (n cm$^{-2}$ sec$^{-1}$)

In practice the calculation involves computation over a series of parallel circuits which are summed.
Argon is both chemically and biologically inert and the only significant effect is whole body dose from individuals exposed to or immersed in the plume. The decay scheme for $^{41}$Ar is illustrated in Figure 1. Although the gamma dose will greatly exceed the beta dose in all practical cases of discharge from reactor buildings because of the significant attenuation of the beta radiation from the plume it is the beta emission which is primarily utilised for measurement. As a result of these estimates calculations were made of the dose rates and annual doses which were expected to result from the discharge of shield cooling systems from U.K. reactors.

![FIG. 1. Decay scheme for $^{41}$Ar.](image)

At Trawsfynydd Nuclear Power Station for example, the predicted stack discharge of $^{41}$Ar was 7.5 mCi/sec which produced theoretical annual doses of 0.43 rad/year at the Turbine Hall, 0.24 rad/year at the Administration Block, 0.39 rad/year at the Control Room and 0.31 rad/year at the Cooling Ponds. Although these doses were within the levels recommended by the International Commission on Radiological Protection they were significantly important to justify measurements to confirm the levels.

In consequence a request was put to the APC Health Physics Division to produce simple light weight equipment to measure the specific activity of the shield cooling discharge.

### 2. DESCRIPTION OF PROTOTYPE (MARK 1) EQUIPMENT

The prototype for the equipment consisted basically of a cylindrical canister of $5.97 \times 10^4$ cm$^3$ volume into which was fitted a standard G.M. tube (Fig. 2). The size of the collecting chamber was chosen to give adequate sensitivity whilst being small enough to transport by hand conveniently around the Station. Prior measurements utilising a B12 G.M. tube in an 'infinite' balloon indicated a sensitivity of 1850 cpm/pCi. Brown measured $^{41}$Ar effluent in a 9" x 26" duct with a sensitivity of 296 cpm/pCi. From these results it was evident that adequate sensitivity could be obtained with a
3. CALIBRATION OF THE PROTOTYPE

The prototype was calibrated by introducing a standard quantity of \(^{41}\)A into the chamber. To achieve this the chamber was evacuated, the ampoule broken and air introduced via the breaking device to purge the \(^{41}\)A and bring the chamber back to atmospheric pressure. The drum was then sealed and the count rate recorded for a significant period of time.

After making the standard corrections for decay and background the sensitivity of the prototype was determined as 572 cpm/pCi \(^{41}\)A. The accuracy of the calibration was estimated as ± 20% [Table I].

4. DESCRIPTION OF THE MARK 2 MEASURING CHAMBER

After the prototype had been utilised for measurement at Bradwell Nuclear Power Station and Calder Hall it was decided to develop and manufacture a production model. This model manufactured by M.C. Engineering Co. Ltd. [6] included the following practical refinements:

a. Aluminium alloy was utilised to reduce the weight of the chamber to a minimum.

b. A cylindrical shape was selected to produce minimum size without significant decrease in volume.

c. A sparge pipe was fitted to ensure adequate purging in operation.

d. Lifting handles were fitted.

e. A filter was provided on the inlet to protect the internals against particulate contamination. (This was in anticipation of the extended use of this equipment for direct measurements of reactor coolant).

The equipment is illustrated in Fig. 3. It consists of an aluminium sphere of diameter 18.5 inches, fitted with three ports which carry, respectively, the entry pipe, the exit pipe and the thin-walled geiger tube.

The entry pipe is fitted with a diaphragm valve and a filter and the exit pipe with a diaphragm valve. Both pipes terminate in connectors arranged to screw on to the flexible pipes which are provided for the shield cooling air particulate monitors.

To take a sample, the vessel is connected to these flexible pipes with the filter chamber facing upstream so that any particulate matter is intercepted. The sample is obtained by displacement. The effectiveness of this displacement was measured by counting samples after various sampling times and finding the minimum purging time required to give the maximum activity. The mid-time of the sampling period is regarded as to.
FIG. 2. Isometric sketch of the prototype (Mark 1) equipment.
Both valves are then screwed down and the vessel is removed to a Health Physics Laboratory for counting. The geiger tube is connected via a quench unit to a scaler and the sample is normally counted for some hours. Only one reliable count is necessary but if successive counts are taken, the half life of the radiation may be measured to check that it is characteristic of Argon $^{41}$. By extrapolation the count rate at $t_0$ and thus the $^{41}A$ activity in picocuries per millilitre is estimated.

### 5. CALIBRATION OF MARK 2 CHAMBER

A quartz ampoule containing Argon gas was irradiated in the BEP0 pile at Harwell at Pile Factor 4 for some minutes. It was then removed and the activity measured by the AERE Isotope Production Unit.
FIG. 3. Isometric sketch of the Mark 2 equipment.
The vessel was fitted with a special manifold which carried a thick walled polythene tube with a valve, a pressure gauge and a second valve leading to a vacuum pump. This manifold was plugged into the exit pipe of the vessel in order to avoid the dead space of the filter vessel. Both vessel valves were closed.

The ampoule was placed in the polythene tube which was then closely stoppered. The vessel was evacuated to 20 inches of mercury. The vacuum connection valve was then closed and the valve leading from the polythene tube to the vessel was opened. The ampoule was then crushed inside the polythene tube and air was allowed to sweep through the tube and into the vessel, carrying the Argon with it.

### TABLE II

| EHT | 1150 volts |
| Discriminator Bias | 10 volts |
| Quench time | 300 μs |
| Background (Before calibration) | 46 c.p.m. |
| Background (After calibration) | 68 c.p.m. |
| Source calibrated as a mean of | 104.4 μc/s |

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Mean 7418

403 c.p.m. per μCi/cm³
The geiger tube was already connected to a scaler and background counts had been taken.

The sample was then counted for several hours and after applying the usual corrections, the activity of the air/argon mixture was interpreted as counts per minute per picocurie per millilitre.

A second background count was taken after the calibration.

The results of a typical calibration are illustrated in Table III. A typical vessel has a sensitivity of about 400 cpm/pCi \(^{40}\text{A}\).

The accuracy of the calibration is estimated to be \(\pm \) 20%.

<table>
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<tr>
<th>Table III</th>
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</thead>
<tbody>
<tr>
<td>Cross Calibration of Mark 1 and Mark 2 Vessels at Bradwell Nuclear Power Station</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time of commencement of period (hours)</th>
<th>Decay time since ( t_0 ) to ( t_1 ) (mins)</th>
<th>Counts</th>
<th>Period (mins)</th>
<th>c.p.m.</th>
<th>c.p.m. corrected for background</th>
<th>Activity of source (pc/ml)</th>
<th>Activity at ( t_0 ) (pc/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1 North Stack 504 MW(th) power 44,000 cfm + 20,000 cfm flow, 214 cfm nominally through vessels ( t_0 = 1100 ) hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mark 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1117.5</td>
<td>13</td>
<td>1170</td>
<td>1</td>
<td>1170</td>
<td>685</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>1122.5</td>
<td>27.5</td>
<td>10979</td>
<td>10</td>
<td>1097</td>
<td>812</td>
<td>2.02</td>
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<tr>
<td>1201</td>
<td>66</td>
<td>9099</td>
<td>10</td>
<td>910</td>
<td>669</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>Mark 1</td>
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<td>1118.5</td>
<td>19</td>
<td>1615</td>
<td>1</td>
<td>1615</td>
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<td>2.34</td>
<td>2.64</td>
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<tr>
<td>1135</td>
<td>40</td>
<td>1747</td>
<td>10</td>
<td>1746</td>
<td>1466</td>
<td>2.57</td>
<td>3.02</td>
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<td>1212</td>
<td>75</td>
<td>14265</td>
<td>10</td>
<td>14264</td>
<td>1724</td>
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<td></td>
</tr>
<tr>
<td>Reactor 1 South Stack 504 MW(th) power 40,000 cfm + 20,000 cfm flow ( t = 1615 ) hrs. 15 mins. purge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mark 2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1462.5</td>
<td>17.5</td>
<td>13796</td>
<td>10</td>
<td>1380</td>
<td>1095</td>
<td>2.72</td>
<td>3.0</td>
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<td>42.5</td>
<td>11216</td>
<td>10</td>
<td>11217</td>
<td>932</td>
<td>2.31</td>
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<tr>
<td>1439.5</td>
<td>29.5</td>
<td>25884</td>
<td>10</td>
<td>2588</td>
<td>2408</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>1509</td>
<td>34</td>
<td>28168</td>
<td>10</td>
<td>2819</td>
<td>2339</td>
<td>4.1</td>
<td>3.2</td>
</tr>
<tr>
<td>1536</td>
<td>75.5</td>
<td>1437</td>
<td>1</td>
<td>1437</td>
<td>1157</td>
<td>2.02</td>
<td>3.32</td>
</tr>
<tr>
<td>Reactor 2 South Side 590 MW(th) power 47,000 + 45,000 cfm flow ( t_0 = 1638 ) hours</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1649.0</td>
<td>16</td>
<td>13513</td>
<td>10</td>
<td>1351</td>
<td>1066</td>
<td>2.64</td>
<td>2.9</td>
</tr>
<tr>
<td>1744</td>
<td>41</td>
<td>11776</td>
<td>10</td>
<td>1177</td>
<td>892</td>
<td>2.21</td>
<td></td>
</tr>
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<td>Mark 1</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>1701</td>
<td>28</td>
<td>15447</td>
<td>10</td>
<td>1545</td>
<td>1265</td>
<td>2.21</td>
<td>2.7</td>
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<td>1725</td>
<td>52</td>
<td>14346</td>
<td>10</td>
<td>1435</td>
<td>1155</td>
<td>2.02</td>
<td>(mean)</td>
</tr>
<tr>
<td>Reactor 2 North Side 590 MW(th) 47,000 + 40,000 cfm flow ( t_0 = 1822 )</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Mark 2</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1832</td>
<td>15</td>
<td>15980</td>
<td>10</td>
<td>1598</td>
<td>1313</td>
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<td>3.6</td>
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<td>14287</td>
<td>10</td>
<td>1429</td>
<td>1144</td>
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<td>Mark 1</td>
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<tr>
<td>1843.5</td>
<td>26.5</td>
<td>22445</td>
<td>10</td>
<td>2245</td>
<td>1665</td>
<td>3.44</td>
<td>4.0</td>
</tr>
<tr>
<td>1907</td>
<td>50</td>
<td>18740</td>
<td>10</td>
<td>1874</td>
<td>1594</td>
<td>2.89</td>
<td>(mean)</td>
</tr>
</tbody>
</table>

* GM tube faulty
6. RANGE OF THE EQUIPMENT

The lower limit to sensitivity is set by the background at the counting laboratory. Shielding to the chamber is impracticable and we have found that the background has varied from about 60 to 120 counts per minute. Thus the lower level of sensitivity will vary from $2.5 \times 10^{-12}$ Ci/cm$^3$ to $10^{-12}$ Ci/cm$^3$. The upper level of detection is determined in practice by the dead time of the quench unit. We have found that a quench time of 300 µsec can be utilised giving a practical upper limit of $7.5 \times 10^{-10}$ Ci/cm$^3$.

7. CROSS CALIBRATION OF MARK 1 AND MARK 2 VESSELS AT BRADWELL NUCLEAR POWER STATION

As a further check upon the independent calibrations of the Mark 1 and Mark 2 vessels it was decided to make simultaneous measurements with both vessels on the Bradwell reactors. Measurements were made on the north and south stacks of Reactor 1 operating at 504 MW(th) and Reactor 2 when operating at 590 MW(th). The results of these tests are summarised in Table III and indicate a consistent relationship with earlier measurements made with the Mark 1 vessel at lower power (Fig. 4).

![Graph showing specific activity vs. MW(th) with data points for North Stack and South Stack.]

**FIG. 4.** Measurement of the specific activity of the shield cooling air discharge from Bradwell Reactor 2 utilising the prototype chamber. Specific activity $^{41}$Ar $2.54 \times 10^{-12}$ Ci/cm$^3$(t0), background 69 cpm.

8. MEASUREMENTS OF THE $^{41}$A ACTIVITY IN SHIELD COOLING AIR DISCHARGES UTILISING THE MARK 2 VESSEL

Subsequent to the measurements at Bradwell the Mark 2 equipment was transported to Calder Hall for measurements at full power prior to use for the commissioning measurements at Hunterston 'A', Trawsfynydd, and Tokai Mura (Fig. 5). At the latter stations a number of separate measurements were made at a range of powers. Each of the measurements included a half-life check for $^{41}$A. The results at full power are given in Table IV. The measurements showed a good fit to a linear relationship between thermal power and specific activity. The rate of increase of specific activity with thermal
power was significantly different for each reactor (Fig. 6). This is not surprising in view of the complexity of the different shield coolant systems and the individual nature of each design, although it was not possible to ascribe these differences to any particular design feature.

**TABLE IV**

Measurements of the Specific Activity of the Shield Cooling Air at Full Power from Bradwell, Calder Hall, Hunterston 'A,' Trawsfynydd and Tokai Mura Nuclear Power Stations Utilising the Mark 2 Vessel

<table>
<thead>
<tr>
<th>Power of Reactor (MW(th))</th>
<th>Average Specific Activity of Shield Cooling Air pCi/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bradwell I</td>
<td>3.3</td>
</tr>
<tr>
<td>Calder Hall</td>
<td>8.3</td>
</tr>
<tr>
<td>Hunterston 'A'</td>
<td>4.78</td>
</tr>
<tr>
<td>Trawsfynydd</td>
<td>7.8</td>
</tr>
<tr>
<td>Tokai Mura</td>
<td>1.83</td>
</tr>
</tbody>
</table>
9. CONCLUSIONS

The equipment which has been developed although simple in concept has proved practical to operate and has provided reproducible measurements.

It has been operated over ranges of specific activity from $2.5 \times 10^{-13} \text{ Ci/cm}^3$ to $2 \times 10^{-11} \text{ Ci/cm}^3$ $^{41} \text{Ar}$ in air at temperatures up to 50°C. The sampling device together with its counting equipment has been operated to an accuracy estimated to lie between the range of ±20%.

This accuracy is considered to be adequate since greater errors are likely to have arisen from the problems of obtaining a representative sample of the discharged air.

The measurements taken have confirmed that there is no significant discharge of isotopes other than $^{41} \text{Ar}$ in the shield cooling air of the reactors measured.
The results also showed that the levels of discharge were below those initially predicted. At Trawsfynydd Nuclear Power Station the discharge level was measured at about 2 mCi/sec from the station operating at full power compared with a predicted level of 7.5 mCi/sec. The discrepancy between predicted and measured levels arises from two sources. There is firstly the prediction of activation flux at points of interest and secondly inaccuracies in the assumptions made in modelling the complex geometry of the varying shield cooling passages. At Bradwell Nuclear Power Station measurements of the thermal flux were made in order that the possible error from the first component could be assessed. From Reactor 2 a total discharge of 0.31 mCi/sec was evaluated using estimated fluxes. Measurement of the fluxes enabled this prediction to be modified to 0.36 mCi/sec [7]. Measurements with the $^{41}$Ar chamber indicated an actual discharge rate of 0.28 mCi/sec.

These measurements were able to confirm that the site dose rates from the discharge of shield cooling air were well below the levels recommended by the ICRP [8].

The same equipment will be utilised to measure the routine discharge of small quantities of reactor coolant discharged from Tokai Mura since it has been demonstrated that the range of the equipment can be extended beyond that for which it was initially designed.

In addition it is anticipated that this equipment could also be utilised to measure the small quantity of reactor coolant which may leak from the concrete pressure vessel of the first commercial Advanced Gas-Cooled Reactor at Dungeness 'B'. The station ventilation plant is arranged to remove all leakage to the ventilation air stack. This leakage will contain small quantities of $^{41}$Ar. The discharge from this source is expected to be of the same order as the shield cooling discharge from one of the later magnox stations. Although this will not present a radiation hazard, confirmatory measurements will be made.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the co-operation of the Central Electricity Generating Board, the South of Scotland Electricity Board, the United Kingdom Atomic Energy Authority and the Japan Atomic Power Company in providing access and staff for the measurements quoted in this report. They are further indebted to the Commissioning and Laboratory Staff of Atomic Power Constructions for valuable practical assistance.

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**APPENDIX I**

**Specified Characteristics of Geiger Counter**

20 Century Ltd., 312 Cat. No. CV 494 which is an organic quenched
thin walled borosilicate glass counter.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating potential (average)</td>
<td>1100 volts</td>
</tr>
<tr>
<td>Plateau (mm.)</td>
<td>200 volts</td>
</tr>
<tr>
<td>Operating length of anodes</td>
<td>12 cm</td>
</tr>
<tr>
<td>Diameter of operating length</td>
<td>1.6 - 1.8 cm</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>30-35 mg/cm$^2$</td>
</tr>
<tr>
<td>Life</td>
<td>$\sim 3 \times 10^8$ counts</td>
</tr>
<tr>
<td>Background (shielded 38 mm lead)</td>
<td>19 - 32 cpm</td>
</tr>
</tbody>
</table>
PARTICLE-SIZE SPECTROMETRY OF AEROSOLS BY LIGHT SCATTERING IN A LASER BEAM AND ITS APPLICATION TO AIR MONITORING AND FILTER TESTING

W. JACOBI
HAHN-MEITNER INSTITUT FÜR KERNFORSCHUNG, BERLIN, FEDERAL REPUBLIC OF GERMANY

Abstract

PARTICLE-SIZE SPECTROMETRY OF AEROSOLS BY LIGHT SCATTERING IN A LASER BEAM AND ITS APPLICATION TO AIR MONITORING AND FILTER TESTING. A new type of a particle-size spectrometer for aerosols was developed using a low-power He-Ne laser as light source. The light scattered from single particles crossing the laser beam is measured in nearly 4π-geometry by a suitable light conductor which is connected to the cathode of a photomultiplier. The multiplier pulse is transformed by a special pulse forming and integrating circuit whose output signal is proportional to the area of the original light pulse and can be fed into a standard multichannel analyser. As no optical lens systems are used, the design of the instrument is rather simple and a low background of undesired, scattered light can be reached.

The spectrometer was calibrated with monodisperse latex aerosols of different size. The lowest detectable particle diameter of the first working model was 0.3 μm. The spectrometer is distinguished by its good size resolution of 5-15%, depending on particle size, and its small scattering volume of only 0.05 mm³. This permits the direct spectrometry of aerosols with concentrations up to a few 1000 particles/cm³ without dilution. The instrument was developed especially for air monitoring in normal, unfiltered air, for measurements of filter efficiency versus particle size, and for studies on coagulation and inhalation of aerosols. Some of these applications are discussed.

INTRODUCTION

The most important physical parameter for the characterization of an aerosol is its particle-size distribution. This concerns the behaviour of aerosols in free air, the removal of aerosols in filters, and the deposition of inhaled aerosols in the human respiratory tract. Considering the increasing importance of air pollution problems, resulting either from radioactive or non-radioactive toxic aerosols, automatic and rapid methods for in-situ analysis of the size of aerosol particles are required.

Several types of light-scattering instruments for size spectrometry of aerosols above particle diameters of about 0.3 μm were developed in recent years [1-5]. These spectrometers measured the light pulse scattered from a single particle which traverses the collimated light beam of a conventional light source.

In the following a new type of light-scattering aerosol spectrometer is described, whose construction differs remarkably from the previous spectrometers of this kind. A continuous gas laser of low power was used as light source. No optical lenses are included, thereby reducing the background of scattered light and simplifying the design and adjustment of the spectrometer. Furthermore, by applying a light conductor the light scattered in nearly all directions was measured. Finally a new method for the analysis of the scattered light pulses was developed.
In the following a brief description of the spectrometer and its properties is given; a detailed description will be published elsewhere [6].

DESCRIPTION OF THE SPECTROMETER

Light source and scattering chamber

As light source a He-Ne laser with a beam power of 0.5 mW at a wavelength of 6328 Å was used. The laser beam had a diameter of 1.2 mm at the laser output and a divergence smaller than 0.7 mrad. After passing a stop system the beam entered the scattering chamber whose cross-section is shown schematically in Fig. 1.

The scattering chamber consists of an encapsulated cylindrical light conductor made of Plexiglass with a diameter of 25 mm and a height of 20 mm. Vertical to its axis the light conductor has two bore channels of 5-mm diameter which intersect in the centre of the cylinder. The laser beam passes through the horizontal channel and is absorbed on the other side in a light trap, which includes a Si photodiode to check the beam intensity. Through the other, vertical channel a laminar stream of filtered air flows at a definite rate in the range of 10-30 litre/h. A narrow thread of the measuring air containing the aerosol whose size distribution is to be measured is injected into this clean-air stream. The injection is done with a narrow tube of 0.2-mm inside diameter just above the laser beam. By suitable adjustment of the flow rate, the measuring air with its aerosol passes in the form of a narrow perpendicular thread through the centre of the laser beam.

Each aerosol particle crossing the laser beam generates a pulse of scattered light whose length is given by the transit time of the particle through the beam and therefore depends only on the flow rate. In our experiments the pulse length was in the range of 0.8-2.5 ms. The form of the scattered light pulse corresponds to the Gaussian intensity profile of
the laser beam. As the diameter of the aerosol-containing air beam is small compared with the laser beam diameter, all aerosol particles traverse nearly the same light intensity profile. This is an important condition of obtaining a good particle size resolution with the spectrometer.

A characteristic feature of the system described is the small size of the scattering volume in which scattering takes place. It is given by the air volume in which the laser beam and the aerosol-containing air beam cross. In our device the scattering volume was only about 0.05 mm$^3$. As discussed later, the small size of the scattering volume permits the direct spectrometry of air with concentrations up to about 1000 particles/cm$^3$ without dilution.

No optical lenses were used in sampling the scattered light. The scattered light pulse is directly measured by a sensitive photomultiplier whose cathode is attached to one base of the cylindrical light conductor. As the light conductor surrounds the scattering volume on all sides, the multiplier takes up the light scattered over nearly the whole angle of 4π.

Pulse analysis

The pulse height of the output pulse from the multiplier is a function of the size of the scattering particle. In previous aerosol spectrometers the pulse height distribution of the counted particles is measured directly. Unlike this method we measured the pulse area distribution of the output pulses from the multiplier. The advantage of our method is a reduction of the background noise and a higher signal to noise ratio. We could use this method because at a given flow rate the pulse length is independent of the size of the scattering particles.

For pulse integration the output pulses from the multiplier are fed into a Miller integrator with a variable integration capacity. As shown in Fig. 2, the pulse integration is started by a Schmitt trigger 50 μs after the negative input pulse exceeds a fixed threshold of about -30 mV. This threshold was set just above the noise level. The integration is stopped when the back-flank of the pulse decreases below another threshold of about -10 mV. At this point a linear gate is opened and the integration capacity is discharged in a time of about 2 μs. The height of the output pulse from this gate is equal to the pulse area of the input pulse. Its length of about 2 μs permits after amplification direct connection to a conventional pulse-height analyser. In our case a 256-channel analyser was used. The particle-size spectrum measured is written out either on a recorder or a printer.

Parallel to the integration circuit a counting circuit permits the simultaneous measurement of the total number and the concentration of particles above a given size.

EXPERIMENTAL RESULTS

Calibration

The spectrometer was calibrated with monodisperse latex aerosols of different particle diameters in the range of 0.3 - 3 μm. These aerosols were generated in the usual way by atomization of strongly diluted, monodisperse latex hydrosols.
Figure 3 shows the measured pulse spectra for six, nearly monodisperse test aerosols of different particle sizes. The channel number of the pulse analyser is given on the abscissa. For better comparison the six spectra have been drawn as one figure. Each test aerosol produces
a sharp single peak at a definite channel number, clearly separated from the other test peaks. This good size resolution exists also for small-sized test aerosols with particle diameters of 0.36 and 0.56 μm. Another important feature is the absence of any background spectrum from noise down to particle sizes of about 0.3 μm.

The relation between particle size and channel number depends on the amplification, the multiplier voltage and the air flow rate through the scattering chamber. Figure 4 shows the measured calibration curves — channel number versus particle size — for amplification factors $V = 1$ and $V = 2$ at different values of the air flow-rate $v_N$ through the scattering chamber. The multiplier voltage was held constant at 1200 V. The curves show a non-linear, but straightforward relation between particle size and channel number. By appropriate selection of the parameters, the calibration curve can be adapted to the particle size range desired. The minimum particle diameter detectable with the spectrometer system described is 0.25 - 0.3 μm.
Scattering efficiency

The calibration curves given are primarily valid for spherical particles with a refraction index $n$ corresponding with the values $n = 1.58$ (polystyrol latex) and $n = 1.49$ (polyvinyl-toluene-latex) of the test aerosols. The observed, non-linear correlation between particle size and channel number is mainly due to the scattering properties of the particles. In Fig. 5 the measured, normalized calibration curves are compared with the theoretical, total scattering cross-section computed from Mie’s theory for $n = 1.44$, $1.50$, $1.55$ [7]. For particles smaller than about 2 μm the response of the spectrometer agrees within an error range of lower than ±20% with the theoretical curves. In this size range therefore the measured calibration curves for latex particles can be corrected to other $n$-values with the aid of the Mie theory. At larger particle sizes the spectrometer response is too low compared with the scattering cross-section. This difference is probably caused by the increasing amount of light scattered forward into the horizontal bore channel of the light conductor.

![Fig. 5. Spectrometer response in comparison with the theoretical scattering cross-section of particles with different refraction index $n$.](image)

Particle-size resolution

One of the most important quantities which characterize the quality of an aerosol spectrometer is the size resolution which follows from the standard deviation of the observed pulse distribution in the peak of a monodisperse test aerosol. In the following the size resolution is given as the ratio of the peak width at half the maximum peak amplitude to the mean particle diameter of the test aerosol, in analogy to the definition of energy.
resolution in nuclear radiation spectroscopy. Calibration measurements showed that within the error limits the size resolution of the spectrometer is independent of the air flow rate $v_N$ through the scattering chamber in the range of 10-25 litre/h. The measured size resolution is plotted as a function of particle size in Fig. 6. The resolution is about 6% for 0.3 and 2.7-μm particles. Between these sizes the resolution is higher and reaches a maximum value of 15% for 1-μm particles. This lapse of the resolution curve can be explained from the slope of the scattering cross-section versus particle size. The given resolution values include the size inhomogeneity of the latex test hydrosols used, given in the lower curve of Fig. 6. After subtraction of this inhomogeneity an effective size resolution of 5-15% for the spectrometer described is given. This corresponds to a standard deviation of about 2 - 6%. These low values indicate the great accuracy of the particle size distribution measurements which can be obtained with this laser spectrometer.

![Fig. 6. Measured size resolution of the spectrometer as a function of particle size.](image)

**Maximum detectable particle concentration**

To avoid the coincidence of light pulses resulting from the simultaneous presence of two or more particles in the scattering volume, this volume should be as small as possible. As pointed out earlier, the spectrometer described has a very small scattering volume of only about 0.05 mm$^3$, which is 1-2 orders of magnitude smaller than all other aerosol spectrometers of the light-scattering type described hitherto. This permits the direct spectrometry of high aerosol concentrations without dilution. From the value given for the scattering volume it follows that for a concentration of 1000 particles/cm$^3$ the percentage of coincident pulses is smaller than 3% and increases to 5% for concentrations of 2000 particles/cm$^3$.

**APPLICATIONS AND CONCLUSIONS**

The laser-spectrometer described was especially developed for research studies in our laboratory on aerosol physics and aerosol inhalation. However, it may also be a useful instrument for air monitoring and filter testing in the detectable particle size range. For example, we have
JACOBI measured the short-time variations of the size distribution in the atmospheric aerosol with the spectrometer to get information on the wash-out efficiency. The spectrometer also permits a rapid determination of the efficiency of filters as a function of particle size. For this purpose the size distribution of a heterogeneous aerosol is measured in the air flow before and after the filter. The ratio of both distributions gives directly the filter transmission as a function of particle size at the adjusted flow rate.

The preliminary results presented in this paper indicate that the laser-spectrometer described satisfies the requirements for aerosol spectrometers of high quality in the detectable size range above 0.3-μm particle diameter. As no optical lens system is required, its design is rather simple. The spectrometer is distinguished by its good size resolution and its low scattering volume which allow the direct spectrometry of aerosols at high particle concentrations without dilution. Further work is being done in our laboratory to improve the spectrometer and to calibrate it for different kinds of aerosols.

ACKNOWLEDGEMENTS

I would like to express my thanks to my co-workers J. Eichler, H.J. Barz, H.J. Pangritz and N. Stolterfoht, who participated in the construction and operation of the spectrometer. Furthermore I am indebted to the Bundesinnenministerium of the Federal Republic of Germany which gave financial support to this project.

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DISCUSSION

O. L. CORDES: Is the 0.3 micron lower limit for the size of particles that can be resolved by this type of spectrometer a theoretical lower limit, or a practical one 9

W. JACOBI: This detection limit of the present design of our spectrometer is caused by the noise level of the scattered light background, which is mainly due to the Rayleigh-scattering of the air molecules in the laser beam. However, at the given wavelength, the scattering cross-section decreases strongly with decreasing particle size. We therefore cannot expect to reach a much lower detection limit.
D. W. BALLARD: We developed a laser spectrometer similar to yours at Sandia Laboratories, employing a 1-mW He-Ne continuous gas laser. We did not treat the laser beam optically, in order to improve the shape of the sensing zone, which is rectangular, rather than circular. We used forward-light scattering instead of right-angle scattering, to take advantage of forward-lobe scattering efficiency. Our instrument operates at 10 cfm and the photomultiplier can discriminate up to 100 000 cps. I am pleased to see that we have independently pursued the same instrument improvement in both West Germany and the USA, and I have high hopes that this effort will enable us to develop a high volume, real-time monitor that all of us in the airborne contamination field recognize as an urgent requirement.

W. JACOBI: Thank you for your information about the instrument developed at the Sandia Laboratories. I share your opinion about the great need for such spectrometers. I must point out one misunderstanding: We don't apply right-angle scattering in our instrument. As I have mentioned, the scattering volume is surrounded by a light conductor, which receives nearly all the light scattered in an angle of 4π.

R. D. RIVERS: What is the upper count rate, or the upper mass concentration measurable by your instrument?

W. JACOBI: If we tolerate a maximum coincidence rate of 2%, we can analyse about 5000 particles/minute in the detectable size range.

E. W. BLOORE: What is the effect of irregular particles and of particle colour or refractive index?

W. JACOBI: So far, we have calibrated the spectrometer only for spherical particles with refractive indices of 1.49 and 1.56. For particle diameters lower than about 2 microns, the spectrometer response for other refractive indices can be estimated from these calibration curves with the help of the Mie-theory.

E. BRAVO S.: Can your instrument accept only a constant particle size?

W. JACOBI: The lowest detectable particle diameter with our instrument is about 0.3 microns. The upper limit of the size-range can be changed by varying the air flow-rate or the pulse amplification, as is shown in Fig. 4 of the paper. However, only monodispersed latex hydrogels up to 2.7 microns in diameter have been available for calibration so far.

J. J. COHEN: Have you considered the possibility of using lasers of shorter wavelength to permit the classification of smaller particles?

W. JACOBI: It would be very interesting to do so because of the greater scattering cross-section and if we had enough money we would use an argon laser. Unfortunately, short-wavelength lasers are too expensive.

D. A. NITTI: Have you done any experiments to see if passing the aerosol sample through the small orifice or capillary that you use for sample injection perturbs or biases the measured particle-size spectrum?

W. JACOBI: The length of the small injection tube is about 10 mm. At the normal flow-rate used, the mean residence time of the particles in this tube is only about 5 msec and coagulation of particles during this time is negligible. It is a more difficult problem to prevent clogging of the tube inlet if very large particles are present in the measured air.
However, this effect can be reduced considerably by proper design of the air inlet of the tube. Clogging of the tube can be recognized by a change in either the flow-rate or the pulse length.

A. LIEBERMAN: You indicate a pulse of 0.8 – 2.5 msec. Is this a variable pulse length?

W. JACOBI: Yes. The pulse length can be varied by changing the air flow-rate. The time-range of the scattered light pulses depends only on the flow-range for which calibration measurements were done. However, at each measurement of a size spectrum, the flow-rate is fixed and the pulse length therefore also remains constant, independent of particle size. Normally, the spectrometer was operated with a pulse duration of about 1 msec.
CHARACTERISTICS OF AIR CONTAMINANTS FROM NUCLEAR REACTORS

(Session II)
Chairman: R. E. HOLMES
CHARACTERIZATION OF SODIUM SPRAY AEROSOLS*

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Abstract

CHARACTERIZATION OF SODIUM SPRAY AEROSOLS. The consequences of pool and spray fires require evaluation in the safety analysis of liquid metal-cooled fast breeder reactors. Sodium spray fires are characterized by high temperature and pressure, produced during the rapid combustion of sodium in air. Following the initial energy release, some fraction of the reaction products are available as aerosols which follow the normal laws of agglomeration, growth, settling, and plating.

An experimental study is underway at Atomics International to study the characteristics of high concentration sprays of liquid sodium in reduced oxygen atmospheres and in air. The experiments are conducted in a 31.5 ft³ (2 ft diam. by 10 ft high) vessel, certified for a pressure of 100 lb/in² (gauge). The spray injection apparatus consists of a heated sodium supply pot and a spray nozzle through which liquid sodium is driven by nitrogen pressure. Spray rate and droplet size can be varied by the injection velocity (nozzle size, nitrogen pressure, and sodium temperature).

Aerosols produced in 0, 4, and 10 vol.% oxygen environments have been studied. The concentration and particle size distribution of the material remaining in the air after the spray injection and reaction period are measured. Fallout rates are found to be proportional to the concentration of aerosol which remains airborne following the spray period.

INTRODUCTION

Although it is recognized that the probability of a system failure leading to a large sodium spill is very remote, consideration of such accidents is required in the safety analysis of an LMFBR, due to the presence of radioactive sodium isotopes and other possible contaminants which can become airborne in the event of a sodium fire, and overpressurization of containment. The chemical reaction of sodium burning in the building atmosphere, the thermal effect of the sodium heat capacity, and the radioactivity of the sodium may establish design requirements of engineered safety features. These characteristics influence the design and maintenance procedure restrictions for the main heat transfer and service vaults (inner containment barrier) and for the reactor building (outer containment barrier).

The sodium-oxygen reaction and its effects will depend on the mode of release, prevailing environmental conditions, and physical characteristics of the area into which the release occurs. For purposes of defining the potential air reactions and effects, it is convenient to consider two representative conditions as typical

1) Reaction at the surface of a pool of sodium (static or burning pool), and

2) Reaction associated with a spray-type release (pressurized spray or explosive ejection).

* Based upon studies conducted for the US Atomic Energy Commission under Contract AT(04-3)-701.
While affected by many variables such as heat transfer to walls and oxygen depletion in an enclosed system, the energy released by the burning pool to the surrounding atmosphere would tend to cause a slow increase in pressure. In the case of pressurized spray and explosive ejection, pressure rise and peak pressures at considerably higher rates can occur. The explosive ejection, although the least likely, is potentially the most severe. The significant difference between the explosive ejection and the pressurized spray is one of reaction rate. Under given temperature conditions, the rate of reaction is a function of the rate of sodium surface exposure which depends upon the mass rate and particle size of the sodium discharge. In a pressurized spray discharge (orifice or nozzle type), it is improbable that both a very large discharge rate and the fine particle dispersion could exist simultaneously. Only in the explosive ejection of a large mass of sodium into a fine dispersion sodium are optimum conditions for the most severe reactions possible.

This paper describes some preliminary studies of the aerosol characteristics of sprays produced by discharging liquid sodium through nozzles.

PREVIOUS EXPERIMENTAL PROCEDURES

In most previous work\textsuperscript{[1,2]} on sprays of sodium, the experimental parameters of concern have been the reaction rate, energy release, and pressure and temperature rise associated with the spray. Following the release of the sodium, there are rapid rises and falls of air temperature and pressure, and from these observations one assesses whether or not a building or cell would be irreparably damaged. The excess of Na or O\textsubscript{2} and measurement of oxygen and sodium consumption allow one to assess whether or not Na\textsubscript{2}O\textsubscript{2} or Na\textsubscript{2}O would be formed. In most previous work, the concentration of sodium released for reaction has been \(\sim 800 \mu g/cm^3\). Such an aerosol concentration is extremely unstable and difficult to characterize. The fraction of the released mass and/or fission products which remain airborne and available for leakage has not been measured but it is undoubtedly small, and subject to the laws of gravitation and agglomeration.

EXPERIMENTAL STUDIES

In these studies, sodium sprays are generated in a 31.5 ft\textsuperscript{3} (2-ft diameter by 10-ft high, certified at 100 lb/in.\textsuperscript{2} (gauge)) spray test vessel (STV) where the oxygen content of the vessel atmosphere is varied. The spray injection system consists of a heated sodium supply pot connected to a full cone 15° spray nozzle through which up to 1 lb liquid sodium can be driven with 40 to 100 lb/in.\textsuperscript{2} (gauge) nitrogen gas pressure.

During the tests, observations are made of the rate of decrease of oxygen and changes in temperature and pressure. In addition, the mass of sodium which is airborne, and that which settles on the floor, walls and ceiling, are monitored as a function of time. After the sodium injection is terminated, round jet impactors are used to measure the airborne particle size distribution by mass as a function of time.

Three experiments have been performed in the STV to date. These tests are preliminary and scoping in nature. Table I presents a summary of these tests.
<table>
<thead>
<tr>
<th>Row Number</th>
<th>Parameter</th>
<th>Test Number</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na released (g)</td>
<td>68 24 83</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Spray time (sec)</td>
<td>20 20 7 sec</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Initial O₂ (%)</td>
<td>4 10 0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Initial Na temperature (°F)</td>
<td>600 1000 1200</td>
<td>See fallout rate during spray (Row 12)</td>
</tr>
<tr>
<td>5</td>
<td>Spray size</td>
<td>coarse finer finer</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>O₂ consumed (% oxygen)</td>
<td>0.35 0.92% 0</td>
<td>During spray</td>
</tr>
<tr>
<td>7</td>
<td>Na oxidized from ΔO₂ (μg/cc)</td>
<td>9.5 22.5 0</td>
<td>During spray, Na in Na₂O₂ is computed</td>
</tr>
<tr>
<td>8</td>
<td>Time to consume O₂ (sec)</td>
<td>2.6 26 0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Measured pressure change</td>
<td>2.8 9.5 -</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Computed, ΔP (lb/in.²)</td>
<td>3.0 9.0 -</td>
<td>From ΔO₂ forming Na₂O₂ (for Test 1 and 2)</td>
</tr>
<tr>
<td>11</td>
<td>Na₂O₂ produced (g)</td>
<td>14.5 38 0</td>
<td>During spray</td>
</tr>
<tr>
<td>12</td>
<td>Spray fallout rate (g Na/sec)</td>
<td>60 0.1 7.5</td>
<td>During spray</td>
</tr>
<tr>
<td>13</td>
<td>Aerosol deposition T₅₀ (min)</td>
<td>6 3 15</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Equivalent size of Row 13 of Na (V_d-r₅₀)</td>
<td>6.8 9.8 4.4</td>
<td>Aerodynamic radius, d = density g/cm³</td>
</tr>
<tr>
<td>15</td>
<td>Measured of aerosol after spray conc. of Na (μg/cm³)</td>
<td>5 to 6 24 1.2</td>
<td>Na in Na₂O₂ is measured (for 1 and 2)</td>
</tr>
<tr>
<td>16</td>
<td>Fraction of released spray on floor (%)</td>
<td>18 67 90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wall</td>
<td>37 33 9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>wall and ceiling</td>
<td>40 - -</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Released Na oxidized during spray time (%)</td>
<td>12.5 93 0 0</td>
<td>(Row 7/Row 1) x 0.9 x 10⁶ cm³</td>
</tr>
<tr>
<td>18</td>
<td>Fraction of oxidized Na remaining airborne</td>
<td>0.58 0.92 0</td>
<td>(Row 15/Row 7)</td>
</tr>
<tr>
<td>19</td>
<td>Row (15) converted to Na₂O₂ (g)</td>
<td>9.4 41</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Fraction of released Na remaining airborne</td>
<td>0.0725 0.9 0.013</td>
<td>(Row 15/Row 1) x 0.9 x 10⁶ cm³</td>
</tr>
<tr>
<td>21</td>
<td>Row 19 as μg/cm³</td>
<td>10.5 45.7</td>
<td></td>
</tr>
</tbody>
</table>
The first test determined that the nozzle design was improper for producing sodium droplets which would react promptly in low O\textsubscript{2} environments. The test was conducted in an initial 4 vol. % oxygen environment. The spray lasted for 2 sec. During this time, 60% of the liquid sodium fell and 33% was deposited on the walls. During the spray, only 10% of the initial oxygen was consumed (see Row 6) although the STV has the capability of oxidizing 18.3 g Na per %O\textsubscript{2} by volume if the formation of Na\textsubscript{2}O\textsubscript{2} is assumed. Na\textsubscript{2}O formation uses twice as much sodium per % oxygen.

For Test 1, 73 g Na could have been oxidized to Na\textsubscript{2}O\textsubscript{2} in the 4%O\textsubscript{2} environment. Since such a large fraction of the released sodium was not oxidized it was obvious that there was an excess of O\textsubscript{2} which favors the formation of Na\textsubscript{2}O\textsubscript{2}. This observation was also apparent when a calculation based on oxygen consumption and the heat of combustion per mole of sodium oxidized revealed that the computed pressure rise equaled the measured value only when Na\textsubscript{2}O\textsubscript{2} formation was assumed. This was also true for Test 2 (see Rows 9 and 10), where the initial O\textsubscript{2} was 10% by volume and ∆O\textsubscript{2} was 1% (see Rows 3 and 6).

Test 2 had the advantage of an improved spray nozzle (15° angle), a higher sodium temperature 1000°F, a longer injection time, and more O\textsubscript{2} (10% by volume). The combination of these characteristics gave a higher oxygen consumption and energy release.

Much less material fell out during the spray time (see Row 12) and a higher fraction of the released mass was oxidized (Row 17), resulting in an increased air concentration after the spray (see Row 15). The oxidized sodium and the sodium remaining airborne were nearly equal (see Row 18) for Test 2. This would follow from two facts: (1) If the spray is fine, complete oxidation is easier than when the sodium droplets are large. (2) Oxidation of partially condensed sodium vapor has been shown to produce a smaller initial particle size distribution\textsuperscript{3} than those produced by condensation alone.

Test 3 was performed in a pure argon environment to provide a means of characterizing the liquid sodium spray and, as a result, only condensed sodium remained airborne. The concentration remaining airborne in Test 3 was only ~1μg/cm\textsuperscript{3} (Row 15) and this was the only experiment in which the median radius as measured with impactors increased with time. In the other two experiments, the median radius at the end of the spray injection period was larger than it was at later times.

A heater was used to produce convection currents during the experiment so as to provide a "stirred" environment (uniform concentration at all heights). As a result, the air concentration at any height decreased at the same rate. In a "stirred" environment, the time for the initial air concentration to decrease to one half or the time for 1/2 of the mass to build up on the floor can be used to characterize the 50% size of the distribution (mass median radius or Stokes radius). The floor mass half time (see Row 13) was first used to compute the median aerodynamic radius of the particle distribution, \[ \sqrt{d \cdot \tau_{50}} \] (see Row 14), where d is the density of the aerosol in g/cm\textsuperscript{3} and \( \tau_{50} \) is the mass median (Stokes) radius in microns. The densities of sodium and Na\textsubscript{2}O\textsubscript{2} are 0.9 and 2.8 g/cm\textsuperscript{3}, respectively, and thus the mass median radius for Tests 1, 2, and 3 are 4.06, 5.86, and 4.7 microns, respectively. Note that the mass median size is related to the concentration of aerosol remaining airborne after the spray (see Row 15) except for Test 3. The large value of the mass median radius for Test 3 compared to Tests 1 and 2, whose concentrations are higher, is due to the condensation effect previously mentioned.
Fig. 1 shows how the air concentration for the three experiments changes with time. It appears that the higher the concentration of aerosol, the faster the rate of decrease.

Since the initial particle size distribution of the nozzle-sprayed material was not measured, it is not known whether the apparent relation between the concentration of the airborne material remaining after the spray and the aerodynamic radius is fortuitous. Nevertheless, one observes that the aerodynamic radius \( r = (\rho)^{0.26} \), where \( \rho \) is the concentration remaining airborne following the spray.

The determination of the relationship between the mass released, \( \% O_2 \), and \( \rho \) is planned.
CONCLUSION

When stoichiometric oxidation of a sodium spray occurs in O₂ environments, large pressure pulses may be generated in relatively short times. The fraction of the oxidized sodium which remains airborne is a function of the initial particle size distribution of the aerosol and its agglomeration and settling rate. As the aerosol concentration increases, the initial fallout rate increases. Thus the material available for leakage and/or filtration is inversely proportional to the initial airborne mass remaining after the spray.

In the spray accident the resultant agglomeration initially proceeds very rapidly causing the particle growth and fallout rate to increase. This causes the size relation \( r = \rho^b \) to decrease, since \( b \) is a function of the time available for agglomeration. When \( \rho \) is small, \( r \) does not become large enough to decrease the concentration rapidly and thus growth can be observed.

REFERENCES


DISCUSSION

W. SCHIKARSKI: What is the initial aerosol particle size in your spray fire experiment immediately after the sodium is dispersed? And do you think there is a relationship between this and the characteristics of the spray nozzle?

C. T. NELSON: There may be a relationship between the characteristics of the spray nozzle and the initial sodium oxide aerosol particle distribution. However, it is believed that the oxide aerosol is obtained from oxidized sodium droplets and that these particles are much smaller than those of the droplets from which they are formed. The contribution of sodium droplet size is to allow more and faster oxidation and thus produce a higher initial oxide concentration.
MODELLING CHARACTERISTICS OF AEROSOLS GENERATED DURING LMFBR ACCIDENTS *

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Abstract

MODELLING CHARACTERISTICS OF AEROSOLS GENERATED DURING LMFBR ACCIDENTS. Continuing studies at Atomics International are being conducted to develop experimental information and analytical methods which characterize the release and transport of effluents generated during major Liquid Metal Fast Breeder Reactor (LMFBR) accidents.

Experiments have been conducted in a laboratory test chamber to study the behaviour of oxidized sodium, released from a sodium pool fire at concentrations up to 60 µg/cm³. Various quantities of burning sodium have been dispersed in various oxygen environments in a 6-ft high chamber, 40 ft³ (1.13 x 10⁶ cm³) in volume, with a total surface area of 10⁵ cm² and a floor area of 6260 cm². In all experiments, measurements are made of: (1) the airborne concentration and particle size distribution versus time, (2) the mass and activity deposition rate on the floor and walls, (3) the total amount of activity and mass deposited on the walls and floor, and (4) the initial and remaining quantity of mass in the burn pot. Deposition samples from the floor and at several heights above the floor showed equal amounts of mass, and thus demonstrated 'stirred' conditions.

The conclusions derived from these experiments are: (1) As more aerosols are released into the chamber, the time for clearing the air decreases. The particle size distribution increases to larger maximum sizes as the mass of material released is increased, regardless of the shape of the aggregate (chains or spheres). The relation between the maximum radius and released mass concentration has been found to be approximately \( r = \rho_R 0.4 \), where \( \rho_R \) is in µg/cm³ and \( r \) is the maximum mass mean radius in microns. (2) Wall plating rates indicate that a higher deposition velocity occurs with increase in the airborne concentration, which is associated with higher temperature gradients. (3) The initial size of the released sodium oxide is log normal, with a mass median diameter of \( \sim 1.0 \mu m \) and a geometric standard deviation of 2.33. (4) The experimental results described in this paper have been fitted by an empirical mass model. This model appears to describe the observed spatial and temporal characteristics of the aerosols sufficiently well for use in reactor safeguards evaluations.

INTRODUCTION

Studies are currently being conducted at Atomics International to develop experimental information and analytical techniques which characterize the materials dispersed as aerosols during major Liquid Metal Fast Breeder Reactor accidents. The aerosol studies include vaporization and condensation in inert atmospheres, or vaporization and oxidation in air, of both sodium and \( \text{UO}_2 \). Sodium aerosols are generated in closed test vessels from sprays and pool fires in atmospheres with various oxygen contents. This paper will describe aerosols generated from sodium pool fires. Work on sodium spray aerosols and \( \text{UO}_2 \) aerosols are described in other papers at this conference.[1,2]

* Based upon studies conducted for the US Atomic Energy Commission under Contract AT(04-3) - 701.
By correlating the data from a large number of experiments of the kind described above, it has been possible to relate many of the observed parameters empirically. These empirical relationships allow one to develop simple models whose analytical origin can be justified from more rigorous physical and mathematical principles.

**EXPERIMENTAL TECHNIQUES**

All experiments described in this paper were conducted in a closed laboratory test chamber (LTC). The LTC, described previously,[3,4] is a $1.13 \times 10^6 \text{ cm}^3$, 180 cm high, cylindrical steel vessel with a large wall surface to volume area of $\sim 0.09 \text{ cm}^{-1}$. Sodium pool fires are used to produce sodium oxide aerosols. The experiments are conducted so that the burning time or source time is controlled by (1) the oxygen content of the environment, (2) the liquid quantity of liquid sodium, and (3) the area of the burn pot. Initiation of the fire is controlled by removal of the pot lid after the sodium has reached a temperature of $\sim 540^\circ \text{C}$. This lid is removed by means of a crank-line mechanism which is actuated manually from the exterior of the chamber.

Following the removal of the lid, several automatic sequential samplers begin to collect the sodium oxide aerosols as they deposit on the floor and walls. These samplers measure the deposition rate of the airborne material. The data can be accumulated so that the fraction of the total deposited material can be determined at any time. Air samples are obtained on millipore filters at several heights in the chamber as a function of time. Round-jet impactor samples are collected and the mass distribution of the released oxide is determined as a function of time. Electrostatic and thermal precipitator samples are collected for optical particle sizing. Cumulative mass samples are obtained from the walls, ceiling, and floor, and the sum of the material collected on all surfaces represents the released mass. This quantity is also equal to the initial mass in the burn pot minus that which remains as equivalent sodium. The quantity of material collected per unit area as a function of height above the floor serves as an indicator of the type of environment which exists during the life of the aerosol. If the environment is quiescent and tranquil, the amount of material collected per unit area increases as the distance from the sampling point to the ceiling increases. When a turbulent, stirred environment exists, the material which is airborne remains uniformly concentrated at all heights, hence, the amount collected per unit area is independent of height, i.e., the concentration decreases at the same rate at any height.

By summing the mass collected on deposition samplers with the airborne mass, one can obtain a mass balance throughout the experiment.

This paper describes the data and the interpretation of the results from aerosols produced from sodium pool fires generated in the LTC. The subjects which are discussed are applicable to extrapolating the results to any other geometry.

**Burning rate and release fraction of sodium oxide and fission products from pool fires**

The burning rate of sodium has been found to be a function of the oxygen concentration, the temperature of the liquid sodium, and the flow of gas across the pool surface. In low oxygen environments ($\sim 4 \text{ vol.\%}$) the combustion heat does not maintain the pool temperature. The oxidation
rate is proportional to the flow across the pool and the temperature of the molten sodium. Because of the lower oxidation rate and, hence, reduced surface concentration in low oxygen environments, the release fraction of the oxidized sodium is higher than it is in higher oxygen environments (10 to 21 vol.%). However the release rate is also a function of temperature and flow. In closed vessels the flow across a pool fire is due to natural convection and depends primarily on the surface temperature of the fire, the surface area of the fire, and the height of the enclosing vessel. For the purpose of modeling the aerosol behavior, the release fraction of the oxidized sodium determines the concentration of sodium which is airborne. The fraction of fission products in the sodium which are released during a fire is a function of the solubility and vapor pressure, etc., of the individual fission product and the sodium fire temperature, flow, and oxide crust formation.

The result of the experiments performed to date for oxidation and release rate are summarized as

<table>
<thead>
<tr>
<th>Closed Vessel (LTC) — Natural Convection</th>
<th>1000°F (4%O₂)</th>
<th>1200 to 1300°F (21%O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na Burning Rate (lb/hr ft² %O₂)</td>
<td>0.4</td>
<td>0.35</td>
</tr>
<tr>
<td>Na Release Fraction</td>
<td>0.35 to 0.4</td>
<td>0.15 to 0.2</td>
</tr>
<tr>
<td>Na¹³¹I Release Fraction</td>
<td>0.8 to 1.0 (0%O₂)</td>
<td>0.3 to 0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Dependence for 3 ft² Area</th>
<th>Flow Rate (ft³/min)</th>
<th>20</th>
<th>90</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°F Na Burning Rate (lb/hr ft² %O₂)</td>
<td>0.25</td>
<td>0.36</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>1000°F Na Release Fraction</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000°F NaI Release Fraction</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 to 1300°F NaI Release Fraction</td>
<td>0.15 to 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 to 1300°F Na Burning Rate (lb/hr ft² %O₂)</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 to 1300°F Na¹³¹I Release Fraction</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the above listings, the Na¹³¹ release fraction is defined as the ratio of the specific activity of ¹³¹I in the gas to that in the liquid. The Na release fraction is the ratio of the release rate to the oxidation rate expressed in the units, Na/hr ft² %O₂.

The burning rate constant in LTC which is approximately 0.4 lb Na/ft² %O₂ hr has also been observed from the rate at which the oxygen concentration decreases in the closed LTC experiments. The results imply that for a given area and volume, that the oxygen decreases with a constant half time regardless of the initial O₂ content; i.e., the rate of decrease is proportional to the concentration.
Initial particle size of the released sodium aerosol

In typical aerosol experiments, the particle size distribution is representative of the distribution until plating, settling, or agglomeration removes some particle size preferentially and thus changes the distribution. If no agglomeration occurs, the removal rate is proportional to the concentration and, regardless of the amount introduced, the half time for removal is a constant.

For liquid sodium fires in which the release fraction and burning rates are those described previously, the released particle distributions are log normal and the initial mass median radius in microns has been found to be

\[ r_{50}' = 0.4 \rho^{0.2} \]

where

\[ \rho = \text{concentration measured near the surface of the fire (} \mu\text{g/cm}^3) \]

\[ \rho(\mu\text{g/cm}^3) = \frac{\text{release rate (lb Na/hr)}}{\text{flow (ft}^3/\text{hr})} \times 1.6 \times 10^4 \]

In the LTC for air fires, \( r_{50}' \) (initial) = 0.58 \( \mu \text{m} \) and \( \sigma \), the geometric standard deviation, is 2.1. It should be noted that the dependence of the initial particle size on concentration is weak. This is due to the relationship of particle growth, agglomeration, and time. In the case of the initial particle size, the time for agglomeration is only that time between the oxidation (and release) of the aerosol, and the time that it takes to reach the sampler. The combination of concentration, flow, and time are all interrelated.

Observations of particle growth

During each experiment in the LTC, a measurement of the initial airborne particle size distribution is made when the concentration in the chamber is low. Measurements of the distribution are repeated as more aerosol is introduced into the chamber and as the concentration decreases due to settling and plating. One observes for each test that a maximum mass mean radius, \( r_a \), occurs in a time which is greater than the production time of the aerosol. As long as a given initial size is being produced, the airborne distribution is governed somewhat by the source.

The collection of the settled mass per unit time and area, \( dM_F/dt \), is related to the settling velocity, \( v_s \), and the instantaneous concentration \( \rho(\mu\text{g/cm}^3) \) as

\[ \frac{dM_F}{dT} = v_s \left( \frac{\text{cm}}{\text{sec}} \right) \cdot \rho \left( \frac{\mu\text{g}}{\text{cm}^3} \right) \]  \hspace{1cm} (1)

Thus, as the concentration of a given particle with a settling velocity, \( v_s \), is increased, the rate of deposition \( dM_F/dt \) should increase. However, if a distribution exists,

\[ \frac{dM_F}{dT} = \frac{dM_F}{dT} \]
is not constant, i.e., as the larger particles settle out, $v_s$ would decrease as $\rho$ decreases. Since both the deposition rate and the concentration are observables, one can easily compute $v_s$ vs time. Note also that $v_s$ is proportional to the Stokes radius. For each experiment which has been performed the value of $v_s$ or $r_{\text{Stokes}}$, computed in the above manner, increases to a maximum value at some time after the maximum concentration, $\rho_{\text{max}}$, occurs. The maximum Stokes radius, $r_m$, is larger than the maximum value of the mass median radius, $r_a$, measured in the air. Figs. 1 and 2 show the air concentration vs time and the accumulated mass vs time for some of the experiments which have been performed in the LTC. It is easy to note that high air concentrations decrease faster than lower concentrations.

\[ \frac{dn}{dt} = -Kn^2 \]
If \( n = n_o / 2 \), it can be shown that the half time, \( T_{50} \), is

\[
T_{50} = \frac{1}{n_o K} = \frac{(\pi/6) d D_o^3}{M_R \frac{V}{K}}
\]  

(3)

where:

- \( K \) = agglomeration constant
- \( d \) = material density (g/cm\(^3\))
- \( M_R \) = grams released
- \( V \) = volume of container
- \( D_o \) = initial diameter of particles = 2\( r_o \)
Thus, the time to reduce the initial concentration of material is related inversely to the mass concentration when the initial size is a constant. When the concentration of airborne material decreases uniformly at all heights in a chamber (stirred settling) it can be shown from computation that the time, \( T_{50} \), for the concentration of a log normal distribution to decrease to 1/2 of the initial value is very nearly

\[
T_{50} = \frac{0.693H}{v_s} = \frac{0.693H}{0.012r_{50}^2C} \text{ (sec)}
\]

where,

- \( H \) = height of the chamber (cm)
- \( v_s \) = settling velocity of particles (cm/sec)
- \( C \) = Cunningham correction factor.

The quantity \( v_s \) is defined as the settling velocity for \( r_{50} \), the mass median radius of a log normal distribution. If \( \sigma = 1 \), then \( v_s \) is the settling velocity of a monosized distribution. When \( \sigma \) varies between 1 and 2.5, the mean value of \( T_{50} \) is

\[
\frac{T_{50}}{H} = \frac{50}{dr_{50}^2} \frac{(sec)}{cm} \quad (5)
\]

In the LTC experiments with sodium oxide, the time, \( T_{50} \), is defined in terms of the airborne mass which has settled. Note that not all of the released mass settles, but that fraction which does settle in a stirred environment follows the above relationship. Thus \( T_{50} \) represents the time for 1/2 of the mass on the floor at \( t = \infty \), to settle. A further definition of \( T_{50} \) is that it is the time for 1/2 of the mass to settle on the floor after the production or source term has ceased.

For the experiments performed to date in the LTC, we observe that

\[
T_{50} = \frac{70 \text{(min)}}{\rho_R^{0.8}} = \frac{4200 \text{(sec)}}{\rho_R^{0.8}}
\]

The height \( H \) (cm) in the LTC is 180 cm and \( d \) for sodium oxide is 2.27 gm/cm\(^3\), thus normalizing we obtain

\[
\frac{T_{50}}{H} = \frac{53}{d\rho_R^{0.8}} \quad (6)
\]

This is the empirical observation between \( T_{50} \) and \( \rho_R \). Therefore, Eqs. 5 and 6 can be used to formulate a relation between \( r_{50} \) and \( \rho_R \):

\[
r_{50} = (\rho_R^{0.4})
\]

This relation has been shown to hold for released mass concentrations of sodium oxide in the range from 2 to 60 \( \mu g/cm^3 \). For concentrations much less that 1 \( \mu g/cm^3 \), i.e., \( 10^{-2} \mu g/cm^3 \) or so, the agglomeration time constant is less than that for settling and thus \( T_{50} \) would be a constant and independent of concentration. Fig. 3 shows the dependence
of the observed maximum mass mean radius on $\rho_R$, the released mass concentration of sodium oxide aerosols for the LTC experiments. This figure summarizes the most important empirical relationship observed for sodium aerosols.

![Graph of mass mean radius vs. $\rho_R$](image)

**Fig. 3.** Experimental observations of $r$ versus $\rho_R$ in LTC for sodium oxide aerosols.

### OTHER CONCENTRATION EFFECTS

A simple model can be used to describe the behavior of an aerosol in a closed container. With an equation of the form

\[
\frac{d\rho}{dt} = S - \alpha \rho - \beta \rho = S - \lambda \rho
\]

where

- $\rho$ is concentration ($\mu g/cm^3$)
- $\alpha = \nu_s/H$, the settling removal rate
- $\beta = \nu_w A_w/V$, the plating removal rate
- $\lambda = \alpha + \beta$
- $S = \text{source term} (\mu g/cm^3 \text{ sec}) = \rho_R/\tau$
- $\tau = \text{generation time of aerosol} (\text{sec})$
there are a number of other observations that one can make in order to formulate a model. If we solve Eq. 8, we obtain

\[
\rho = \frac{S}{\lambda} (1 - e^{-\lambda t}) \quad 0 \leq t < \tau
\]

\[
\rho(\tau) = \frac{S}{\lambda} (1 - e^{-\lambda \tau}) \quad \text{at } t = \tau
\]

\[
\rho(\tau) = \rho_{\text{max}} \quad \text{at } t = \tau
\]

\[
\rho = \frac{S}{\lambda} (1 - e^{-\lambda t}) e^{-\lambda (t - \tau)} \quad t > \tau
\]

Also one can show that

\[
M_F + M_w = M_R
\]

where

\[
M_F + M_w = \text{total mass on the walls and floor at } t = \infty, \text{ thus }
\]

\[
M_F = \frac{\alpha}{\lambda} M_R
\]

\[
M_w = \frac{\beta}{\lambda} M_R
\]

\[
\frac{M_F}{M_R} + \frac{M_w}{M_R} = \frac{\alpha}{\lambda} + \frac{\beta}{\lambda} = 1
\]

In all experiments conducted in the LTC, observations are made of \(\rho(\tau) = \rho_{\text{max}}\), the ratios \(M_F/M_R\) and \(M_w/M_R\), and \(\tau\) the time that \(\rho_{\text{max}}\) occurs.

The following general observations have been made:

1. As \(\rho_R\) increases, \(\rho_{\text{max}}/\rho_R\) decreases from a value of 1 to lower values

2. As \(\tau\) increases for a constant \(\rho_R\), \(\rho_{\text{max}}/\rho_R\) decreases

3. As \(\rho_R\) increases, \(M_F/M_R\) increases

4. As \(\rho_R\) increases, \(M_w/M_R\) decreases.

The wall plating of an aerosol in a quiescent environment will be negligible since the aerosol diffusion constant and concentration gradient are very small. When a high temperature gas is generated in an enclosure with initially cold walls, an ideal environment exists for wall deposition of the aerosol.

The empirical observation of the wall plating half time in the LTC is

\[
T_{50} \text{ (wall)} = \frac{77 \text{ (min)}}{(\rho_R)^{0.6}}
\]
and, if normalized for any size container of $V(\text{ft}^3)$ and $A_w(\text{ft}^2)$,

$$T_{50}^{\text{wall}} = 208 \frac{V}{A_w (\rho R)^{0.6}} \text{ (min)}$$

Thus large buildings have wall plating half times which are long.

The time constants $\alpha$ and $\beta$ can be shown to be

$$\beta = \nu \frac{A_w}{V} = 1.67 \times 10^{-3} \frac{A_w}{V} (\rho)^{0.6} (1/\text{sec})$$

and

$$\alpha = \frac{\nu_s}{H} = \frac{0.03 \rho^{0.8}}{H}$$

Thus, one can substitute for $\alpha$ and $\beta$ in Eq. 8 a function which depends on $\rho$, the mass concentration. The empirical relations for $\alpha$ and $\beta$ fit the experimental results if $\rho R$ is placed instantaneously in the chamber; i.e., no source term in Eq. 8. When a source term is used, the values of the exponents and coefficients must be modified.

**DISTRIBUTION SHAPE AND AGGLOMERATION**

Whether an initially heterogeneous distribution of aerosols agglomerates or settles without agglomeration, the process provides a means of narrowing the distribution. In the latter, larger particles escape by settling and in the former small particles are agglomerated. If both removal mechanisms occur, the distribution changes by both mechanisms.

In the experiments which have been described, the spread expressed by $\sigma$ decreases from a value of 2.1 to 1.5 as the airborne concentration ratio decreases from 1 to $10^{-3}$.

Electron microscope photographs of samples obtained with electrostatic precipitators show that the number of particles decreases with time and the sizes increase.

The classical relation between the mass median diameter (mmd) and the count median diameter (cmd) is only observable at low concentrations or for the initial size. Subsequent samples obtained after the concentration increases cannot be observed on the microscope because there are too many particles per field.

**SUMMARY**

The experimental results for Na$_2$O particulates described in this paper appear to fit the general behavior of an agglomerating aerosol in a stirred environment. Because of numerous experimental results and the empirical relations which have been observed it has been possible to formulate models which effectively predict the results which have been generated in a laboratory test chamber (LTC). These models, in turn, can be used to extrapolate predictions for accidents which may occur in Liquid Metal Fast Breeder reactors. When the growth in particle size
is allowed for a given released mass concentration, a considerable reduction in the radiological source term occurs since the fallout rate is increased thus reducing the concentration which is available for leakage. The primary empirical relationship which has been developed from these studies is that the mass mean radius or Stokes radius, \( r \), which determines the fallout characteristics of a released concentration \( \rho_R(\mu g/cm^2) \) is greater than \( r = (\rho_R)^{0.4} \) for Na\(_2\)O aerosols.

REFERENCES


DISCUSSION

W. SCHIKARSKI: What process, such as sedimentation or convection, governs the concentration decrease? Does your concentration time function hold for long periods of the order of days, or does the concentration level off and, if so, when?

R. L. KOONTZ: The concentration decreases as a result of sedimentation to the floor, and deposition on the walls. The latter process is due to diffusion, convection and thermal gradients. Concentration levels have decreased to as low as \( 10^{-6}\mu g/cm^3 \) in 1 day, even when the initial levels were from \( 10-30 \mu g/cm^3 \). We have not observed a levelling off in the concentration. The air is stirred throughout the measuring period by means of a heater, thus eliminating stagnation.
THE CHARACTERIZATION OF UO₂ AEROSOLS BY AERODYNAMIC PARAMETERS *

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CANOGA PARK, CALIF., UNITED STATES OF AMERICA

Abstract

THE CHARACTERIZATION OF UO₂ AEROSOLS BY AERODYNAMIC PARAMETERS. Information on the behaviour of PuO₂ aerosols is required for the analysis and design of safeguards for fast breeder reactors. Experimental investigations of U₃O₈ aerosols (as a simulant for PuO₂) produced by arc vaporization of UO₂ - stainless steel mixtures in air have been conducted, and the particle characteristics of the aerosols studied as a function of initial concentration and time. The increasing complexity of the three-dimensional, chain-like, multibranched agglomerates which are produced in increasing number with prolonged aging has been investigated by electron microscopy. It was evident that characterization of the aerosol particle size distribution could not be performed by microscopic examination, since the effective size of the agglomerate was difficult to determine.

The spatial and temporal distribution of U₃O₈ aerosols were studied in a 40 ft³ test chamber. Measurements were obtained for the mass concentration and aerodynamic particles size of the airborne material, the settling rate on the floor of the test chamber, and the deposition rate on the wall, all as a function of time. It was found that the removal functions were related to the aerodynamic particle size of the aerosol, rather than to an optically measured 'size'. The particle size of the aerosols was characterized by both the settling velocity of the released mass and the round-jet cascade impactors. Both methods yielded similar results. Using the settling times of the airborne material, it was possible to relate size and concentration. The concentration was proven to be homogeneous.

Mixtures of aerosols produced by vaporizing UO₂ - stainless steel in air and burning liquid sodium simultaneously were also studied. Both materials agglomerated together to form a complex branched aggregate which settled to the floor at a rate proportional to the combined mass concentration.

Analyses of cascade impactor data show that the aerodynamic median diameter increases to a maximum value as a function of the released materials. The material collected on each stage revealed that the iron, sodium, and uranium oxides have identical distribution patterns. Complete characterization of the complex behaviour of such mixed aerosols can only be made by the use of well-calibrated impactors and microchemical techniques.

INTRODUCTION

The evaluation and control of the potential hazard from aerosolized mixed plutonium-uranium fuels during a major fast breeder reactor accident is dependent upon knowledge of the temporal dependence of concentration and rate of leakage of the airborne material from the containment vessel. The characteristics of any aerosol of mixed particle sizes continually change, due to settling and due to agglomeration of particles to produce larger particles. Previous work by Atomics International on aerosols generated during sodium fires indicates that the particle size to which the airborne material grows, due to agglomeration, increases as the concentration of the sodium aerosol increases.¹ The increased

* Based upon studies conducted for the US Atomic Energy Commission under Contract AT(04-3)-701.
particle size effect corresponds to an increased settling rate as the concentration increases.

If this phenomenon can be proved to exist for all aerosols, regardless of the chemical species, then credit can be taken for natural removal functions in the safety evaluation of fast breeder reactors, where plutonium oxide, uranium oxide, and fission products are to be released during the design basis accident (DBA).

It has been shown by Brookhaven National Laboratory\cite{2} that there are close similarities between the branched chain agglomerates of particles resulting from vaporization of PuO$_2$ and those resulting from the vaporization of UO$_2$. In addition, a large fraction (~80\%) of mixed oxide fast reactor fuel is UO$_2$. Thus, vaporized UO$_2$ can be used to characterize the behavior of aerosols formed from the release of mixed oxide fuels.

**EXPERIMENTAL PROCEDURES**

A laboratory test chamber, 6 ft high with a volume of 40 ft$^3$, previously used for sodium aerosol studies\cite{3} was modified for use in UO$_2$ aerosol studies.

A d.c. arc generator (Fig. 1) was used to produce vaporized UO$_2$. The vaporizer itself consists of a central, UO$_2$-covered tungsten electrode and a stainless steel cup electrode filled with compacted UO$_2$ powder. To start the arc, a fine iron wire is placed in the UO$_2$ powder. As the tungsten electrode and UO$_2$ powder are consumed, the cup electrode is advanced by a motor whose speed and direction are controlled by the current flowing through the electrodes. During the UO$_2$ vaporization cycle, some of the stainless steel cup and the tungsten electrode are also vaporized, resulting in a mixed element vapor. Fig. 2 shows the appearance of the electrodes after use in a test. As much as 3.6 g/min of mixed oxides have been released for as long as 3.5 min. When mixtures of UO$_2$ and sodium aerosols are studied, a separate pot is used to heat the sodium to 1000°F before ignition to form sodium oxides.

During the experiments the following samples were taken

1) Automatic devices were used to collect incremental samples of wall-plated material and settled material.

2) Air concentration samples were collected on millipore filter papers.

3) Mass size distribution samples were taken, using modified round hole jet impactors.

4) Specimens for electron microscopy were taken with a point-to-plane electrostatic precipitator and with thermal precipitators.

X-ray fluorescence analyses of the samples are performed for uranium, iron, and tungsten. The validity of this method was checked with spot samples by means of colorimetry and u.v. fluorescence analysis, and it was found to be within ±3\%. Additionally, weights of the mixed oxides in selected samples, measured prior to analysis, compared favorably with the total weights obtained by summing the separate weights for each material obtained from x-ray fluorescence. The nondestructive fea-
ture of the latter method allowed the determination of sodium to be performed by means of flame photometry. During these analyses, x-ray diffraction studies indicated that the UO$_2$ had been oxidized to U$_3$O$_8$, the iron to Fe$_3$O$_4$, and the tungsten to a mixed oxide similar to WO$_3$.

EXPERIMENTAL RESULTS AND DISCUSSION

Six experiments have been completed to date, one of these being a sodium-UO$_2$ experiment. The general results and experimental parameters are presented in Table I. Maximum airborne mass concentrations of the mixed oxides ranged from 0.06 to 12.0 μg/cm$^3$. In all experiments, the time required for the air concentrations to decrease to one-half of its maximum value was lessened as the concentration was increased (See Fig. 3 and Table I). Fig. 3 also shows that the half-time during any one experiment increases as the concentration decreases. The removal rate is related to the settling velocity of the aerosol, which can be described by the Stoke's relation

\[ v_s = 0.012 \frac{d^2}{\rho} \]

where

- $v_s$ = settling velocity (cm/sec)
- $d$ = density of particles (g/cm$^3$)
- $r$ = particle radius (μm).  

FIG. 1. UO$_2$ sample in arc-melting apparatus.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Initial Oxygen (%)</td>
<td>21</td>
</tr>
<tr>
<td>Mass of Oxides Collected in Chamber, $M_R$ (g)</td>
<td>0.30</td>
</tr>
<tr>
<td>Released Air Concentration, $\frac{M_R}{V} = \rho_R$ ($\mu g/cm^3$)</td>
<td>0.26</td>
</tr>
<tr>
<td>Measured Maximum Air Concentration, $\rho_{max}$ ($\mu g/cm^3$)</td>
<td>0.056</td>
</tr>
<tr>
<td>Time of Maximum Air Concentration, $\tau$ (min)</td>
<td>2.0</td>
</tr>
<tr>
<td>Half-Time of Air Concentration, $T_{50A}$ (min)</td>
<td>160</td>
</tr>
<tr>
<td>Maximum Airborne Median Aerodynamic Radius, $\sqrt{d} r_{50}$</td>
<td>-</td>
</tr>
<tr>
<td>Fraction of Total Mass on Floor</td>
<td>0.86</td>
</tr>
<tr>
<td>Fraction of Total Mass on Wall</td>
<td>0.14</td>
</tr>
<tr>
<td>Half-Time of Floor Deposit, $T_{50F}$ (min)</td>
<td>80-140</td>
</tr>
<tr>
<td>Half-Time of Wall Deposit, $T_{50W}$ (min)</td>
<td>-</td>
</tr>
<tr>
<td>Mean Aerodynamic Equivalent Radius, $\sqrt{d} r_{50}$ (Based on $T_{50F}$)</td>
<td>1.43-1.1</td>
</tr>
<tr>
<td>Maximum Aerodynamic Equivalent Radius (Based on floor deposition rates)</td>
<td>-</td>
</tr>
<tr>
<td>Time of Maximum Aerodynamic Equivalent Radius (min)</td>
<td>-</td>
</tr>
<tr>
<td>Composition of Aerosol (%)</td>
<td></td>
</tr>
<tr>
<td>Uranium oxide</td>
<td>-</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>-</td>
</tr>
<tr>
<td>Tungsten oxide</td>
<td>-</td>
</tr>
<tr>
<td>Sodium oxide</td>
<td>-</td>
</tr>
</tbody>
</table>

* Mixed sodium-UO$_2$ fire
Thus, the data of Table I and Fig. 3 infer that larger particles are produced at higher airborne concentrations, since a faster rate of decrease occurs at these levels, which must be due to higher settling velocities.

During Test No. 4, as shown in Fig. 4, the airborne concentrations of sodium oxide, uranium oxide, and iron oxide decreased at similar rates, indicating that the aerosol particles are behaving as a composite of all the oxides, rather than as individual materials (Fig. 4).

Since the airborne concentration decreases faster with increasing concentration, the deposition rate on the floor or wall should also increase at higher airborne concentrations. The cumulative settled masses,
as plotted in Fig. 5, show that as the concentration is increased, the slope or deposition rate increases with concentration. In Tests 3, 5, and 6, the deposition rates are very similar, and therefore the air concentration and floor half-times for these tests should be similar, as indeed they are (See Table I). For mixed composition aerosols, there is a great deal of uncertainty about the effective material density, $d$, which affects the settling characteristics. The variation in composition can be seen in Table I.
The arc-generated, airborne uranium oxide, collected by means of electrostatic precipitators and examined by means of electron microscopy, shows comparable structure in all tests. The basic structure of the metal oxide aerosol consists of spherical particles, 0.1 µm and less in diameter, agglomerated in a branched-chain configuration (Fig. 6). As the airborne material is allowed to age, the chains become larger in size and more complex. Fig. 7 shows the rapidity with which this occurs. The sample times of 0.5, 3.5, and 5.0 min, with their corresponding chain sizes, are representative of all uranium oxide aerosols generated during these tests.
FIG. 5. Cumulative settled components of mixed oxide aerosols in laboratory test chamber.

The particle chains in Fig. 7 also indicate the problem which can arise when photomicrographs are used to determine the particle size distribution of a sample with such complex chains. It is extremely difficult to assign an equivalent size, using projection techniques obtained with instruments like the Zeiss particle size analyzer. In addition, measurements of the horizontal projection of particles assume that there is a third dimension to the particles which is equal to the horizontal projection. It has been found, by electron microscopy shadowing techniques, that, while the chain length may be as long as 10 μm, the thickness of the chain can be as little as 0.1 to 0.2 μm. For these reasons, microscopy has only been used to examine structural detail, not to obtain particle size distributions. With the microscope, the uranium oxide chains can be seen to act as nuclei on which other materials agglomerate. In Fig. 8, sodium oxide is seen to be associated with the UO₂. However, it is the chemical analysis of the deposition samples which allows one to state that the air and floor half-times for Na and U are the same.

Particle size distributions may be correlated, through the use of cascade impactors with stage calibrations, in terms of aerodynamic equivalent diameters, as proposed by Mercer[4]. The aerodynamic equivalent radius (AER) is related to radius by

\[
AER = \sqrt{d \cdot r}
\]

where

- \(d = \text{density of aerosol particle (g/cm}^3\)\)
- \(r = \text{radius (μm)}\).

The use of aerodynamic equivalent sizes to describe particle distributions is helpful, in that settling velocities are proportional to \((\sqrt{d \cdot r})^2\), thus,
FIG. 8. Na₂O and U₃O₈ aerosol in air sampled at 2.0 and 6.0 min respectively after addition of the Na₂O to the U₃O₈.

FIG. 9. Example of aging effects on particle size during test No. 2.
the particle density is not needed for deposition rate calculations. Impactor studies of several of the tests indicate a growth in particle size from some initial size to a maximum at a time later than that at which the peak concentration occurs (Fig. 9 shows the data for Test 2).

![Graph showing comparison of airborne aerodynamic particle size and settled aerodynamic size.]

Samples taken within 1 min of the start of vaporization for particle size analysis by electron microscopy are already complex chains which are difficult to evaluate for size. Cascade impactor samples taken during this period to evaluate the initial aerodynamic size show a range of aerodynamic equivalent radius from 0.8 to 1.2 \( \mu \text{m} \) with geometrical standard deviation, \( \sigma \), of 2.4 to 2.6. If the effective density for the aerosol is assumed to be 4 g/cm\(^3\), then the initial mass median radius is 0.4 to 0.6 \( \mu \text{m} \). Similar data from all experiments show that the maximum size to which the airborne aerosol grows is directly related to the released mass concentration. Analyses of the deposits on the impactor stages show that the mass fraction of each material on each stage is the same for all materials which comprise the aerosol, this indicates that a composite particle is present whose aerodynamic properties are a function of the mixture, rather than any single component.

The rate at which settled material is accumulated can also be used to determine aerodynamic sizes of the settled material. If the system is stirred (uniform concentration at all heights and at all times), the time for 50% of the settled material is related to a mean aerodynamic equivalent size by

\[
T_{50} = \frac{0.693H}{V_s} = \frac{0.693H}{0.012 \text{ dr}^2}
\]
where
\[ T_{50} = \text{half-time for fallout (sec)} \]
\[ H = \text{height of chamber containment (cm)} \]
\[ v_s = \text{particle settling velocity (cm/sec)} \].

Since there is a certain amount of fallout occurring during the time it takes the air concentration to reach a maximum, a normalizing time (\( r \)), the time of the peak concentration, is used as the initial point for half-time calculations. Therefore, all half-time (\( T_{50} \)) calculations and mean aerodynamic equivalent sizes are based on that material which settles after the peak air concentration is reached.

\[
(\sqrt{d} \cdot r)_{50} = (\rho R)^{0.31}
\] (3)
CONCLUSION

When UO$_2$ is arc vaporized in air, an aerosol of U$_3$O$_8$ is produced which forms branched-chain agglomerates composed of many sphere-like particles, less than 0.1 µm in diameter. The chain complexity increases with time and concentration, producing larger effective particles with faster settling velocities. The agglomerate consists of an intimate mixture of the uranium oxide and other metal oxides which might be produced during the vaporization phase. The chained structure, with much void volume, and the high ratio of horizontal projection to vertical projection on samples deposited on electron microscope grids, make it difficult to assign aerodynamic particle sizes by microscopic techniques.

A more suitable measurement parameter is the aerodynamic equivalent radius, which can be obtained from cascade impaction sampling of airborne particulates or from analysis of deposition rates of the settled component. All tests show that an increase in particle size, from an initial value to a value which is dependent on the mass of aerosolized material, occurs. Knowledge of the aerodynamic size characteristics allows one to predict both the aerosol depletion rate and the settled component accumulation.

In the presence of other metal oxides such as sodium oxide, the uranium oxide chains and the other aerosols agglomerate to form a larger aggregate. The removal rates of the sodium oxide - uranium oxide mixture is different from either pure sodium oxide or uranium, iron, and tungsten oxides. This aspect of the problem is the focus of future work, although some preliminary results indicate that, at a given released concentration, the sodium oxide - uranium oxide mixture falls out faster than either of the constituents would if they were released separately and at the same individual concentration.

The results of the present study can be used to relate the rate of fallout to the mass of material released during a design basis accident of a liquid metal fast breeder reactor.

If the experimentally determined relation (between concentration and the mean particle size to which the initial distribution grows) can be extrapolated to the higher concentrations and larger volumes in LMFBR, then one can expect a considerable reduction of airborne core materials as a function of time for the DBA. This reduction decreases the radiological source term, and thus the dose at the site boundaries.

REFERENCES

DISCUSSION

J. D. JOUBERT: You pointed out quite correctly that in the case of a uranium oxide (U\(_3\)O\(_8\)) aerosol made up of complex chains of varying length insufficient knowledge is available on the size of the basic particles. You have characterized the aerosol by the hydrodynamic, or Stokes, diameter. If we want to trap the aerosol with paper, glass-fibre or electrostatic filters, can we say that the Stokes diameter characterizes the aerosol in these specific cases or is it not rather characterized by the sizes of the links or some other parameter? This is a fundamental problem in the study of aerosol capture in the case of aerosols composed of more or less merged chains.

L. BAURMASH: The properties which we have measured, settling velocity and impaction efficiency, are both functions of the aerodynamic or Stokes size. We feel that any aerosol property which is dependent on particle transport, such as filtration and electrostatic precipitation, would also be a function of the aerodynamic size. However, there may be properties which are not functions of the aerodynamic size, such as optical extinction.
THE KARLSRUHE RESEARCH PROGRAM ON NUCLEAR AEROSOLS AND ITS RELATION TO THE PLUTONIUM HAZARD OF FAST SODIUM REACTORS

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Abstract

THE KARLSRUHE RESEARCH PROGRAM ON NUCLEAR AEROSOLS AND ITS RELATION TO THE PLUTONIUM HAZARD OF FAST SODIUM REACTORS. The Karlsruhe Aerosol Research Program was started in 1967 at the Nuclear Research Center Karlsruhe to study nuclear aerosols which may be generated in nuclear accidents. In particular, aerosols from accidents in fast reactors, their processes of generation, transport and impairment in reactor buildings are under investigation.

The test facility used for the investigation of nuclear aerosols (called TUNA) is described together with the various steps of the experimental program. Theoretical analysis of the possible accidental plutonium release from fast reactors has shown the importance of the problem. The aspects of plutonium release via formation of aerosols are discussed, particularly in respect to the uncertain or unknown parameters and number involved. The conclusions drawn from these considerations which led to the present outline of the Karlsruhe Research Program on Nuclear Aerosols are discussed. The first results from experiments on UO₂ aerosols produced under simulated accident conditions by the exploding-wire technique are also given.

1. INTRODUCTION

Reactor siting is mainly a problem of activity release due to a major accident. In estimating the accidental activity release and assessing the hazard to the public, accident and activity release models are used. Many parameters which are not well known or even not well understood enter the calculations. Since data are lacking, numerous conservative assumptions are made. In particular, the physical and chemical nature of the activity-carrying material released from the reactor fuel, its behaviour in a post-accident containment atmosphere, its leakage and transport characteristics, and the potential radiation exposure still pose many unresolved questions. The importance of the subject is illustrated by the number and size of research programs conducted in various countries on the various aspects of activity release.

The Karlsruhe Research Program on Nuclear Aerosols in its present phase is directed at some specific problems connected with the accidental activity release of fast breeder reactors. In particular, in sodium-cooled fast breeders some specific questions exist with respect to activity release and to activity-release-reducing engineered safeguards. A better understanding of the phenomena involved would certainly give better insight in the unresolved questions of accidental activity release from thermal reactors.
This paper discusses characteristics of activity release models, the role of aerosol formation in activity release; and the objectives of the Karlsruhe aerosol program.

2. CHARACTERISTICS OF ACTIVITY RELEASE MODELS

The inventory of radioactive material in a reactor core can be as high as $10^8$Ci, depending on isotope and burn-up. The maximum permissible free handling activity can be as low as $10^{-6}$ Ci, depending on isotope and burn-up. Therefore, 14 decades of activity is the range which must be treated in assessing activity release in core destructive accidents.

Just how much of the activity released from the fuel in an accident could reach a person in the vicinity of the reactor depends on various parameters, such as reactor design, design of the containment system and meteorological conditions. The most important problems, however, are (1) the function of activity release from the core; and (2) decontamination of the containment atmosphere from airborne activity.

At present most reactor accident analysts use what may be called the 'evaporation model' in describing the amount and time function of activity release from reactor fuel. This model in its most simple form assumes that fission products and fuel material can escape from the core into the containment atmosphere according to the fuel temperature encountered in the accident and the corresponding vapour pressure of the fission-product isotope under consideration.

Therefore, in core destructive accidents like core melt-down due to loss of coolant of a thermal reactor, the part of the activity inventory which is assumed to be released from the fuel can be calculated in terms of the percentage of core melting since the boiling point of most fission products, particularly the important ones in respect to radiation burden, do not exceed the melting point of $\text{UO}_2$. More or less all important fission products are released from the fuel on reaching melting point. In accidents like core vaporization due to a reactivity excursion of a fast reactor, the activity release is even easier to predict. Since essentially all elements or compounds existing in reactor fuel after burn-up have boiling points lower than the $\text{UO}_2$ boiling point, all fission products, fuel isotopes, cladding and coolant elements will be vaporized and released to the containment atmosphere.

It can be concluded that in the 'evaporation model' the percentage of released radioactive material is fairly high and probably overestimated. This approach is certainly both conservative and pessimistic.

The 'evaporation model' can describe the primary activity release 'on the safe side'. However, it is inadequate in one important point, namely, it does not take into account the physical form of the material released which is responsible for a number of decontaminating processes taking place in the atmosphere. Here a better approach, what we call the 'aerosol model', can improve the situation. This model is based on the following arguments:

(1) Large accidents in nuclear reactors set free very large amounts of radioactive material which must stay airborne for long times (hours) to leak through the containment barriers and present a hazard to the environment.
(2) The released material may be in the form of gases, vapours or aerosols. Since vapours behave very much like gases if their droplets are small enough, and since some vapours may be considered as aerosols, the released material exists essentially in the form of gases and aerosols.

(3) The release of gases out of the reactor plant can be predicted fairly accurately. The problems to resolve lie in understanding the transport characteristics of nuclear aerosols generated in core-destructive accidents and suspended in the containment atmosphere.

The aerosol model provides several advantages which could lead to a more realistic description of activity release. In the aerosol model we do not ask how much active material is released from the fuel, but rather how much active material can stay airborne in the containment atmosphere during the accident. Therefore, we do not ask for release fractions of specific fission products which will be subject to doubt as long as accident models are not sufficiently verified. We ask rather for aerosol behaviour and aerosol parameters which provide much better access to experimental investigation and justification. Furthermore, the aerosol model illuminates which parameters are of importance in the attempt to reduce the activity release in an accident. For instance, the containment volume is directly proportional to the airborne aerosol mass and therefore, activity. Minimizing the free containment volume can help to reduce the gross activity release considerably. Studying post-accident aerosols would lead also to optimized engineered safeguards, such as filter systems, spray systems etc.

3. ACTIVITY RELEASE FROM THE FORMATION OF AEROSOLS IN FAST REACTOR ACCIDENTS

Accidental activity release in fast reactors differs from that in thermal reactors in two aspects. First, the initiation and course of large accidents in fast reactors are different, secondly, the amount of radioactive inventory capable of being released to the containment atmosphere is different. At present large accidents in fast reactors are assumed to produce reactivity excursions with subsequent melting and vaporization of reactor fuel and of other core materials. Therefore, activity release from the core is nearly complete due to vaporization of all core material and depends only on the percentage of core vaporization. Consequently, solid materials, such as high melting oxides, can also be released.

Since almost all core materials can be released from the core, there is no sense in defining release fractions for any specific radioactive elements. We should rather ask how the released material behaves after vaporization. Depending on pressure, temperature and other conditions, it will certainly recondense and form aerosols which then can be the subject of various processes such as coagulation, diffusion, thermophoresis, sedimentation and plate-out. Fortunately, most of these processes tend to decrease the airborne aerosol concentration, i.e. the containment atmosphere has a self-cleaning effect. However, because these decontamination processes depend on many parameters which are not well known, the amount and the time function of these air-cleaning processes cannot be predicted reasonably.

A number of aerosol parameters must be known to estimate activity transport in containment systems after accidents. First of all the primary
FIG. 1. Large accident dose to different organs of typical fast sodium reactor.
The particle size distribution is important. It depends strongly on the energy inserted into the fuel during vaporization. Particles created by recondensation in most cases are observed to be spherical. Soon after production of the primary particles coagulation takes place, forming larger agglomerates. These agglomerates differ in size, form, weight, porosity etc. depending on the primary particle size and on the conditions under which the agglomerates are formed. The particle coagulation depends strongly on the particle concentration. Therefore, the most important parameters in the description of aerosol formation and behaviour after a large accident with core vaporization are:

1. Primary particle size distribution and time behaviour
2. Primary particle concentration and time behaviour
3. Particle coagulation.

Knowing these parameters, most other processes, such as sedimentation or diffusion can be estimated. It has been mentioned that the various accident conditions, such as presence of vapours and gases, gas temperature, pressure, temperature gradients, gas flow etc., influence aerosol behaviour considerably. Because of the presence of various elements in the phase after vaporization, various chemically different aerosols can be formed which may coagulate to mixed aerosols. Since most of these effects cannot be predicted reliably, experimental studies are necessary to investigate the importance of the various postulated effects and conditions.

The second aspect in which accidental activity release of fast reactors differs from that of thermal reactors is the radioactive inventory. Fast reactors can contain 8 times more plutonium. This emphasizes the importance of the accidental release of solid fuel and fission products due to a core vaporization accident. Plutonium is a major hazard to the public in such an accident if it is all released. This is illustrated by Fig. 1 which shows the contribution to the environmental accident dose in the absence of any activity-decreasing engineered safeguard.\(^1\) Plutonium as a bone seeker and entering through the lung makes the major contribution to these doses. It should be mentioned, however, that plate-out factors representing the self-cleaning effect of the containment atmosphere have a considerable influence and are assumed to be pessimistic. As shown earlier [1], plutonium doses can be reduced by up to a factor of 10^4 if the aerosol model with reasonably extrapolated but not yet experimentally or theoretically confirmed and justified parameters is applied.

Accident dose calculations are rather complex because of the numerous reactor and site data involved. They are significant only if they are related to a real reactor plant or reactor design. Therefore the answer to the problem of which isotope in the event of accidental release is the limiting factor in siting may vary with reactor design, accident analysis and site conditions. In our example the doses are calculated taking into account all fuel and fission-product isotopes produced during operation of a 300 MW(e)

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\(^1\) Dose calculations are based on following assumptions:
- Reactor power: 750 MW(th), load factor: 0.7, operation time: 430 d
- Release fractions: halogens 10%, solids 1%, volatile solids 50%, noble gases 100%
- Plate-out half-time: 1 h, 10 h, 1 h
- Double containment (leak rate 1: 50%/d, leak rate 2: 0.5%/d), stack release.
sodium-cooled fast reactor. All doses are calculated according to the ICRP recommendations [2]. Only in the case of the lung dose was a shorter biological half-time for PuO₂ reported in [3] used.

Whether the bone or the lung is the critical organ for plutonium aerosol inhalation depends on several aerosol parameters. First of all, the element composition in the aerosol is important since not only PuO₂ or Pu aerosols will be created. Much more probable is the formation of mixed aerosols containing several elements of the vaporized core material. The degree of mixing depends on coagulation which depends in turn on primary particle concentration. Mixed aerosols may be much more soluble in the body fluid than insoluble metal oxides. Furthermore, particle size influences the internal body transport of inhaled particles. The probability of entering the bloodstream will increase with decreasing particle size.

Another aspect is the off-gas filter system. We do not know very much about how filter systems behave if hundreds of kilograms of dust, i.e. the vaporized core material, become airborne and clog and heat up (because of decay heat) the filter system. The high-efficiency filter may encounter a considerable loss of efficiency. Again particle size and other aerosol parameters are important. In view of these considerations we did not take into account filter factors in the dose calculations of Fig. 1, although a reasonable factor of between 90 to 99% may be justified even for long-term availability and efficiency of off-gas filters. These factors could reduce the bone and lung dose to the external dose which is mainly due to irradiation by noble gases.

4. THE KARLSRUHE AEROSOL RESEARCH PROGRAM

4.1. Status of the problem

Nuclear aerosols, i.e. aerosols generated in large core-destructive reactor accidents, have not been studied very much in the past. This is due to a number of reasons, to mention a few.

Iodine is the most important fission product to be released in a thermal reactor accident. Most iodine escapes from the failed fuel in vapour form creating aerosols only if certain conditions of the containment atmosphere are given.

Large accidents in thermal reactor cores produce relatively small amounts of nuclear aerosols.

Since the activity is the important factor, most release studies concentrate on the measurement of activity transport characteristics rather than on the characteristics of the transported material such as state, particle form, particle size and others.

Nevertheless, the accident analysis of large fast reactors and the growing use of plutonium has put emphasis on the importance of nuclear aerosols. Here, as has been explained in the foregoing chapters, plutonium-bearing aerosols are of prime interest.

Several investigators have attempted to determine the aerosol characteristics of airborne plutonium. Carter [4], Stewart [5] and Ettinger [6] studied the aerosol produced from burning plutonium. They found mass median diameters around 1 - 16 μm [4, 5] and 0.03 - 0.13 μm [6]. The aerosols were almost spherical. No chains were observed. Sherwood
[8], Moss [9] and Brunskill [10] studied plutonium aerosols from radiochemical laboratories. Here mass median diameters fo 0.14 - 0.65 \( \mu m \) [8] and aerodynamic diameter of 5 - 20 \( \mu m \) [9] were found. No information on aerosol concentration, particle density or mass concentration was determined in these measurements which could be used for the estimation of plutonium aerosol behaviour as function of large core-destructive accidents.

Besides the large discrepancy in measured particle size, little information can be drawn from these measurements for the accidental release problem because of the difference in the aerosol production process. It has been known for a long time that aerosol properties, particularly particle size and form, depend on the energy involved in the production process. Other parameters such as temperature, pressure etc., can play a role too. Therefore, the method of aerosol production is of great importance in this context. Experiments carried out by Karioris and co-workers [10] confirmed the influence of energy on particle size. They found a decrease in the particle size of metal oxide aerosols produced by exploding metal wires with increasing voltage of the capacitor bank. Unfortunately no attempt was made to evaluate the electrical energy actually introduced into the metal wire which, of course, is only a small percentage of the electrical energy available in the capacitor bank.

Information on the particle size of metal oxides is also available from industrial processes, such as ore mining, welding etc. Here, again, a tendency to small particles of the sub-micron range \(< 0.5 \mu m\) can be observed [11]. However, direct information on the particle size of plutonium-bearing aerosols cannot be deduced from all these experiments, because of unknown parameters such as aerosol-producing energy, aerosol mass density, particle concentration, and mass concentration.

In principle, metallic dusts and fumes can have particle sizes with molecular diameters around 0.001 \( \mu m \) up to 100 \( \mu m \). Therefore at present the size of plutonium aerosols created in nuclear accidents is quite unknown, although small particles below 1 \( \mu m \) are more probable than larger ones. Unfortunately, data on the other important aerosol parameters such as particle density and particle concentration are not available. From the theory of coagulation we know that high concentrations of particles are not stable. Concentrations higher than \( 10^7 \) particles/cm\(^3\) may stay airborne only a few minutes. Although we probably will have lower concentrations, the possible concentrations must still be studied because of the irregular forms (chains, agglomerates etc.) the aerosols actually will have. The influence of irregular particle forms on mass concentration under typical accident conditions has to be studied.

Well-established theories are available on deposition, diffusion, thermophoresis and other decontamination processes. In most cases, however, they are valid for spherical particles only. Therefore, experimental investigation of irregular particles is necessary to provide sufficient data on the effectiveness of these processes in decontaminating a containment atmosphere.

4.2. Objectives of the program

In view of the foregoing considerations the Karlsruhe aerosol program is aimed at providing information on the following subjects:
(1) Particle size of fuel and fission-product aerosols as a function of energy involved and as a function of other important accident conditions. Upper and lower limits of particle sizes shall be established to give accident analysts a guide if the accident conditions assumed are changed.

(2) Particle and mass concentration as function of vaporized material, energy and accident conditions. Upper and lower limits shall be established to provide information for the assessment of the maximum transported aerosol mass in a reactor containment system. Direct or indirect measurement of particle density shall be made.

(3) Particle chemical composition as function of the accident condition. Because of the mixed aerosols expected the amount of the chemical elements involved and the corresponding specific activity shall be determined.

(4) Time function of the aerosol mass concentrations to estimate the decontamination processes taking place after the accident in the containment atmosphere. Variation of typical accident parameters, such as temperature, gas, gas volume, will help understand the mechanism involved.

(5) Aerosol transport and decontamination studies from the theoretical point of view. Modelling of most important processes shall make the phenomena computable.

The overall objective of the Karlsruhe research program on nuclear aerosols is the complete understanding and the reliable description of activity release and transport in large nuclear reactor accidents. Since nuclear aerosols play an important role in the activity release, the understanding of aerosol behaviour will contribute considerably to the understanding of accidental activity release.

4.3. Program outline

The first phase of the program is concerned with fuel aerosols and their production and measurement under simulated accident conditions. In a pre-operational research and development program the detailed outline of the experimental program and of the necessary facilities were established and supporting theoretical studies were carried out. Since the aerosol formation process is of important influence on particle size and other aerosol parameters, three aerosol production techniques are employed.

(1) The exploding wire technique
(2) Resistance heating
(3) Burning.

The first aerosol production method used is the exploding wire technique. A small pin of UO₂ is preheated to produce electrical conductivity. The electrical energy is inserted by discharge of a bank of capacitors. The electrical energy available is 54 kWsec with time constants of discharge around 1 msec. Both parameters are variable. This allows for the investigation of energy-time effects according to data obtained from the reactor-accident analysis.

The second aerosol production method is based on the well-known electrical heating of solid material in a boat. To avoid any influence of the boat material, different materials, such as tungsten and tantalum carbide, will be compared. Both methods will be used in the same aerosol production chamber on top of the main vessel and comparison of both methods will show how much the aerosol production process influences particle size and form.
Aerosol measurement takes place in a 2-m³ vessel (main vessel) which is equipped with various devices based on the following methods: sedimentation sampling; thermal precipitation; electrostatic precipitation; optical counting; filter column; filter pack; and scintillation spectral analyser.

The whole particle size range (from 100 to 0.001 μm) is covered by these instruments. The thermal precipitator collects particles of all sizes from 10 μm down to 0.001 μm, but needs long times in case of small concentrations to collect statistically sufficient particle populations. The electrical precipitator also collects essentially all particles but allows for better differential sampling. Samples are photographed by light and electron microscope and sized on the basis of equivalent area (projected diameter). The large particle sizes and the particle concentrations are measured by optical counters (Bausch & Lomb). An improved version of present optical counters using a laser instead of light beam is currently under development at Battelle, Frankfurt. It will be available to the program in the near future. Filter methods are used as integral methods for mass concentration measurement, and it is hoped, for differential mass concentration measurement. The whole range of expected particle concentrations from 10⁶ particles/cm³ down to 10 particles/cm³ can be measured. The scintillation spectral analyser which was first described by Binek and co-workers [12] and which is under further development and improvement at Sartorius, Göttingen, will be used to differentiate the various chemical elements in mixed aerosols and to measure their particle size.

There are four test series of the experimental program in the first phase:

Test series No. 1 consists of test runs of the electrical and preheating equipment, calibration and energy and insertion time, and tests of the various aerosol measurement techniques.

Test series No. 2 consists of the production of UO₂ aerosols by small excess energies² in air and measurement of particle size and concentration as a function of time.

Test series No. 3 consists of the production of UO₂ aerosols by various excess energies² in N₂, Ar and He and vapours including sodium vapour with normal and elevated temperatures up to 200°C. Measurement of particle size and concentration as function of time will be performed and the creation of mixed aerosols will be investigated.

Test series No. 4 consists of production of UO₂ aerosols by other methods as resistance heating or induction heating. Comparison will be made to the aerosol produced in test series No. 3 to evaluate influence of aerosol production on aerosol properties.

The main objective of the first phase of the program is to demonstrate the validity of the aerosol model described and to verify the upper limits of mass concentrations of fuel aerosols that are stable in a typical fast reactor accident containment atmosphere and their time behaviour.

The second phase of the program is concerned with aerosols other than those consisting of fuel material. In particular those fission product aerosols will be investigated which are most hazardous to the public. Also nuclear aerosols produced in large accidents of thermal reactors will be studied.

² Excess energy is defined as the energy which is introduced into the probe to exceed the melting point. This energy is responsible for release of particles from the probe.
Aerosols produced by melt-down of fuel in shipping casks and aerosols produced by burning will also be studied.

As an integrated effort computer codes have been developed [13] and will be improved by tracing the most important problems to the resolved.

4.4. Description of facilities

The facility built for the experiments in phase 1 is called "Teststand für die Untersuchung Nuklearer Aerosole (TUNA)" and shown in Fig. 2. The 2-m³ vessel consists of stainless steel for better cleaning. The aerosol production chamber with the preheating device for UO₂ pins (Fig. 3) sits on top of the vessel. Low inductance cables connect the capacitor bank.
Several flanges allow the connection of the aerosol measurement equipment and detectors for temperature, humidity, pressure and temperature gradient measurements. Very low leakage even at higher pressures can be achieved. Filling with gases and vapours including sodium vapour and steam is possible. Heating of the vessel is possible up to 200°C. The capacitor bank has an electrical energy of 54 kWsec. This energy is sufficient to vaporize about 1 cm³ of UO₂. Discharge with several time constants between 100 μsec and 10 msec is possible, depending on the resistance characteristics of the probe to be vaporized and other electrical properties of the facility. Penetrations are designed for high voltage. Aerosol production by electrical resistance heating can be done in the aerosol chamber as well.

4.5. First results

First results from test series No. 1 and 2 have been obtained. In these experiments Cu and UO₂ aerosols were produced by means of the exploding wire technique.

The expected decrease in particle size with increasing energy inserted into the material to be vaporized was found. The primary aerosols were collected by sampling the particles evaporating from the probe directly and depositing them on foils, minimizing any effect of particle size change by coagulation etc. between the creation and sampling of the aerosol particles.

Figure 4 shows the typical copper aerosol produced by the insertion of specific excess energies of the order of 1000 Wsec/g in a copper wire in about 0.05 msec. The aerosol has a logarithmic normal distribution. Mean size of the aerosol is 0.087 μm with a geometrical standard deviation of 1.6.
FIG. 4. Primary Cu aerosols.

FIG. 5. Primary UO$_2$ aerosols.
Figure 5 shows a primary UO$_2$ aerosol produced by the exploding wire technique. This experiment was done in helium. Small chains and single particles were observed. The small chains may be created by some coagulation during the preheating period in which, depending on the vapour pressure, UO$_2$ particles are already emitted from the probe. The aerosol follows a logarithmic normal distribution with a mean diameter of 0.062 $\mu$m and a geometrical standard deviation of 2.1.

A typical single UO$_2$ particle formed within the first minutes after vaporization is shown in Fig. 6.

In Fig. 7 a coagulated UO$_2$ aerosol is shown. Samples were taken by the sedimentation sampler 80 minutes after vaporization collecting for a longer time period. Large agglomerates were formed, although smaller chains still existed. Particle concentrations were not measured in these experiments.

Since typical post-accident containment atmosphere conditions as postulated by the accident analysis of sodium-cooled fast reactors have not yet been applied to these experiments, conclusions as to the most important decontamination processes for UO$_2$ aerosols taking place in a reactor containment cannot be drawn from these results. However, at this stage the following points can be concluded:

(1) The primary UO$_2$ particles are spherical and form chain coagulates.
(2) The particle size decreases with increasing energy inserted.
FIG. 7. UO₂ aerosol in air after 80 min.

(3) There is a tendency towards small primary aerosol particle sizes around 0.1 μm and below, depending on energy inserted.

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REFERENCES

DISCUSSION

H. ISBIN: Are you recommending that we improve safety by making the containment smaller?

W. SCHIKARSKI: Yes, you gain much more by reducing the aerosol concentration, i.e. the airborne activity, than you lose because of higher pressure in a smaller volume. There is an upper limit to the aerosol concentration which can stay airborne for the duration of the accident and this concentration will certainly be proportional to the airborne activity.
PuO₂ - UO₂ - Na AEROSOLS PRODUCED BY VAPORIZATION OF FAST REACTOR CORE MATERIALS *

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Abstract

PuO₂ - UO₂ - Na AEROSOLS PRODUCED BY VAPORIZATION OF FAST REACTOR CORE MATERIALS. A hypothetical accident for fast reactors predicts expulsion of sodium coolant from the core, gross melting and vaporization of fuel into a containment vessel which may contain air or an inert gas for safety reasons. The vaporized fuel subsequently condenses into an aerosol composed of PuO₂ and UO₂ mixed with Na. The characteristics of these aerosols were studied by vaporizing fuel and sodium into various atmospheres to simulate accident conditions.

In all atmospheres, the individual PuO₂ and UO₂ particles formed are cubic in shape and range in size from 40 to 400 Å on an edge. Initially, these particles rapidly coagulate into chain and cluster aggregates measuring 0.06 to 0.3 μm in equivalent diameter. In humid air, the sodium oxide forms spheres and clusters of spheres with an initial count median diameter (CMD) of 0.17. However, in dry nitrogen the sodium shapes are more irregular and have a 0.30-μm initial CMD. The coagulation constant for PuO₂ in dry nitrogen ranges from 3 x 10⁻⁹ to 9 x 10⁻¹⁰ cm³/sec during the 24 hours after generation. At a mass concentration of 22 mg Pu/m³, a typical initial CMD for PuO₂ is 0.14 μm with a geometric standard deviation of 2.6. The mass concentration decreases rapidly with time but tends to reach a "stable" value of 10 μg Pu/m³ after many hours.

The combined aerosols of PuO₂, UO₂, and Na produce fairly constant size distributions depending upon the atmosphere in which they are formed. These agglomerates are composed of twisting chains of cubic shaped particles into which are incorporated sodium spheres and clusters. Dry nitrogen atmospheres produce agglomerates with a CMD of 0.6 to 0.8 μm, while humid air produces much smaller agglomerates having a CMD of 0.25 to 0.39 μm.

A CDC 6600 computer was used to integrate numerically the coagulation relationships formulated by Smoluchowski, with terms added to account for particle formation and settling. Using the experimental data on the particle size distributions and the aerosol number density as a function of time, agglomeration coefficients were evaluated. In addition, the time dependence of the total airborne mass concentration was evaluated by integrating the product of the number density and particle density over all values of the particle radius.

Introduction

The prospect that the continued development of fast reactors fueled with plutonium will result in an abundance of these reactor types requires careful consideration of their safety aspects. Numerous safeguards engineered into their construction and operation should cope with nearly all foreseeable accident conditions of the first and second level.

When consideration is given to the third level of reactor safety, i.e., to the highly unlikely occurrence of a simultaneous failure of all protective systems at the time of a

* This research was performed under the auspices of the USAEC.
reactor accident, it must be assumed that the coolant is expelled from the core and gross melting and vaporization of the fuel occurs.

In the case of sodium cooled fast breeder reactors fueled with plutonium-uranium oxide, the hypothetical accident predicates gross melting of the fuel, compaction of the core producing a prompt critical reactor period, followed by vaporization of fuel and coolant to the containment vessel. The resultant vapor will condense into an aerosol composed of PuO$_2$ and UO$_2$ mixed with Na. The time dependent behavior of the aerosol with respect to coagulation, settling, wall plating, particle size distribution, and particle density is of interest to persons concerned with the possible effect of such an accident on the rate of leakage from the reactor containment and its impact on siting considerations and salvage operations.

The extremely low human tolerance for plutonium is for many situations the determining factor over the radiation effects of fission products$^{[11]}$; therefore, fission products have been excluded from the initial phases of this study.

Experimental Apparatus and Procedure

All of the experiments were carried out using a resistance heater to rapidly vaporize the materials into a flowing gas stream. The heater assembly consisted of a high resistance ribbon filament suspended between two water-cooled copper blocks. Utilizing a power-stat and a 12-volt a.c. power supply, a current of 500 amperes was passed through the filament on which the sample was placed. A temperature of 3000°C could be attained in 3 to 5 seconds. The compound PuC$_2$ melts at 2390°C, while UO$_2$ melts at a somewhat higher temperature of 2840°C.$^{[2]}$ Therefore, the PuO$_2$ vaporization experiments were carried out at ≈2700°C, while a temperature near 3000°C was required to vaporize equal quantities of UO$_2$ and PuO$_2$-UO$_2$ mixtures in similar periods of time. The vaporization usually required from 30 to 45 seconds to be completed, depending upon the sample size. In some of the initial PuO$_2$ experiments, the vaporization was done in a small chamber and the aerosol transported by a gas stream through a duct to the settling chamber. In these experiments, the gas flow was maintained at ≈50 cc/min during vaporization and was terminated after the visible aerosol fume was carried into the settling chamber. The fuel vaporization apparatus was installed directly on the floor of the main settling chamber for all runs with UO$_2$ and the latter ones with PuO$_2$.

Although experiments were carried out in which the sodium and fuel oxide were both placed on the heater filament, it was generally more satisfactory to vaporize the sodium with a separate resistance heater located adjacent to the main filament. Because of the widely differing vapor pressures of PuO$_2$ and sodium, the sodium could be readily vaporized at tempera-
tures below 900°C, considerably lower than those required to vaporize the fuel. Experiments were done in atmospheres of argon, nitrogen, and air with relative humidities as high as 70%. Numerous preliminary screening experiments showed tantalum carbide to be the best filament material, producing no detectable aerosol in all "blank" experiments except in those of high moisture levels.

Several settling chambers were employed during the course of these experiments. Due to the health hazard associated with plutonium, all components of the apparatus were enclosed within a glove box. This severely restricted the maximum size of the settling chamber which could be employed in these studies and necessitated the use of chambers which could be readily removed from the glove box and replaced. Therefore, the larger chambers of 1 cubic meter and 0.75 cubic meter in size were constructed of a specially treated polyethylene material, 0.006 gauge Antistatic Polyethylene Film. The height of both of these enclosures is one meter. A Lucite settling chamber, 0.40 meters in height, was also employed. The surface-to-volume ratio of each of these enclosures was 6.0, 6.6, and 30 m⁻¹, respectively.

Since the primary objective of these studies was an investigation of the quantity of plutonium oxide remaining airborne, emphasis was placed on sampling the airborne concentration and size distribution as a function of time. This was accomplished using thermal precipitators. Their principle of operation is based on the thermophoresis effect. Briefly, a gas sample is withdrawn from the aerosol enclosure at the rate of \( \approx 7 \) cc/min for several minutes. The gas stream containing the aerosol particles is drawn past a hot wire. The aerosol particles deposit on electron microscope grids located in the center of the plugs inserted in each precipitator. The carbon-coated microscope grids are attached to the face of each plug. These are then inserted into the hole adjacent to the wire for each sampling operation. The plugs are removed after the sample is taken and the grids are mounted in a Phillips EM 100B electron microscope for examination.

Pictures are taken of the representative particles deposited on the carbon coating. The count mean diameter of the aerosol particles is determined using a Zeiss TGZ3 particle-size counter.

A number of calibration experiments showed the over-all particle collection efficiency of these precipitators to be better than 95% for the particle size ranges of interest in this study. The plutonium mass concentration data was obtained by alpha-counting of the plutonium deposited on the grids. In addition, plate-out sampling of the floor and walls of the enclosure was done in some experiments.
FIG. 1. Typical PuO$_2$ chain agglomerates.

FIG. 2. Cubic-shaped particles of UO$_2$. 
Results

The vapor of both PuO$_2$ and UO$_2$ condenses into cubic crystals that form into long twisting chains characteristic of metal oxides. See Figures 1 and 2. The experimental results showed that the nature of PuO$_2$ vaporized into nitrogen, argon, and dry air was essentially the same. In each case the individual nucleated particles rapidly agglomerated into branched chains typified by those shown in Figures 3 to 5. Figure 3 is an enlargement of one opening of an electron microscope grid and shows the typical flocculent appearance of the particles and their widely varying size distribution. Figure 4, an enlargement of several of the agglomerates, shows the cubic structure of the individual particles making up the agglomerate with some sodium present. These structures are typical of oxide particles nucleating from a vapor phase.

Experiments in which sampling time and gas flow rate through the thermal precipitator were varied, clearly showed
that these agglomerates accurately represent the characteristics of the airborne material and are not built up on the collection surfaces. Unlike cascade impactor sampling, the thermal precipitators do not have the tendency to destroy the original gas phase agglomerate structures. Figure 5 reveals the three-dimensional nature of the particles. This photograph is a shadow-graph of a PuO₂ aerosol deposit which was made by vaporizing chromium oxide onto a collection grid tilted at an angle of 30° to the vaporizing source beam. The light areas are due to a lack of deposited chromium oxide caused by the vertical structure of the particle protruding between the vapor path and the inclined grid surface.

Visually, deposits of PuO₂ and UO₂ aerosols appear to be similar as seen in Figures 6a and 6b. It is evident that both

FIG. 4. Cubic-shaped PuO₂ particles from > 50 Å to 0.1 µm in size with light coloured Na coating.
FIG. 5. Shadow-graph of PuO$_2$ agglomerates showing their three-dimensional nature.

UO$_2$ and PuO$_2$ aerosols are composed of chainlike agglomerates made up of small cube-like particles. The UO$_2$ agglomerates are usually somewhat larger in physical size than the corresponding PuO$_2$ ones, resulting in a more rapid settling of the pure UO$_2$ as well as mixed PuO$_2$-UO$_2$.

A plot of the change in airborne plutonium mass concentration as a function of time is shown in Figures 7 and 8 for the 17.4 liter and 0.75 cubic meter chambers, respectively. Invariably, the aerosol mass concentration initially drops very rapidly, leveling off to a much slower rate of decrease after the initial period. Usually, several days of settling time are required before the airborne plutonium oxide concentration drops below $10^{-7}$ g/m$^3$, the limit of detection. The behavior
FIGS 6a, b. Comparison of UO$_2$ and PuO$_2$ agglomerates, respectively, indicating similarity.
FIG. 7. Mass concentration variation of PuO$_2$ aerosol with time in 17.4 litre chamber.

INITIAL CONCENTRATION GENERATED WAS 2.0 g Pu/m$^3$.

FIG. 8. Mass concentration variation of PuO$_2$ aerosol with time in 0.75 m$^3$ chamber.

INITIAL CONCENTRATION GENERATED 0.050 g Pu/m$^3$.
of pure PuO$_2$ shown on Figure 8 indicates the concentration drops through three orders of magnitude in two days with a leveling off at 10$^{-5}$ g Pu/m$^3$ which is four times the background alpha-count. This aerosol was generated directly in the chamber. The concentration reaches zero or background count after one week's time in the three-quarter m$^3$ chamber.

The aerosol particles within the agglomerates, as well as the size distribution of the agglomerates themselves, are well represented by a log-normal distribution. That is, the number of particles per unit volume of diameter $d$, $n_d$, are adequately represented by the relationship:

$$n_d = \frac{N}{\log \sigma \sqrt{2\pi}} \exp \left[ \frac{-(\log d - \log d_m)^2}{2 \log^2 \sigma} \right]$$

where $N$ is the total number of particles per unit volume, $d_m$ is the count mean diameter (CMD) and $\sigma$ is the standard deviation. The individual particles of an agglomerate range in size from 30 Å to 0.04 μ and have a standard deviation around 2.0.

The count mean diameters of the PuO$_2$ agglomerates were usually found to be within the range 0.15 to 0.20 μ with $\sigma$ ranging from 1.7 to 2.0. Typical plots of the log-normal distribution of an aerosol sampled at 10 minutes, one hour, and seven hours are shown in Figures 9a, 9b, and 9c, respectively. The particle sizes for Figure 8 are initially 0.128 μ to 0.178 microns after 27 hr. The geometric standard deviation went from 2.0 to 2.8 at 27 hr.

To investigate the nature of mixed PuO$_2$-Na aerosols, an aerosol with a Na/PuO$_2$ ratio of 12.5:1 was generated in the 0.75 cubic meter chamber containing dry nitrogen gas. The aerosol was found to consist largely of composite Na-PuO$_2$ aggregates after one hour of settling. After 48 hours, no particles were observed in the samples, and the alpha count had dropped to about four times background. These results are similar to the ones obtained with a Na/PuO$_2$ ratio of 75:1. The variation of count mean diameter with time for this experiment is shown in Figure 10. The CMD is seen to reach a maximum between 0.6 and 0.8 microns in one to two hours of settling time. Subsequently, the larger particles settle leaving airborne ones with a CMD of around 0.23 microns. A plot of the PuO$_2$ mass concentration as a function of time is shown in Figure 11. The PuO$_2$ mass concentration was found to decrease by three orders of magnitude in 24 hr from a measured value of 10 mg/m$^3$ sampled at 5 min. The nominal initial PuO$_2$ mass concentration was 56 mg/m$^3$, based on the quantity of PuO$_2$ vaporized into the chamber.
FIGS 9a, b, c. Comparison of PuO$_2$ size distribution at 10 min, 1 h, and 7 h.
FIG. 10. Variation of Count Median Diameter with time for Na–PuO₂ aerosol.

Na–PuO₂ AEROSOL C.M.D.*
IN 0.75 M³ CHAMBER
NOMINAL CONCENTRATIONS——
Na 0.67 g/m³
PuO₂ 0.0535 g/m³

σ's = 1.7 ± 0.1
*C.M.D. = COUNT MEDIAN DIAMETER

FIG. 11. Mass concentration variation of Na–PuO₂ aerosol with time in 0.75 m³ chamber.

AEROSOL CONCENTRATION
BY ALPHA COUNTING PuO₂
CHAMBER VOLUME: 0.75 m³
WEIGHT VAPORIZED
40 mg PuO₂
500 mg Na
A picture of the PuO$_2$-Na aerosol taken at a magnification of 224,000 clearly shows the cubic structure of the PuO$_2$ crystals as seen in Figure 12. A coating of lighter density sodium or sodium hydroxide along with larger sodium spheres is also visible. The PuO$_2$ cubes range in size from $<50$ Å to about 0.1 microns, and are generally smaller in size than the UO$_2$ cubes shown in earlier reports. The aggregates of PuO$_2$ are composed of many of these small cubic particles.

The possibility of aerosol resuspension as a result of the agitated movement of the settling chamber walls was investigated. The chamber was sampled prior to and after the chamber was collapsed from the sides and bottom following a plutonium aerosol run. No particles were found on the thermal precipitator sample grids before or after the agitation, indicating little or no resuspension due to movement of the chamber sides. Therefore, the persistent nature of the airborne plutonium concentration is evidently associated with the physical characteristics of the aerosol.

A UO$_2$ aerosol was generated in the 0.81-m$^3$ chamber containing nitrogen gas with a relative humidity of 70%. The aerosol had an initial mass concentration of 30 mg/m$^3$ and a
CMD of 0.13 microns, with a $\sigma_g$ of 2.4. A plot of the CMD measured over a period of two days is shown in Figure 13. The CMD peaked at five hours, reaching a maximum value of 0.365 microns and leveling off to 0.088 microns at 52 hours. The nearly spherical agglomerates typical of high humidity are shown in Figure 14. This aerosol sample has a $\sigma_g$ of 2.49. These data are similar to those obtained in the Na-UO$_2$ experiment at 27% R.H. In the earlier Na-UO$_2$ experiment, the particle size reached a peak value of 0.390 microns at 5 hours.

A log-normal size distribution is observed in nearly all runs as shown in Fig. 15 with pure UO$_2$ at 70% humidity at 5 hr 18 min; however, after 28 hr 18 min, an anomaly is found (see Figure 16). There is a break in the curve below the 50% point, the sigma increases to 3.47. This was also observed in a Na-UO$_2$ run at 70% humidity below the 20% point when additional high magnification photographs of the smaller particles were analyzed (see Figure 17a and 17b). This size distribution is not produced by separate Na and UO$_2$ particles but by combined Na-UO$_2$ particles as shown in Figure
18. The break is at about 0.3 microns and continues below 0.1 micron at which point the curve resumes its original slope. Less than 2% of the particles are below 0.05 microns. It is possible that with high humidity chemical reactions occur and spherical agglomeration with moisture absorption lead to a particle size distribution that is not log normal.

Discussion

It is a well-known fact that high number density aerosols rapidly coagulate. Most experimental evidence indicates that coagulation results in nearly every collision. Consequently, the reduction in airborne plutonium concentration is mainly due to settling, while plateout on walls generally accounts for only 10 to 15% of the total material in our experiments. Airborne particles are known to settle according to Stokes equation for Reynolds numbers below 0.1. The Stokes velocity is given by the equation

\[ V_S = \frac{1}{18} \frac{g \rho d^2}{\eta} \]
where \( d \) is the diameter of the particle, \( \rho \) its effective density, \( g \) the acceleration due to gravity, and \( \eta \) the viscosity of the gaseous medium in which settling is occurring.
FIGS 17a, b. Particle size distribution of Na-UO₂ aerosol in 70% relative humidity at 5 h and 18 min and 28 h and 18 min, respectively.
Following the work of others\[9,10\] a computer program was developed to solve the equations expressing the simultaneous agglomeration and Stokes settling of an aerosol. Using the experimental data on the particle size distribution and number density of some \(\text{PuO}_2\) aerosols, agglomeration coefficients were evaluated. Values ranged from \(3 \times 10^{-9}\) to \(9 \times 10^{-10}\) cm\(^3\)/sec. For the particle radius, \(r_\text{p}\), dependence versus time, the computer predicted trend was in general qualitative agreement with the experimental data. In addition, the time dependence of the total airborne mass concentration was evaluated by integrating the product of the number density, the individual particle volumes and the particle density over all values of the particle radii. The calculated mass concentration behavior with time did not quantitatively agree with the leveling off observed experimentally, indicating that the particle density varies with time.

Due to the relatively large different time scales in which the two processes operate, it is possible to use simplified equations in a semiquantitative manner. That is, initially agglomeration is very rapid while settling is relatively unimportant; for intermediate times of several minutes to several
hours, settling is the dominant process while relatively little agglomeration takes place.

Sinclair[5] has developed an approximate solution to an equation expressing the time dependence of the airborne mass concentration accounting for the settling of heterogeneous stirred aerosols.

\[- \frac{d}{dt} \ln M_t = 3.0 \times 10^5 \frac{\rho d_g^2}{h}, \quad \text{(where } V_s/t/h<1)\]

In this relationship, h is the height of the enclosure in centimeters, \( \rho \) the particle density, and \( d_g^2 \) is given by the equation

\[\log d_g^2 = 2 \log d_g + 18.424 \log \sigma_g\]

The use of the diameter \( d_g \), in conjunction with Stokes law, adequately accounts for the distribution of particle sizes. The use of the mass mean or count mean diameter is not appropriate. Integration of \( d \ln M_t/dt \) yields an equation for the fraction, \( f \), of an aerosol remaining airborne as a function of time. Therefore,

\[f = \exp\left(-3.0 \times 10^5 \frac{\rho d_g^2}{h} t\right)\]

CGS units are to be employed here. Consequently, the settling behavior of an aerosol can be determined from the product \( \rho d_g^2 \).

In our experiments, the initial behavior of the pure PuO\(_2\) and the mixed PuO\(_2\)-UO\(_2\) aerosol is in good agreement with the approximate theory. Figure 19 shows that all of the PuO\(_2\) data, within experimental scatter, can be represented by a single semilog plot of the fraction of PuO\(_2\) remaining airborne as a function of \( t/h \). The deviation from a straight line after a decrease of approximately one order of magnitude is undoubtedly due to a decrease in the product \( \rho d_g^2 \) with time. Although in theory the particles are growing with time, they are forming chain-like "fluffy" agglomerates whose density is much less than the theoretical (11.46 g/cm\(^3\)). The particles are likely to be of theoretical density immediately following nucleation. Particle densities ranging from 4 g/cm\(^3\) to <1/2 g/cm\(^3\) were experimentally observed after several hours of agglomeration.

Our preliminary work indicates that the time dependence of UO\(_2\) and mixed PuO\(_2\)-UO\(_2\) aerosol mass concentrations is somewhat different from that of pure PuO\(_2\). This difference is shown in Figure 19 for the case of a 20 wt % PuO\(_2\)-80 wt % UO\(_2\) aerosol. The UO\(_2\) and PuO\(_2\)-UO\(_2\) aerosols settle more rapidly, probably due to a larger over-all \( \rho d_g^2 \). It is not too surprising to expect UO\(_2\) and PuO\(_2\) aerosols to differ somewhat in behavior since the vapor pressure relationships for these two oxides are considerably different, and they vaporize by different processes.[6,7,8]
The fraction remaining airborne shown on Figure 19 indicates the effect of mass concentration on settling rate. At 0.050 \( \text{g Pu/m}^3 \) the fraction decreases one order of magnitude before leveling off. At 2.0 \( \text{g Pu/m}^3 \) the fraction decreases two orders of magnitude; however, the initial \( \rho d^2 \) line remains constant at \( 0.458 \times 10^{-6} \). Therefore, the product of the initial densities and diameters are equal. The lower mass concentration gives smaller particle sizes after several hours by a factor of two and the sigma increases to 2.8. No peak in CMD is observed as it was in the Na-PuO\(_2\) run (Figure 10). It is evident that the Na contributes to the peak at 0.78 microns, while in PuO\(_2\) alone, the range of values is 0.128 to 0.22 at the end of the run. A slight peak at 0.275 \( \mu \) is observed at three hours.

A conservative estimate of the product \( \rho d^2 \) can be obtained from the slope of the dotted straight line shown in Figure 19. This value should be adequate for estimating the first one to two orders of magnitude drop in concentration. It is worthwhile noting that the product of the theoretical density and
FIG. 20. Behaviour of mixed PuO$_2$-Na aerosols.

The presence of sodium has some effect on the PuO$_2$ aerosol mass concentration behavior as seen in Figure 20. For sodium to PuO$_2$ ratios of 1, the long-time behavior of the aerosol is very much like that without sodium. However, with larger sodium-to-PuO$_2$ ratios, the experimental results indicate that the aerosol remains airborne for a much longer period of time. This observation is not unexpected. Since the densities of both sodium and its oxide are quite low compared with PuO$_2$, the composite agglomerates, although larger in size, have a smaller density than the agglomerates of pure aerosols. This leads to a smaller value of $d_3$ and a more persistent aerosol.

At this time, we recommend the use of the following equation for making conservative estimates of the fractional $d_3$ calculated from experimental $d_9$(CMD) and $s_9$ values is in good agreement with that obtained from the figure. Obviously, whenever possible, it is preferable to use the product $d_3^2$ deduced from the time dependence of the airborne mass concentration. Since this value is based on the aerodynamic character of the particles, no correction for their nonsphericity is needed.
decrease in aerosol concentration with time. In the absence of large excess of airborne sodium,

$$f = \exp \left( -\frac{1.37 \times 10^{-3}}{h} \right)$$

Where large quantities of sodium (or its oxide) are vaporized together with PuO$_2$, this relationship may be a valid conservative estimate for very short times. In this equation, $h$ is the height of the reactor vessel in meters and $t$ is time in hours.

Acknowledgments

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REFERENCES


DISCUSSION

W. SCHIKARSKI: Have you any idea why cubic crystals were formed in your experiments? And did you sometimes change the vaporization time?

F. L. HORN: We vaporize the PuO$_2$ and UO$_2$ as rapidly as possible, by first melting the solid and then evaporating the liquid completely. We purposely do not heat the liquid so rapidly that droplets are sprayed out, although we could do so. The gaseous vapour formed is dispersed by the flowing stream of argon.
The cubic crystals are apparently formed by condensation of the vapour directly into the known cubic crystal structure of PuO$_2$ and UO$_2$, rather than by solidification of liquid spheres.

W. SCHIKARSKI: I believe that the crystallization process involves much smaller sizes — of the order of Ångstroms — than the particle sizes we are investigating.

F. L. HORN: As I see it, on cooling, the gaseous vapour crystallizes onto condensation nuclei in the pattern of the cubic structure, which continue to grow into the various-sized cubic particles observed.
AIRBORNE RELEASE OF PARTICLES IN OVERHEATING INCIDENTS INVOLVING PLUTONIUM METAL AND COMPOUNDS *

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Abstract

AIRBORNE RELEASE OF PARTICLES IN OVERHEATING INCIDENTS INVOLVING PLUTONIUM METAL AND COMPOUNDS. Ever-increasing utilization of nuclear fuels will result in wide-scale plutonium recovery processing, reconstitution of fuels, transportation, and extensive handling of this material. A variety of circumstances resulting in overheating and fires involving plutonium may occur, releasing airborne particles. This work describes the observations from a study in which the airborne release of plutonium and its compounds was measured during an exposure of the material of interest containing plutonium to temperatures which may result from fires.

Aerosol released from small cylinders of metallic plutonium ignited in air at temperatures from 410 to 650°C ranged from 3 x 10^-6 to 5 x 10^-5 wt%. Particles smaller than 15μm in diameter represented as much as 0.03% of the total released. Large plutonium pieces weighing from 456 to 1770 g were ignited and allowed to oxidize completely in air with a velocity of around 500 cm/sec. Release rates of from 0.0045 to 0.032 wt% per hour were found. The median mass diameter of airborne material was 4 μm. Quenching the oxidation with magnesium oxide sand reduced the release to 2.9 x 10^-4 wt% per hour.

Many experiments were carried out in which plutonium compounds as powders were heated at temperatures ranging from 700 to 1000°C, with several air flows. Release rates ranged from 5 x 10^-4 to 0.9 wt% per hour, depending upon the compound and the conditions imposed. The airborne release from boiling solutions of plutonium nitrate were roughly related to energy of boiling, and ranged from 4 x 10^-4 to 2 x 10^-1 % for the evaporation of 90% of the solution. The fraction airborne when combustibles contaminated with plutonium are burned is under study. The data reported can be used in assessing the consequences of off-standard situations involving plutonium and its compounds in fires.

INTRODUCTION

As the use of nuclear energy grows, the circumstances under which plutonium can be involved in an accident increase. Since the potential hazards attendant to each different set of conditions must be realistically assessed, data on the behavior of plutonium under a variety of conditions are required. The authors have conducted a series of studies to determine the fraction of plutonium made airborne and characteristics of aerosols produced by overheating plutonium metal and several plutonium compounds. Plutonium in various phases of processing and use commonly appears in three forms -- plutonium metal, plutonium compounds as powders, and liquids containing soluble plutonium compounds. All these forms can be found in various atmospheres and configurations. If we attempted to obtain quantitative data on all plutonium forms under all conditions, we would be faced with a never ending array of experiments. Thus, we have attempted to study a representative cross-section of each form under some overheating conditions. The results obtained are indi-
ative of the nature and amounts of materials produced under these conditions. The values reported here are not to be taken as definitive in any specific case but must be interpreted in light of the conditions prevailing. We have thus far determined the fractional releases from:

1. The oxidation of small, ignited rods of unalloyed plutonium metal in low air flows.
2. The oxidation of large, ignited pieces of plutonium metal in moderate air flows.
3. Heating plutonium bearing powders in low air flows.
4. Heating plutonium nitrate solutions and the solids remaining after evaporation in low air flows.

We are currently engaged in determining the fractional release of plutonium in various forms mixed with flammable materials and dried on sand. These studies will continue. The data obtained are expected to prove useful in assessing consequences of off-standard incidents involving overheating of plutonium and its compounds.

SUMMARY

Of these materials used in these studies, plutonium compounds in the form of powders released the largest amounts of plutonium aerosol. Plutonium oxalate powder had as high a release rate as was found under the conditions used in these studies — 0.90 wt.% per hour when heated to 1000°C in air with an upsweep velocity of 100 cm per second. The high rate under this set of conditions appears to be due to a combination of circumstances which favored release. Lower rates of release were obtained under other conditions imposed. Partially oxidized plutonium oxalate was the most readily airborne under most conditions imposed during these experiments. The highest rate found for the partially oxidized plutonium oxalate, 0.82 wt.% per hour at 1000°C in 100 cm per second air, was comparable to that found for the plutonium oxalate. Significant plutonium release resulted using the partially oxidized oxalate under a greater variety of less rigorous temperatures and air velocities. Release rates ranged from 0.057 to 0.82 wt.% per hour. Plutonium fluoride release rates were the lowest for the compounds considered, 0.007 to 0.05 wt.% per hour. The material remaining after heating was a free-flowing entrainable powder.

Overheating plutonium metal created less airborne material. The amount of material entrained during the oxidation of ignited, unalloyed plutonium metal in low air flows, 3.3 to 50 cm per second, was small — 3 x 10^-6 to 5 x 10^-5 wt.%. The size distribution of the oxide produced can vary with the oxidation conditions and, since the oxide is friable, the mechanical work to which it is subjected. Under the conditions of the study, as much as 0.03 wt.% of the oxide was smaller than an aerodynamically equivalent sphere with a diameter of 15 microns.

In moderate air flows, 525 cm per sec, 0.0045 to 0.032 wt.% per hour was released during the oxidation of large pieces of ignited, metallic plutonium. The Median Mass Diameter (MMD) of the particles airborne during one of the experiments was 4.2 microns.

Heating a finely divided fraction of oxide, greater than 15 and less than 44 microns diameter, in a stream of flowing air entrained a similar amount — 5 x 10^-6 to 0.025 wt.% per hour.
Heating liquids containing soluble plutonium compounds released the smallest amounts of material. Using slow heating rates, the maximum amount airborne from a concentrated plutonium nitrate solution in a shallow pool during a two hour heating-cooling cycle was 0.03 wt.%. When a higher heating rate and greater volume were used the maximum amount airborne was 0.18 wt.% during a 63 minute sampling period at a full rolling boil.

The fraction released by overheating the solids remaining after the evaporation of plutonium nitrate solutions is in the same range as from the oxides. The maximum amount was 0.125 wt.% with the remaining values ranging from 0.0046 to 0.0125 wt.%. The amounts airborne showed a general correlation with air velocity but more probably reflect the physical state of the source material.

DISCUSSION AND RESULTS

I. Plutonium Metal

A. Fractional Release from the Oxidation in Low Air Flows of Small, Ignited Pieces of Unalloyed Metal.

Six rods of unalloyed plutonium metal, 1/4 in. diameter and 3/4 in. long, were ignited in a stream of dry air and the amount of plutonium entrained determined. The metal rods were fairly uniform in size and appearance. Weights ranged from 9.89 to 11.3*+ grams. The metal specimen was suspended above a quartz boat which was centered in a horizontal quartz combustion tube. Filtered air was drawn around the specimen and the temperature elevated by a resistance-type, clam-shell furnace. After the metal was ignited, temperatures in the combustion tube were maintained at the desired level by means of a variable transformer connected to the furnace power inlet. The material entrained was caught on a membrane filter. Microscopic examination of the filter indicated that this material is primarily submicron in size. The filters were then dissolved and the plutonium content determined by alpha counting.

After cooling, the remaining oxide was collected, weighed and classified. All the oxides produced in these experiments were very similar in appearance -- a dark brown, loosely-joined mass with patches having a greenish hue. Under magnification, two types of particles were distinguishable, the larger portions were a dark brown, elongated rectangle and the remainder a yellowish-brown, very small particle. The oxide was classified by means of a combination sieve-air elutriator-cascade impactor technique. During a few of the later runs, the apparatus was rapped to dislodge particles which might be trapped in the oxide mass.

The entrainment of particles under these conditions is not large. During the oxidation-cooling cycle, the amount released ranged from $3 \times 10^{-6}$ to $5 \times 10^{-5}$ wt.%. Drawing air through the oxide mass entrained about an equivalent amount but as much as 0.03 wt.% could be made airborne with rapping. The material airborne was of very small particle size -- 70 to 80% had equivalent diameter less than 0.1 micron. (See Table I.)
## Table I

**Oxide Produced During the Oxidation of Ignited Unalloyed Plutonium Rods**

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<thead>
<tr>
<th>Temperature Range, °C</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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<tr>
<td></td>
<td>Amb-900</td>
<td>Amb-560</td>
<td>Amb-650</td>
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<td><strong>Fractional Release During</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation &amp; Cooling, wt.%</td>
<td>$2.8 \times 10^{-6}$</td>
<td>$3.1 \times 10^{-5}$</td>
<td>$5.3 \times 10^{-5}$</td>
<td>$4.1 \times 10^{-6}$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>$3.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sampling Time, Min.</td>
<td>155</td>
<td>74</td>
<td>75</td>
<td>146</td>
<td>153</td>
<td>117</td>
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<tr>
<td><strong>Fractional Release During</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elutriation, wt.%</td>
<td>$8.1 \times 10^{-6}$</td>
<td>$2.3 \times 10^{-4}$</td>
<td>$8.9 \times 10^{-4}$</td>
<td>$8.5 \times 10^{-4}$</td>
<td>0.0311</td>
<td>0.016</td>
</tr>
<tr>
<td>Sampling Time, Min.</td>
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<td>20</td>
<td>80</td>
<td>90</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td><strong>Calc. Oxide Recovery, wt.%</strong></td>
<td>98.8</td>
<td>99.8</td>
<td>97.4</td>
<td>100</td>
<td>99.4</td>
<td>100</td>
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<td><strong>Size Distribution Residual Oxide</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>wt.% oxide &lt; 250 microns</td>
<td>7.72</td>
<td>18.23</td>
<td>8.04</td>
<td>10.25</td>
<td>12.47</td>
<td>12.22</td>
</tr>
<tr>
<td>wt.% oxide &lt; 125 microns</td>
<td>3.57</td>
<td>7.66</td>
<td>3.05</td>
<td>4.27</td>
<td>5.03</td>
<td>4.95</td>
</tr>
<tr>
<td>wt.% oxide &lt; 74 microns</td>
<td>2.39</td>
<td>3.75</td>
<td>1.76</td>
<td>2.64</td>
<td>2.96</td>
<td>2.84</td>
</tr>
<tr>
<td>wt.% oxide &lt; 44 microns</td>
<td>0.99</td>
<td>2.63</td>
<td>1.17</td>
<td>1.76</td>
<td>1.89</td>
<td>1.81</td>
</tr>
<tr>
<td>wt.% oxide 15-44 microns</td>
<td>0.66</td>
<td>0.80</td>
<td>0.68</td>
<td>0.63</td>
<td>0.60</td>
<td>0.76</td>
</tr>
</tbody>
</table>
B. Fractional Release from Large, Ignited Metallic Pieces Oxidizing in Moderate Air Flows.

As an adjunct to a separate study, the amount of plutonium entrained during the oxidation of four large pieces of plutonium metal was determined. Three pieces of alpha plutonium of varying quality and shapes plus a hemi-cylindrical, as-cast, delta plutonium ingot were ignited and oxidized under a 2-5/8 in. diameter by 17-3/8 in. long, bell shaped, Vycor chimney. The entire upper surface of the metal piece was ignited with an arc welding unit. The ignited piece was placed under the chimney and air was drawn through the chimney at a velocity of 525 cm per second. Particles airborne were collected on a glass fiber filter and the plutonium determined by dissolution of the material collected and alpha particle counting. During the second run using alpha metal, samples for particle sizing were taken via a side arm sampler operating at a flow slightly higher than in the chimney. The samples were collected on membrane filters and selected portions mounted for electron microscopy.

The amount of fine particulate material airborne under these conditions varied from 0.0045 to 0.032 wt.% per hour (see Table II). Covering the oxidizing material with magnesium oxide sand decreased the release rate several orders of magnitude. Release rates from the alpha metal were slightly higher than found for the delta metal. The MMD of the particles airborne during the oxidation of ignited, bare metal was 4.2 microns.

II. Plutonium Compounds as Powders

Four plutonium compounds representing the type of material commonly encountered were heated in an upsweep of air and the amount of material airborne determined. The powders selected were the oxide produced from the ignited metal, partially oxidized plutonium oxalate, plutonium oxalate and plutonium fluoride. The powders were placed in a shallow depression, 1-1/2 in. diameter by 3/32 in. deep, in a stainless steel furnace cap. Air was drawn up and around the source via a 42.2 mm diameter by 11 in. long, Vycor chimney lined with 0.003 in. mild steel shimstock. The temperature of the material was raised rapidly to the desired level and maintained during the 60 min. heating cycle by a 10 KHz, 15 KW induction heating unit. Temperatures during the run were taken by a platinum-platinum 13% rhodium thermocouple. Air flow and sampling continued during the 60 min. cooling cycle. Particles passing through the chimney were caught by the glass-fiber filter sealing the upstream end of the chimney. Those particles which became airborne but deposited in the chimney were determined by analysis of the shimstock liner. At the completion of each run, the residues and chimney filters were examined and characterized.

A. Plutonium Oxide

The source material for the study of fractional release from the oxide was the greater than 15 and less than 44 micron fraction produced by the oxidation of unalloyed metal rods in low air flow. The material did not undergo any visible changes during the experiments.

The amount released by the oxide during heating in a flowing air stream appears to be similar to that previously reported for entrainment.

Registered trade name of Corning Glass Co.
<table>
<thead>
<tr>
<th>Metal Phase</th>
<th>Physical Description</th>
<th>Metal Phase</th>
<th>Physical Description</th>
<th>Metal Phase</th>
<th>Physical Description</th>
<th>Metal Phase</th>
<th>Physical Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alpha</td>
<td>2</td>
<td>Alpha</td>
<td>3</td>
<td>Delta</td>
<td>4</td>
<td>Alpha</td>
</tr>
<tr>
<td></td>
<td>Wedge-Shaped</td>
<td></td>
<td>Cylindrical, As-Cast</td>
<td></td>
<td>Hemis-Cylindrical</td>
<td></td>
<td>Rough Triangular</td>
</tr>
<tr>
<td></td>
<td>Section, Low</td>
<td></td>
<td>Ingot, Metal Purity</td>
<td></td>
<td>As-Cast Ingot</td>
<td></td>
<td>Pieces, Stratified</td>
</tr>
<tr>
<td></td>
<td>Density Metal,</td>
<td></td>
<td>&gt; 99.99 wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2000 ppm Metallic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Impurities</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wt. Plutonium, grams</td>
<td>569.8</td>
<td>Wt. Plutonium Released, g</td>
<td>0.268</td>
<td>Wt.% Released</td>
<td>0.049</td>
<td>Wt. Plutonium Released, g</td>
<td>0.257</td>
</tr>
<tr>
<td>Release Rate, wt.%/hour</td>
<td>0.032</td>
<td>0.019</td>
<td>0.0045</td>
<td>0.00039</td>
<td>0.00029</td>
<td>Oxidizing metal covered with MgO sand.</td>
<td></td>
</tr>
<tr>
<td>Total Sampling Time, min</td>
<td>90</td>
<td>1770</td>
<td>997</td>
<td>455.5</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III

AMOUNTS OF PLUTONIUM OXIDE ENTRAINED IN FLOWING AIR FROM THE HEATED OXIDE

(Source material was the greater than 15 and less than 44 micron fraction from the air oxidation of unalloyed plutonium metal rods.)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>10 cm per sec</th>
<th>117 cm per sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Temperature</td>
<td>6.1 x 10^-6</td>
<td>0.56</td>
</tr>
<tr>
<td>800°C - 900°C</td>
<td>5.3 x 10^-6</td>
<td>0.025</td>
</tr>
</tbody>
</table>

The release rates varied from 3.2 x 10^-6 to 0.025 wt.% per hour (see Table III). The release rate at high temperature and air velocity is similar to that found for ignited, bare metal in 525 cm per min. air and that re-entrained when air flow and transfer of momentum are involved. At ambient and elevated temperatures and lower velocities, the rate is similar to that found during the classification of this material. The high release rate found at ambient temperature and an air velocity of 117 cm per sec is believed anomalous and the explanation is not readily apparent.

B. Partially Oxidized Plutonium Oxalate

The source material used in these runs was production-line plutonium oxalate oxidized for six months in a dry, glovebox atmosphere. The powder was a tan, finely divided, free-flowing material. Examined microscopically, the powder was made up of cream-colored and brownish spheres with a MMD of 32 microns.

Of the four powders studied, the partially oxidized plutonium oxalate appears to be the most readily made airborne under the conditions used. The release rate increased with both increasing temperature and air velocities (see Table IV). At an air velocity of 100 cm per sec, rates ranged from 0.057 wt.% per hour at 400°C to 0.82 at 1000°C. At 1000°C the release rate was 0.25 wt.% per hour with an air velocity of 10 cm per sec, increasing to 0.82 at 100 cm per sec. The MMD of the particles airborne was 25 microns during the run at 700°C in 100 cm per sec air. The values found for the material deposited in the chimney was much more scattered probably due to the proximity of the source material. The values for the material deposited in the chimney averaged approximately 7% of the material carried through the chimney.

Since the material remaining after an accident can be a significant factor in the hazards associated with dealing with the conditions produced, the residues were examined. For partially oxidized plutonium oxalate heated to 1000°C, the residues were hard-crusted cakes requiring a significant amount of force to break the surface. For the lower temperatures, the residues were bulky, yellow powders which were readily dispersed.
TABLE IV
PARTIALLY OXIDIZED PLUTONIUM OXALATE RELEASE RATES
(Source material -- production-line oxalate oxidized in dry air for 6 months.)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Air Velocity (cm/sec)</th>
<th>Release Rate, Wt.%/Hr. Airborne Deposited in Chimney</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>10</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>*</td>
</tr>
<tr>
<td>400</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0075</td>
</tr>
<tr>
<td>700</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.735</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.041</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.82</td>
</tr>
</tbody>
</table>

* Less than lower detection limit, 4 x 10^-3 wt.%/hour.

C. Plutonium Oxalate

Normal production-line powder as received was used as source material for these runs. It was a moist powder with the color and consistency of brown sugar and contained a few larger lumps up to approximately 1/8 in. in diameter. Under magnification, the individual particles were spherical with a MMD of 50 microns. Over the four months required to conduct these experiments, the physical appearance of the source material altered considerably to a free-flowing, olive-green powder. The probable cause for the change in physical appearance is a loss of moisture to the dry glovebox air (a dewpoint of -70°F).

Although the plutonium oxalate produced the highest release rate found in these studies, 0.90 wt.% per hour, this material does not appear to produce an aerosol as readily as the partially oxidized material. The release rates show a strong dependency on the air sweep velocity only producing significant rates at 100 cm per sec (see Table V). This relationship of release rate to air velocity is not surprising considering the steep slope of the particle size distribution of the source material. The very high value found for the release at 700°C in air with a velocity of 100 cm per second probably represents a combination of maximum shrinkage of the particle without sintering. The particles airborne ranged in size from 5 to 60 microns in diameter. Only 3% to 5% of the material passing through the chimney appears to have deposited on the walls.
Table V
PLUTONIUM OXALATE RELEASE RATES
(Source material: as-received production-line material.)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Air Velocity (cm/sec)</th>
<th>Release Rate, Wt.%/Hr</th>
<th>Airborne</th>
<th>Deposited in Chimney</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>*</td>
<td>*</td>
<td>0.0096</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>*</td>
<td>0.0087</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>*, 0.38, 0.073, 0.054, 0.006, 0.023, 0.025, 0.036</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>.48</td>
<td>.016</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>.0044</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>.90</td>
<td>.047</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>.007</td>
<td>.005</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>.25</td>
<td>.075</td>
<td></td>
</tr>
</tbody>
</table>

* Beneath lower detection limits, < 4 x 10^-5 wt.%/hour.

Crusts of varying thickness resulted from the conditions imposed during this study. These crusts were broken easily and the material underneath was a free-flowing powder. The size distribution of the particles airborne appears to decrease slightly with increasing temperature reflecting the speed at which the hard crust is formed. Thus the heating rate may play a part in the amount and size distribution of the material released.

D. Plutonium Fluoride

The source material was normal production-line powder. As-received, it was a green, finely-divided, free-flowing powder with a few large lumps. The powder was made up of individual spheres with a MMD of 26 microns and agglomerates with a MMD of 38 microns. The amount of material released by heating plutonium fluoride in moving air was lower than found for either type of oxalate and also was dependent on the air velocity used — significant rates were only detected in air with a velocity of 100 cm per second. Release rates ranged from 0.007 wt.% per hour at 400°C to 0.05 wt.% per hour at 1000°C (see Table VI). The size distribution of the material reaching the filter appeared to decrease with increasing temperature. The material remaining after heating was a free-flowing, easily dispersed material.
### TABLE VI

**PLUTONIUM FLUORIDE RELEASE RATES**

(Source Material: as-received, production-line fluoride.)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Air Velocity (cm/sec)</th>
<th>Release Rate, Wt.%/Hr</th>
<th>Airborne</th>
<th>Deposited in Chimney</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>10</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>400</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>--</td>
<td>--</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0073</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>700</td>
<td>10</td>
<td>--</td>
<td>--</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>--</td>
<td>--</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.022</td>
<td>0.048</td>
<td>*</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.005, 0.02, 0.016</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* Below lower detection limits, < 4 x 10⁻³ wt.%/hr.

### III. Liquids Containing Soluble Plutonium Compounds

For our studies, various concentrations of plutonium nitrate in dilute aqueous nitric acid were used. Plutonium nitrate was chosen as the source material since it is a frequently used soluble compound of plutonium.[3] The stock solution was a dark brown liquid containing 288 g of plutonium as nitrate per liter. Various dilutions of this liquid were prepared in nitric acid as required.

#### A. The Fractional Release from Shallow Pools of Liquid Heated in a Stream of Air

Concentrated plutonium nitrate solution was evaporated in a shallow stainless steel dish in a stream of dry air (dewpoint of air was less than -50°F). The evaporation was performed primarily to obtain plutonium nitrate sources for use during a later part of these studies. Release rates from shallow pools were obtained during this operation.

The liquid containing 0.72 g of plutonium was pipetted into the shallow depression in stainless steel cap for the induction furnace. The shallow cap was centered in a Pyrex 50 mm diameter containment vessel. A teflon holder positioned the dish and provided an undisturbed air pattern across the face of the liquid. Filtered, dry air was drawn across the face of the liquid at 10, 50 and 100 cm per second using the building vacuum system. A water-cooled condenser was used to remove moisture in
TABLE VII
FRACTIONAL RELEASE DURING AIR DRYING OF LIQUID PLUTONIUM NITRATE
(0.72 g plutonium as source)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (°C)</th>
<th>Air Velocity (cm/sec)</th>
<th>Wt.% Plutonium Released During Following Evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-1</td>
<td>Ambient</td>
<td>10</td>
<td>&lt; 10⁻⁷</td>
</tr>
<tr>
<td>N-2</td>
<td>75</td>
<td>10</td>
<td>&lt; 10⁻⁶</td>
</tr>
<tr>
<td>N-3</td>
<td>100</td>
<td>10</td>
<td>10⁻³</td>
</tr>
<tr>
<td>N-4</td>
<td>Ambient</td>
<td>50</td>
<td>2.5 × 10⁻⁷</td>
</tr>
<tr>
<td>N-5</td>
<td>100</td>
<td>50</td>
<td>3 × 10⁻³</td>
</tr>
<tr>
<td>N-6</td>
<td>90</td>
<td>50</td>
<td>5.25 × 10⁻⁵</td>
</tr>
<tr>
<td>N-7</td>
<td>Ambient</td>
<td>100</td>
<td>&lt; 10⁻⁸</td>
</tr>
<tr>
<td>N-8</td>
<td>50</td>
<td>100</td>
<td>1.25 × 10⁻⁵</td>
</tr>
<tr>
<td>N-9</td>
<td>90</td>
<td>100</td>
<td>5.73 × 10⁻⁵</td>
</tr>
</tbody>
</table>

the air prior to trapping the airborne particle on a membrane filter. Two variable transformer-controlled infrared heating lamps were used to maintain the desired temperature which was measured by a chrome-alumel thermocouple inserted into a well in the cap. After the residue appeared dry, a second filter was installed to determine the fractional release from the solids remaining on the dish at low temperatures. The filters were examined microscopically to characterize the particles airborne. Due to the small amounts of material involved, very few particles were detected. Alpha counting determined the plutonium content of the filter, containment vessel washes and condensate.

All releases were low (see Table VII). With a 48 hour sampling period, the maximum amount airborne at ambient temperature was only 2.5 × 10⁻⁷ wt.% which is near the lower detection limits for the analysis used. The amount airborne remains under 5.73 × 10⁻⁵ wt.% until boiling temperatures are attained. At 100°C, the rates were 1 to 3 × 10⁻³ wt.%. Even less was released from the dried nitrate -- a maximum value of 2.62 × 10⁻⁶ wt.% was found at a temperature of 90°C in an air velocity of 100 cm per second.

The solids remaining after evaporation, with the exception of run N5, were dark green to brown in color, with a hard glazed, irregular surface. Many had cracks and craters where vapor had been released through the partially hardened surface. In a few of the samples, liquid which had been trapped under the hardened surface was noted. In run N8, an additional 2½ hour drying in the dry glovebox air produced long, thin crystals.

The solids formed during run N5 were significantly different than solids formed during other runs. The liquid bubbled quite violently during most of the heating cycle (~ 45 minutes). The residue had the appearance of dried mud. It was a brown, bulky material which was very unevenly distributed over the cap surface.
B. Fractional Release During the Heating of Pools of Liquid in a Flowing Air Stream

Four evaporation rates were arbitrarily chosen as representing the various degrees of surface disturbance which occur during the heating of liquids. The regimes were designated:

a. Simmer: no breaking of the surface and characterized by an evaporation rate of 0.1 ml per minute.

b. First breaking of the surface: intermittent disturbance of the surface with an evaporation rate of 0.6 ml per minute.

c. Steady breaking of the surface: a slow, continual disruption of the surface with an evaporation rate of 0.8 ml per minute.

d. Vigorous rolling boil: a continuous release of bubbles and vigorous disturbance of the surface of the liquid. Evaporation rate in excess of 1.2 ml per minute.

Fractional releases were determined by drawing air up and around a 180 ml Pyrex beaker holding the plutonium solution and capturing the material airborne on a glass fiber filter sealing the exit of the modified 1-liter Pyrex jar used as a containment vessel. Two and a half ml of a diluted nitrate solution containing 70 or 700 mg of plutonium were pipetted into 97.5 ml of 0.25 M nitric acid held in the beaker. Initially, the surface area of the liquid was 17.8 cm². Air was drawn symmetrically into the containment vessel through an annular ring around the beaker. The beaker was secured by a stainless steel screen attached to the transite vessel support ring. A filter over the entry prevented any losses. An aluminum heating block slotted for viewing surrounded the beaker. The heating block and transformer controlled hot plate were supported on a movable platform which was raised and lowered to provide rapid heating and cooling during the runs. Condensate forming on the walls of the containment vessel was collected in a trough along the inner bottom edge of the vessel. This condensate was analyzed for plutonium.

The plutonium escaping the beaker but not remaining airborne was labelled "fall-out" and was collected on the inlet filter. Attempts were made to determine the air velocities in the containment vessel at the various evaporation rates but they were too low to measure with the instruments available. After some experimentation, a velocity of 2.9 cm per second was chosen as one at which particles airborne could be swept away and yet allow condensation of most of the moisture in the containment vessel under the conditions used. Only 90% of the liquid was boiled off to reduce contamination difficulties associated with handling concentrated solutions. During the last five runs, the exit filter was changed after 30 ml of the solution had been evaporated to determine the effect of concentration on fractional release. The MMD of the particles airborne during run H was found by alpha track counting to be 4 microns.

The amount of material airborne roughly corresponds to boiling rate -- the amount airborne increases with the degree of surface disturbance. The behavior of the liquid ejected during heating also plays an important role. Release values range from $4 \times 10^{-5}$ wt.% during simmering to 0.18 wt.% with a vigorous rolling boil (see Table VIII). The total amount escaping follows boiling rates more closely as would be expected. In the experiments using two exit filters, the amounts of plutonium found on the second filter were consistently higher than on the initial filter.

The results from two of the runs appear anomalous. Run E at the highest boiling rate shows very little activity. The proper amount of
TABLE VIII

FRACTIONAL RELEASE DURING HEATING OF PLUTONIUM NITRATE SOLUTIONS

(2.9 cm per sec air through container, 700 mg plutonium as source.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Average Boiling Rate ml/min.</th>
<th>Wt.% Plutonium Airborne</th>
<th>Fall-Out</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.4</td>
<td>0.18</td>
<td>0.02</td>
</tr>
<tr>
<td>B</td>
<td>0.9</td>
<td>0.084</td>
<td>0.27</td>
</tr>
<tr>
<td>C</td>
<td>0.73</td>
<td>0.024</td>
<td>0.12</td>
</tr>
<tr>
<td>D</td>
<td>0.6</td>
<td>4.5 x 10^-4</td>
<td>4.5 x 10^-4</td>
</tr>
<tr>
<td>E*</td>
<td>2.1</td>
<td>4.2 x 10^-5</td>
<td>2 x 10^-4</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>3 x 10^-6</td>
<td>5 x 10^-3</td>
</tr>
<tr>
<td>G</td>
<td>0.66</td>
<td>8 x 10^-3</td>
<td>0.016</td>
</tr>
<tr>
<td>H</td>
<td>1.2</td>
<td>0.008</td>
<td>0.71</td>
</tr>
<tr>
<td>I</td>
<td>1.4</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>J*</td>
<td>1.4</td>
<td>0.11</td>
<td>1.7</td>
</tr>
</tbody>
</table>

* Only 70 μg plutonium used during this run.

plutonium may not have been added. During run A, the inlet filter clogged due to absorption of moisture. The high vacuum created by the greater resistance of the filter lifted the beaker from its holder creating a different air flow pattern during this run.

C. Fractional Release from Heating the Solids Remaining After the Evaporation of Plutonium Nitrate Solutions in a Flowing Air Stream.

The solids produced during air drying of plutonium nitrate were heated in the apparatus used to measure the fractional release from plutonium compounds as powders. Air was drawn up and around the heated material at one of three standard velocities — 10, 50 and 100 cm per second. The solids were heated to 400°C, 700°C or 1000°C for 60 minutes and allowed to cool for 60 minutes. The particles released were carried up into a 1/2.2 mm ID x 11 in. long Vycor chimney positioned 3/16 in. above the dish. The amount carried through the chimney was determined by analysis of the shimstock liner.

The amount of plutonium airborne from the dried nitrate appears to be independent of temperature and air flow. They range from 0.0046 to 0.12 wt.% which are similar to the values found for entrainment from the oxide (see Table IX). The highest value, 0.12 wt.%, is from a residue which was fragmented prior to heating. Thus, physical state of the source material can be a major factor in the amount released. Only run N5a produced a sufficient number of particles for size distribution. The MMD of the particles airborne was found microscopically to be 20.5 microns. The material remaining after heating was composed of dispersible, grey to greenish colored, thin flakes.
TABLE IX

FRACTIONAL RELEASE DURING HEATING OF SOLIDS REMAINING AFTER THE EVAPORATION OF PLUTONIUM NITRATE SOLUTIONS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. (°C)</th>
<th>Air Velocity (cm/sec)</th>
<th>Wt.% Plutonium Deposited in Chimney</th>
<th>Airborne</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1a</td>
<td>1000</td>
<td>100</td>
<td>0.0067</td>
<td>0.0125</td>
</tr>
<tr>
<td>N2a</td>
<td>700</td>
<td>100</td>
<td>0.004</td>
<td>0.0092</td>
</tr>
<tr>
<td>N3a</td>
<td>400</td>
<td>100</td>
<td>0.0097</td>
<td>0.0068</td>
</tr>
<tr>
<td>N4a</td>
<td>1000</td>
<td>50</td>
<td>0.032</td>
<td>0.125</td>
</tr>
<tr>
<td>N5a</td>
<td>1000</td>
<td>10</td>
<td>0.0016</td>
<td>0.0046</td>
</tr>
<tr>
<td>N6a</td>
<td>700</td>
<td>50</td>
<td>0.015</td>
<td>0.0075</td>
</tr>
<tr>
<td>N7a</td>
<td>400</td>
<td>50</td>
<td>0.0055</td>
<td>0.0064</td>
</tr>
<tr>
<td>N8a</td>
<td>1000</td>
<td>100</td>
<td>0.0012</td>
<td>0.0071</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Airborne release of plutonium from the metal, compounds, and from solutions when these forms are subjected to heat stresses and flowing air streams used in these experiments can range from an almost negligible amount to a few percent. In an assessment of the potential consequences of an airborne release in a given circumstance the nature of the material involved must be known as well as the air flow and the temperature stresses to be imposed. Detailed data on these points are seldom available and estimates must usually suffice. The data obtained for the fraction airborne can be used when the air flow and heat stress of the postulated incidents are similar to those used, however, the data must be regarded as indicative of actual release factors.

Some general conclusions drawn from the observations are as follows:

1. Oxidation of metallic plutonium will cause to be airborne from a very small fraction ($10^{-6}\%$) to a few hundredths of 1%. The higher release fractions were measured for massive pieces of plutonium.

2. The variability in the airborne fraction released from compounds of plutonium masked any consistent trend with temperature. Aerodynamic considerations appear to be more dominant than heating per se to temperatures to 1000°C. The influence of heating on the final physical form of the compound was quite marked. Residues hard and glassy to very fine powders were observed.

3. Evaporation of plutonium can be achieved with an extremely small airborne release if carried out at low evaporation rates. Airborne release accompanying a full rolling boil from a 2-1/2 in. diameter beaker resulted in an airborne release ranging to a few tenths percent.
Although this investigation did not include a comprehensive study of particle sizes of the released materials, the particle size measurements made showed that for the releases measured virtually all could be regarded as particles of respirable size.

Some experiments performed and future experiments are designed to measure the airborne release from plutonium salts contained in combustible materials which burn. It is also planned to conduct experiments to estimate the potential loss of plutonium from soil matrix material by heating. These experiments should yield information with which consequences of shipping accidents can be better assessed.

REFERENCES


BEHAVIOUR OF RADIOIODINE IN GASEOUS EFFLUENTS

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Abstract

BEHAVIOUR OF RADIOIODINE IN GASEOUS EFFLUENTS. Because of the different chemical forms in which radioiodine occurs in the gaseous state, it is important when designing efficient filters to know the chemical forms which may be present in the effluent gases when various operations are being carried out and to know the effect of different gaseous environments on the filtration efficiency. To obtain this information it is necessary to have available reliable means of characterizing different chemical forms and to sample gaseous effluents when these operations are being carried out. This paper describes the use for identifying molecular iodine of metallic screens in a multi-component sampling pack in different gaseous environments.

Using multi-component sampling packs, the fractionation of iodine nuclides between different chemical forms was measured in the effluent gases escaping from an in-pile test loop in which the fuel was deliberately ruptured by restricting the flow of coolant. Sequential samples were taken for six hours after the rupture and it was possible to follow during this period the individual behaviours of $^{131}$I, $^{133}$I and $^{135}$I. Simultaneous samples were also obtained of the noble gases in the effluent gas stream and of the iodine nuclides in the loop coolant.

Similar experiments have been carried out with a view to characterizing the different chemical behaviour of radioiodine as it is released from a variety of operations in the nuclear industry including the cutting of fuel sections in metallurgical examination caves and an incinerator.

Introduction

Airborne radioiodine is a mixture of chemical forms, so that filtering contaminated air efficiently depends on knowing both the behaviour of the various forms with filter media under different operating conditions and the relative amounts of each form in the mixture. Laboratory experiments have been useful for finding out how the various forms behave chemically, but they do not give any information about the composition of the mixture generated in nuclear reactor accidents. In this paper I will give the results obtained using a "May Pack" to separate the mixture of iodine forms following a deliberate rupturing of the sheathing of a single fuel element in a reactor. The accident simulated was reduction of coolant flow caused, for example, by either pump failure or partial block in the entrance to a fuel channel.

Description of Experiment

Water coolant flow to a single closed circuit experimental fuel channel in the NRX reactor at Chalk River was progressively reduced until the fuel sheathing ruptured. The reactor was
then immediately shut down and full cooling restored. A large fraction of the UO₂ fuel from the centre three elements of the seven element string was dispersed throughout the coolant.

Fission products are released dissolved in water escaping from small leaks and subsequently become free when the water evaporates. The piping, valves and pumps etc. for the single fuel channel were confined within a 50m³ room ventilated at a rate of 20m³/min. Air in the ventilating duct was sampled for one hour every hour 6 m from the enclosure using a modified "May Pack".

This consisted of the following filter elements in order:

1. 3 copper screens (100 mesh, 25 mm diameter) etched with hydrogen iodide solution (sp. gr. 1.70) and dried immediately before use.

ii. 1 glass fibre filter (Gelman Type E, 25 mm diameter)

iii. 3 charcoal impregnated filter papers (ACG/B, 25 mm diameter)

iv. 1 tube (16 mm diameter, 40 mm length) containing activated charcoal granules (18/35 mesh)

Coolant water was sampled 15 min. after rupture, separated from suspended solids and analysed 14 days later. The original coolant and water subsequently used to clean out the piping were drained to a catch tank but a leaking pump resulted in flooding of the floor of the small catch tank room. Both the water and air in the room were sampled and analysed four days later.

Each filter in the pack was counted individually using a 100 channel pulse height analyser. Only isotopes of iodine could be detected. All counts were corrected for decay to the time of the rupture.

Results and Discussion

In Table 1 the radioiodine found on each part of the pack is expressed as a percentage of the total in the sample.

During the first two or three hours more than half the iodine appeared on the copper screens, but this decreased slowly thereafter. On the other hand, the fraction found on the charcoal impregnated paper filters increased rapidly and more than doubled during the 6 hr. sampling period.

This trend may have continued as seen from the last column in which is given the composition of the mixture four days later in air above the flooded floor of the catch-tank.
Table 1

Distribution of $^{133}$I in components of the May Packs
(The other iodine nuclides $^{131}$I and $^{135}$I behaved identically).

<table>
<thead>
<tr>
<th>Time</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:25</td>
<td>57</td>
</tr>
<tr>
<td>15:25</td>
<td>59</td>
</tr>
<tr>
<td>16:30</td>
<td>53</td>
</tr>
<tr>
<td>17:10</td>
<td>52</td>
</tr>
<tr>
<td>18:25</td>
<td>46</td>
</tr>
<tr>
<td>19:47</td>
<td>7</td>
</tr>
<tr>
<td>18:10</td>
<td>6</td>
</tr>
<tr>
<td>19:25</td>
<td>1</td>
</tr>
<tr>
<td>20:47</td>
<td>1</td>
</tr>
<tr>
<td>4 days</td>
<td>64</td>
</tr>
<tr>
<td>later</td>
<td>22</td>
</tr>
</tbody>
</table>

room. By this time, less than $1/10$th of the iodine was found on the copper screens and nearly $2/3$rd on the charcoal papers. However, because of the change in conditions the two sets of results are probably not directly comparable.

Throughout the first 6 hours the fraction found on the charcoal column averaged about $10\%$. This is important since it is this fraction which may contain methyl iodide and removing this particular form from air streams by conventional charcoal filters has proved troublesome in some operating conditions.

In fact, the fraction found on the copper screens is most probably elemental iodine (1) which is readily absorbed by surfaces so that by the time the air stream reached the sampling point, the mixture would have been preferentially depleted in elemental iodine. Thus the values in Table 1 are minimal for the copper screen fraction and maximal for the other fractions and the maximum contribution from methyl iodide would have been less than $10\%$.

Despite the large proportion of UO$_2$ dispersed, less than $0.2\%$ of the iodine fission products it contained were dissolved in the water coolant. Their subsequent escape to the atmosphere would thereafter depend on the rate of coolant leakage from the system.
DISCUSSION

F. J. VILES: Did you use a metal or metal oxide fuel? If a metal fuel is used, significant HI may be produced and this raises the question as to where the HI would be collected in the "May Pack".

P. J. BARRY: It was UO₂ fuel. I believe that HI would behave more or less like elemental iodine; i.e. that it would be highly reactive and would be readily absorbed by the copper.

F. J. VILES: We carried out experiments which showed that freshly cleaned copper is not too efficient in collecting HI, but collection would be efficient if oxide were present on the copper.

J. L. KOVACH: Did you calibrate the May Packs used, to see if the copper screen collects all the elemental iodine?

P. J. BARRY: Yes, experiments which we did showed that the three copper screens used would collect at least 90% of the elemental iodine. The remainder could probably be removed by using more screens.

Reference

(1) Barry, P. J., Health Physics (1968), in the press.
METHYL IODIDE FORMATION UNDER POSTULATED NUCLEAR REACTOR ACCIDENT CONDITIONS

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Abstract

METHYL IODIDE FORMATION UNDER POSTULATED NUCLEAR REACTOR ACCIDENT CONDITIONS. The formation of methyl iodide under conditions of postulated nuclear reactor accidents is discussed. Although thermodynamic calculations indicate the equilibrium methyl iodide concentrations would be quite low, calculations based on a simple kinetic scheme involving reaction between small hydrocarbon species and iodine indicate that concentrations higher than equilibrium can occur during the course of the reaction. Such calculations were performed over a wide range of initial species concentrations and a range of temperatures representative of some reactor accident situations. These calculations suggest that little methyl iodide would be expected within the core volume where temperatures are maximum. At the gas leaves the core volume and expands into the plenum region, it cools and the concentration of methyl iodide increases. At the intermediate temperatures which might characterize this region, the formation of methyl iodide from thermally induced reactions could reach its maximum rate. The gas continues to cool, however, and it is probable that by the time it leaves the plenum region it has cooled to the point where thermally induced reactions may be of little importance.

Although the thermally induced reactions will become slower as the gas expands and cools, the radiation-induced reactions will not be slowed to the same extent. The gases leaving the core carry fission products and hence a radiation source is available to initiate reaction by a temperature-independent process. An investigation of the radiation chemical formation and decomposition of methyl iodide in the presence of steam suggests that radiation-induced methyl iodide formation will generally be rapid under the postulated accident situations. Thus, in the plenum region where thermal reactions have become slow, the radiation-induced reaction can still proceed and may well become the dominant factor. The same situation probably pertains as well to the containment region.

INTRODUCTION

The release and subsequent deposition of fission product iodine has been a recognized problem in reactor safety engineering for some time. Considerable effort has been expended to determine the rate and chemical and physical form of radiiodine release from the core, the rate of deposition on various surfaces of a reactor system, and the rate and form of release to the surroundings. Organic iodides as well as other iodine containing species are present in the atmosphere surrounding the core after an accident and experiments indicate that the major organic component is methyl iodide. However, the mechanism by which methyl iodide is formed is largely unknown. Without some knowledge of the mode of formation it becomes exceedingly difficult to extrapolate from laboratory experiment to the reactor situation and to predict with confidence what the methyl iodide concentration might be under given circumstances. The work reported here has been directed toward a fuller understanding of methyl iodide formation under postulated reactor accident situations and has been taken to the point where some tentative conclusions can be made.

In order to develop some insight into the relationship between these studies and the more practical side of the nuclear-reactor-safety
problem it is profitable to look qualitatively at the time-temperature sequence of events for a postulated accident. For this discussion a postulated loss-of-coolant accident for a typical large boiling water reactor [1] has been assumed. The heat-transfer and flow conditions are based on those corresponding to a time of 500 sec after blowdown and assume no metal-water reaction. The temperatures, flow rates, and iodine release rates used in these considerations were determined as part of another nuclear-safety research program conducted at Battelle's Columbus Laboratories [2]. The reactor core was assumed to have a diameter of 199 in. and an active core length of 12 ft. with an effective area for flow in the core of $1.82 \times 10^3 \text{cm}^2$.

The postulated blowdown accident involves a loss of coolant from the primary system with the coolant-water level dropping below the level of the core. The residual heat contained in the pressure vessel causes boiling of the water below the core, thus producing steam which sweeps through the core into the plenum system above the core and then out into the reactor containment building through the rupture in the primary system. Fission products, such as the radiiodine, which are released as the fuel cladding in the core deteriorates can be carried along with the steam. The steam boil-off rate has been estimated to be $3.7 \times 10^6 \text{cm}^3$ per sec. In the heat-transfer analysis the core had been divided radially into 10 annular regions of equal area and each radial region was divided along its length into 11 segments. For the present discussion, the temperature data were averaged over three radial regions, each sectioned axially into three sections. These results and the residence times for the flowing steam in each section based on the effective flow areas for the core and the steam boil-off rate are:

<table>
<thead>
<tr>
<th>Axial Section</th>
<th>Residence Time, Sec.</th>
<th>Center, K</th>
<th>Middle, K</th>
<th>Outer, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>8.4</td>
<td>1370</td>
<td>1283</td>
<td>1051</td>
</tr>
<tr>
<td>Middle</td>
<td>9.6</td>
<td>2112</td>
<td>1978</td>
<td>1627</td>
</tr>
<tr>
<td>Bottom</td>
<td>6.0</td>
<td>1198</td>
<td>1069</td>
<td>863</td>
</tr>
</tbody>
</table>

The center radial core region consists of the three central equal-area sections from the heat-transfer analysis with the middle and outer regions made up of three and four sections of equal area, respectively. Axially, the top, middle, and bottom sections consist of 35, 40, and 25 percent, respectively, of the active core length. The total residence time for gas flowing in the core is about 25 sec.

The time-temperature schedule assumed for the plenum system going from the top of the core to the opening to the containment is:

<table>
<thead>
<tr>
<th>Time, Sec.</th>
<th>Average Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>873</td>
</tr>
<tr>
<td>11</td>
<td>773</td>
</tr>
<tr>
<td>11</td>
<td>673</td>
</tr>
<tr>
<td>22</td>
<td>573</td>
</tr>
</tbody>
</table>

Total residence time in the plenum is about 55 sec. The steam is then assumed to exit to the containment which is at 100 C, or 373 K. Iodine inputs in g mole per liter for the different core section are given below.
Recent measurements of organic content of reactor building atmospheres by ADAMS, et al. [3] at ORNL indicate that total hydrocarbon concentrations could reach levels of $10^{-7}$ moles per liter and were generally in the range of $10^{-9}$ to $10^{-7}$ moles per liter. The majority of this organic material was unsaturated compounds which probably would be quite reactive toward iodine. If the concentrations within the reactor buildings are at all indicative of what might be in the reactors themselves, the ratio of organic species to iodine could vary over many orders of magnitude and probably would be greater than one.

Preliminary calculations indicated that methyl iodide would not be formed in large quantities above about 1200 K. Thus the regions where most thermally induced formation of methyl iodide are likely to occur are the upper region of the core and the plenum where temperatures range from perhaps 500 to 1400 K and iodine concentrations range downward from about $10^{-6}$ g mole per liter.

The gas in the plenum region carries its own radiation source in the form of fission products as well as being irradiated by the core. As fission products are swept into the containment region the gas there also becomes essentially a homogeneous radiation source. Although thermally induced reactions leading to methyl iodide are expected to decrease as the gas cools, the radiation reactions may be largely temperature independent. Radiation induced reactions must also be included, therefore, as a possible mechanism for methyl iodide production in an accident situation. Some of the possible mechanisms involved in the thermal and radiation induced formation of methyl iodide under conditions pertinent to postulated accident situations are discussed in the following sections.

**EQUILIBRIUM AND KINETIC STUDIES OF METHYL IODIDE FORMATION**

The primary objective of the chemical-equilibrium and kinetic studies was to explore possible mechanisms for the formation of organic iodides in nuclear-reactor accident environments. A relatively complex chemical system containing H$_2$O, CO$_2$, HI, N$_2$, CH$_3$OH, I$_2$, CH$_3$I, H$_2$, O$_2$, CO, CH$_4$, CH$_2$O, and, in some cases solid carbon, was considered initially. The results of these calculations show that if equilibrium conditions exist, the CH$_3$I concentration should be several orders of magnitude lower than that which is observed experimentally under comparable conditions, indicating the probable importance of kinetic factors. Additional equilibrium calculations were then made to determine whether the observed CH$_3$I concentrations could be reproduced by suppressing the presence of certain species in the chemical system. These calculations showed that the observed CH$_3$I concentrations could be predicted above 700 K for a simple equilibrium system containing only CH$_4$, I$_2$, CH$_3$I, and HI, with the CH$_4$ present at a concentration of $4 \times 10^{-8}$ g moles per liter which is equivalent to that occurring naturally in the atmosphere. As additional compounds were added to the system, the CH$_3$I was reduced. Neglecting certain species in the equilibrium calculations is considered to be equivalent to the assumption that these species have negligible reaction rates.
<table>
<thead>
<tr>
<th>Type of Chemical System</th>
<th>Case</th>
<th>Elemental Species Concentration, g atoms per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air</strong>(a)</td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>1</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>2</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>3</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>4</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>5</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>6</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>7</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>8</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td>9</td>
<td>7.000 x 10^-4</td>
<td>1.922 x 10^-3</td>
</tr>
<tr>
<td><strong>Steam</strong></td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>10</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>11</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>12</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>13</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
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<tr>
<td>14</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
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<tr>
<td>15</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>16</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>17</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
<tr>
<td>18</td>
<td>7.000 x 10^-4</td>
<td>6.642 x 10^-2</td>
</tr>
</tbody>
</table>

(a) Pure air containing an amount of water vapor equivalent to that in air saturated with water vapor at 70 F
The inability of the equilibrium calculations to reproduce the levels of CH$_3$I observed experimentally led to interest in the chemical-kinetic aspects of the problem. The general approach for these studies has been to use the reasonably simple homogeneous reaction between CH$_4$ and I$_2$ which has been studied by GOLDEN, WALSH, and BENSON [4] over a narrow temperature range from about 600 to 700 K, as a basis for the analysis. This reaction scheme involves three reversible chemical reactions which include CH$_3$I, CH$_3$, HI, and I in addition to the initial reactants, CH$_4$ and I$_2$. Rate data for these reactions are either taken from the literature or determined through standard estimation procedures. Additional details on these studies may be found in References [5,6].

Equilibrium Studies

The total iodine species concentrations of interest in nuclear safety considerations are generally within the range of $10^{-12}$ to $10^{-6}$ moles per liter. Of the total iodine, as much as 15 percent has been observed in experiments as CH$_3$I with the remainder distributed between the I$_2$ and HI forms.

To formulate the complex equilibrium problem it is necessary to postulate a source of carbon. Air normally contains about 0.03 mole percent CO$_2$ and additional carbon compounds are present, particularly in polluted air. Carbon in the solid state may also be present in large quantities in such sources as the carbon steel in a reactor pressure vessel. To cover the range of possible sources of carbon, equilibrium calculations were made for the case where solid carbon is always present in the system and for the case where the carbon present is limited to that associated with the CO$_2$ in normal air. Under certain conditions, where solid carbon must be present to satisfy the equilibrium criteria, the two cases give the same results. To bracket the oxygen and hydrogen concentrations, one set of calculations was based on pure air containing an amount of water vapor equivalent to that in air saturated with water vapor at 70 F and with three different initial oxygen concentrations. The other set of calculations was based on steam. The levels of iodine assumed were $4 \times 10^{-6}$, $4 \times 10^{-8}$, $4 \times 10^{-10}$, $4 \times 10^{-11}$, and $4 \times 10^{-12}$ g atoms per liter at 300 K for both sets of calculations. The concentration values selected for computer processing are based on Table I. In the steam cases, the oxygen and hydrogen concentrations for the higher temperatures were obtained from standard steam tables. The other concentrations for the higher temperatures were determined by multiplying the data at 300 K by the appropriate absolute-temperature ratio. All calculations were made for a pressure 1 atm.

The species present at equilibrium were selected as: H$_2$O, CO$_2$, HI, N$_2$, CH$_3$OH, I$_2$, CH$_3$I, H$_2$, O$_2$, CO, CH$_4$, CH$_2$O, and, in some cases solid carbon. These species were chosen in an attempt to obtain a reasonably good approximation to the true equilibrium concentrations in the carbon, iodine, hydrogen, and oxygen system under the conditions of interest. Iodides of higher hydrocarbons were neglected as they are observed only in very low concentrations. For cases in which the carbon in the gas phase increased at the expense of the solid carbon, it is necessary to perform calculations where the solid carbon is eliminated in order to satisfy the material-balance restraints when the maximum amount of carbon that can be present is equivalent to that based only on CO$_2$.

For the equilibrium calculations, the matrix method described by KOBE and LELAND [7] was used to set up a mathematically independent system of chemical equilibrium and mass-balance equations having a solution in terms of
FIG. 1. Equilibrium species concentrations for carbon, hydrogen, oxygen, nitrogen, and iodine system with solid carbon (air system).
concentration variables. Generally, these equations consist of a set of linear and a set of nonlinear algebraic equations that must be solved simultaneously. The solutions of these equations were obtained using a digital-computer program based on the Newton-Raphson method. The equilibrium constants used in these calculations were derived from standard free-energy values tabulated in LANDOLT-BÖRNSTEIN \[8\] and the NBS tables compiled under the direction of ROSSINI \[9\].

A few of the results of the computer calculations are summarized in Figures 1 and 2, where species concentrations are plotted against the absolute temperature. The curves in the figures are based on points calculated at 100-degree intervals. Only the results for the total iodine concentration of $4 \times 10^{-10}$ g atoms per liter are presented but they are typical of all results. Except for the air system where the total carbon is limited, the results of the other iodine concentrations can be obtained by multiplying the concentrations of the iodine-bearing species by the ratio of initial iodine concentrations. In these cases, the concentrations of the other species are virtually unaffected by the variations in the total iodine concentration at these low iodine levels.

Considering first the air system shown in Figure 1 where an unlimited amount of solid carbon is present, the concentrations of the iodine compounds are affected very little at the higher temperatures by the variation in oxygen. The HI is the predominant iodine compound and remains largely unchanged over the oxygen variation of two orders of magnitude. For the highest oxygen concentration of $1.872 \times 10^{-2}$ g atoms per liter, the CH$_3$I levels off at a maximum of about $4 \times 10^{-17}$ g moles per liter. Reduction of the oxygen by both one and two orders of magnitude gives a peak in the CH$_3$I concentrations of about $7 \times 10^{-17}$ g moles per liter at about 800 K.

Limiting the carbon to an amount equivalent to that associated with CO$_2$ in normal air had only a very slight effect on the HI at the lower total oxygen levels. The maximum CH$_3$I concentration occurred with the lowest oxygen level and peaked at a temperature of about 700 K. The major effect of limiting carbon was on the carbon-containing compounds other than methyl iodide, such as methane and carbon monoxide or dioxide. This is the expected result since CH$_3$I is the carbon-containing species present in the lowest concentration and, hence, the least affected by limitations on carbon availability. The maximum CH$_3$I formation decreased from $10^{-16}$ to $4.5 \times 10^{-17}$ g mole per liter with an order-of-magnitude increase in oxygen. Another order-of-magnitude elevation in the oxygen produced a drastic decrease in the CH$_3$I. All of the carbon was in the form of CO$_2$, leaving virtually none to form CH$_3$I. Most of the hydrogen was also bound in the oxide form, leaving I$_2$ as the major form of iodine. The peak for the intermediate total oxygen concentration occurred at 600 K, while that for the highest oxygen content was apparently above 1000 K. Limiting the carbon tends to drastically reduce the CH$_3$I at the higher temperatures particularly for the two higher levels of oxygen.

The results of typical calculations for the steam system are given in Figure 2. The CH$_3$I concentration for the cases where solid carbon is present (Figure 2) is relatively insensitive to changes in oxygen concentration, with the highest oxygen level showing a small reduction in CH$_3$I. At the lowest oxygen level the CH$_3$I peaks at about 800 K with a maximum concentration of about $1.5 \times 10^{-15}$ g moles per liter. At the two higher levels of oxygen, the peaks move out to 900 K with almost the same maximum CH$_3$I concentration. The CH$_3$I concentrations in the steam cases are over a factor of 20 higher than those for the air system with solid carbon present.
FIG. 2. Equilibrium species concentrations for carbon, hydrogen, oxygen, and iodine system with solid carbon (steam system).
Limiting the carbon in the steam system resulted in an overall reduction in the CH$_3$I, while for the air system the limitations on the carbon caused a reduction only in the cases of the two higher oxygen levels. The magnitudes of the CH$_3$I reduction were also greater in the steam case. The highest oxygen level produced a CH$_3$I profile that peaked at 600 K with a maximum concentration of about 2.5 x 10$^{-17}$. Comparing the air and steam system when the carbon was limited, it was seen that the air system, in general, gave higher CH$_3$I concentrations. The reverse is observed if the two systems are compared when solid carbon is always present.

The results of the equilibrium calculations are summarized in Figure 3 for both air and steam, where the fraction of total iodine in the system appearing at equilibrium as methyl iodide is given for temperatures ranging from 300 to 1200 K. In all cases investigated the maximum methyl iodide appears at about 800 to 1000 K but the methyl iodide fraction is never large. From the previous figures it is apparent that under all conditions investigated hydrogen iodide is the only iodine species present at equilibrium in relatively large concentration. It will, in fact, account for essentially all of the iodine in the system. The results summarized

![Figure 3](image-url)
FIG. 4. Concentrations of CH$_3$I and HI as a function of temperature for the chemical equilibrium systems containing I$_2$, HI, CH$_3$I, and CH$_4$ with and without hydrogen (based on total carbon and iodine concentrations of $4 \times 10^{-8}$ and $2.4 \times 10^{-10}$ g atoms per litre, respectively).
in Figure 3 cover a range of initial iodine concentrations from $4 \times 10^{-12}$ to $4 \times 10^{-6}$ g atoms per liter. Over this range the methyl iodide fraction remains constant for any given set of steam-oxygen-temperature conditions. That is, tenfold increase in total iodine in the system leads to a tenfold increase in methyl iodide but also the same increase in hydrogen iodide. The fraction of total iodine appearing as methyl iodide is unchanged.

Since the complex equilibrium calculations did not reproduce the experimentally observed CH$_3$I concentrations, attention was shifted to the chemical-kinetic aspects of the problem. Rigorous treatment of the kinetics requires detailed knowledge of the reaction mechanisms, which even for fairly simple reactions are sometimes quite difficult to formulate. In fact, very few reactions exist for which all details are known concerning their individual steps and the mechanisms associated with these individual steps. It would, of course, be impossible to perform a detailed mechanistic investigation of all the reactions involving the species considered in the complex equilibrium studies. It is possible, though, to treat many kinetic-rate processes using overall reaction-rate coefficients. Further simplification can sometimes be achieved when certain reactions can be disregarded because their rates are either extremely high or low in comparison to those of the reactions that control the species of interest. A simple equilibrium process can be thought of as a reaction proceeding in both forward and reverse directions with equal rates. Chemical equilibrium constants can then be expressed in terms of rate coefficients. In some instances, the equilibrium constants can be used to determine the asymptotic or maximum values of species concentrations. Thus, in searching for possible kinetic schemes, the equilibrium approach may be used as a basis for choosing reactants that may participate in the formation of the species of interest. This is a somewhat unsystematic approach although it appeared to be one worth pursuing in the present case; here, the equilibrium concentrations do not match the measured concentrations, but are much lower. The obvious explanations for this disparity are that either the theoretical system does not represent the actual system or the actual system is not at equilibrium. The latter explanation is considered to be the appropriate one since the theoretical system was made sufficiently complex to offer a good approximation to the true situation. In applying the equilibrium approach, a few logical species are chosen which could react to give the product of interest, which in the present case is CH$_3$I. Neglecting certain species is considered to be equivalent to assuming that these species have negligible reaction rates. Discovery of an appropriate subset of species that leads to the observed concentrations is assumed to imply that a kinetic scheme can be formulated that will account for the observations.

If it is considered that only CH$_4$, I$_2$, CH$_3$I, and HI are in equilibrium and no other species are contributing to the reaction products, then equilibrium methyl iodide concentrations of the order of $10^{-18}$ g moles per liter are predicted at temperatures above about 700 K. This concentration is consistent with experimental results. In the calculations shown in Figure 4, Curve A represents the CH$_4$, CH$_3$I, I$_2$, and HI system based on the chemical reaction CH$_4$ + I$_2$ $\rightarrow$ CH$_3$I + HI. Total concentrations of iodine, carbon, and hydrogen are $2.4 \times 10^{-10}$, $4.0 \times 10^{-8}$, and $1.6 \times 10^{-7}$ g atoms per liter, respectively. The quantity of carbon and hydrogen is equivalent to that contained in air in the form of CH$_4$. At the highest temperatures, the iodine is essentially all converted to about equal amounts of CH$_3$I and HI.

This is not a very realistic situation, however, since hydrogen and elemental carbon would almost certainly be present. Curves B, C, and D of Figure 4 show the effect on methyl iodide (solid line) and hydrogen iodide (dashed line) of small amounts of hydrogen above that needed to balance the
carbon if it is assumed all carbon is initially present as methane. That is, the difference between $1.6 \times 10^{-7}$ and $5 \times 10^{-7}$, for instance, represents the initial hydrogen in excess of that in the form of methane. Small amounts of hydrogen in excess of methane strongly shift the equilibrium from methyl iodide to hydrogen iodide. The hydrogen iodide predicted in this simple equilibrium system is about that seen in the previously discussed complex systems. Although the "excess" hydrogen has severely depressed equilibrium methyl iodide, the predicted concentrations in the simple system are not quite as low as in the complex system. Curves B, C, and D are based on the two equilibrium reactions: $\text{CH}_4 + \text{HI} = \text{CH}_3\text{I} + \text{H}_2$ and $2\text{HI} = \text{I}_2 + \text{H}_2$.

Considering the kinetic aspects of these equilibrium calculations, it appears that the reactions leading to hydrogen iodide at the expense of methyl iodide are slow compared to the rate of formation of methyl iodide. In this type of situation the approach to equilibrium is slow and the methyl iodide concentration could reach concentrations much higher than equilibrium concentrations.

The situation is somewhat different when solid carbon is present, although allowing the formation of $\text{H}_2$ again depresses the formation of $\text{CH}_3\text{I}$. In the system $\text{CH}_4$, $\text{CH}_3\text{I}$, $\text{HI}$, $\text{I}_2$, and solid carbon, the solid carbon is considered to be an infinite supply. A continual increase in total hydrogen then leads to an increase in methane and, hence, the methyl iodide in equilibrium with it. The change in methyl iodide with total hydrogen concentration is shown in Figure 5. However, essentially all the iodine is in the form of hydrogen iodide at equilibrium under these conditions. At 500 K, for instance, the iodine as HI is about five orders of magnitude greater than in $\text{I}_2$ and $\text{CH}_3\text{I}$ combined. As before, the reaction leading to hydrogen iodide at the expense of methyl iodide must be slow to explain the laboratory results of various experimenters, in light of the predicted equilibrium concentrations.

The results of these equilibrium studies indicate that if equilibrium conditions did exist, the iodine would be expected to occur predominantly as HI, with the $\text{CH}_3\text{I}$ and $\text{I}_2$ concentrations at least several orders of magnitude lower than that of the HI. The higher $\text{CH}_3\text{I}$ and $\text{I}_2$ concentrations found experimentally indicate that kinetic factors are important and must be taken into account to explain the experimental results. Calculations were made to determine whether the observed $\text{CH}_3\text{I}$ concentrations could be reproduced by suppressing the presence of various species in the equilibrium system. It was found that the observed concentrations of $\text{CH}_3\text{I}$ could be calculated using the simple equilibrium system containing only $\text{CH}_4$, $\text{I}_2$, $\text{CH}_3\text{I}$, and $\text{HI}$, with the $\text{CH}_4$ concentration equivalent to that occurring naturally in the atmosphere. As additional compounds were added to the system the $\text{CH}_3\text{I}$ was reduced. This indicates that it should be possible to formulate a kinetic treatment of the problem which will lead to the observed $\text{CH}_3\text{I}$ concentrations. It was also found that in some cases the presence of hydrogen can shift the equilibrium from $\text{CH}_3\text{I}$ to HI.

Homogeneous Kinetics Studies

To establish a basis for the more complex reaction system of interest, it was decided to start with the reaction between $\text{CH}_4$ and $\text{I}_2$ producing $\text{CH}_3\text{I}$. This reaction has been studied at about 600 to 670 K by GOLDEN, WALSH, and BENSON [4] who have reported rate data for the reaction. According to them, the reaction mechanism can be expressed as

$$k_5 \quad \text{I}_2 + \text{M} \rightarrow 2\text{I} + \text{M}$$
where $M$ represents a third body which can be any one of the chemical species present. The reaction-rate constants assumed are given in Table II. The reaction rate constants for Steps 1 through 4 in the above reaction scheme were determined by assuming that the reaction mechanism remains the same outside the temperature range investigated experimentally and extrapolating the data to other temperatures. The data for Reactions 5 and 6 are based on the relationship

$$k_6 = 7.15 \times 10^9 \left( \frac{298}{T} \right)^{1.33}$$

which assumes CH$_4$ as the third body. This relationship was obtained using the results of BUNKER and DAVIDSON [10, 11, 12] for iodine atom recombination in argon, and correcting them to apply to CH$_4$. The rate constant, $k_5$, was then determined from $k_6$ and the equilibrium constant for the reaction.

---

**FIG. 5.** Concentration of CH$_3$I as a function of total hydrogen concentration and temperature for the chemical-equilibrium system containing I$_2$, HI, CH$_4$, CH$_3$I, and solid carbon with and without hydrogen (based on a total iodine concentration of $2.4 \times 10^{-19}$ g atoms per litre at 500°K).
TABLE II. RATE CONSTANTS FOR CHEMICAL KINETIC CALCULATIONS.

<table>
<thead>
<tr>
<th>Reaction Rate Constant</th>
<th>Units</th>
<th>Value at Indicated Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 K</td>
<td>600 K</td>
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<tr>
<td>k1</td>
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<tr>
<td>k8</td>
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</tbody>
</table>
In general, the kinetics problem is formulated in terms of reaction rate equations in the form of first-order differential equations and mass-balance equations, which are algebraic in form and contain no derivatives. The mass-balance equations can be substituted into the differential equations to reduce the total number of equations. These differential equations then constitute a system of simultaneous equations, usually nonlinear, which when coupled with the initial conditions form the mathematical expression of the problem. Analytical solutions can be found only for the most simple problems. To handle most problems it is generally necessary to resort to numerical techniques such as the Adams-Moulton or Runge-Kutta methods using a computer.

To solve the required equations, an existing computer program at Battelle-Columbus based on the Adams-Moulton method was used. Results of these calculations for temperatures of 800 to 1000 K are shown in Figures 6 and 7 in terms of species concentrations as a function of reaction time. Both figures are based on initial concentrations of $4 \times 10^{-8}$ g mole per liter $\text{CH}_4$ and $1 \times 10^{-10}$ g mole per liter $\text{I}_2$ with no other species initially present. The equilibrium concentrations given on the right ordinate in the figures were calculated from free-energy values as described previously. For the most part, the near equilibrium concentrations from the kinetic calculations agree reasonably well with those determined thermodynamically. At temperatures of 800 and 1000 K concentrations rapidly reach a peak and then drop to their equilibrium values. The peaks occur within a period covered by most experiments where CH$_3$I is observed. Thus CH$_3$I concentrations at the levels observed experimentally can be reproduced by this simple calculational model, indicating the possibility that the high CH$_3$I concentrations observed experimentally could be nonequilibrium concentrations produced at high temperatures and then frozen in at low temperatures.

![FIG. 6. Species concentrations as a function of time for the reaction between CH$_4$ and I$_2$ at 800°K (based on reaction system 1 and initial concentrations of $4 \times 10^{-8}$ g mole per litre of CH$_4$ and $1 \times 10^{-10}$ g mole per litre of I$_2$).](image-url)
The first step in expanding the reaction system has been to add the radical reaction (Reaction System 2)

$$\text{CH}_3 + \text{I} \rightarrow \text{CH}_3 \text{I}$$

to the previously described reactions. This reaction was added because of the high apparent radical concentrations predicted by the previous calculations. Appropriate rate constants for System 2 are tabulated in Table 2 for temperatures ranging from 400 to 1200 K. The rate constants for Reaction 8 were obtained from the relation

$$k_8 = 3.93 \times 10^{12} \exp \left(\frac{-43,000}{RT}\right) \text{ sec}^{-1}$$

reported by BAWN [13] for temperatures ranging from about 520 to 600 K. The rate constants for $k_7$ were then calculated from those of $k_8$ and the equilibrium constant.

Species concentrations as a function of time were calculated by computer as before. The results are shown in Figure 8. These results are based on the reaction at 800 K between $\text{CH}_4$ and $\text{I}_2$ with initial concentrations of $4 \times 10^{-8}$ and $1 \times 10^{-10}$ g mole per liter, respectively, and nonreacting inert species at a concentration of $1.269 \times 10^{-2}$ g mole per liter. The inert species, whose concentration level is comparable to that of the nitrogen and oxygen present in air at 1 atm, participates only as the third body in the
iodine dissociation-recombination reaction. The presence of the inert species permits the I and I₂ concentrations to attain equilibrium about five orders of magnitude faster. No overshoot or peaking in the CH₃I concentration occurred as it did in the earlier calculations where neither the inert species nor the reactions associated with k₇ and k₉ were included. Unfortunately, however, it was not possible to carry calculations to equilibrium for cases affording direct comparisons between Systems 1 and 2. Other calculations which were initiated involved the same initial CH₄ and I₂ concentrations at temperatures of 800, 1000, and 1200 K with and without inert species present. The differential equation systems for these cases, however, were found to be stiff, thus requiring impractically long computer times for numerical integration using the Adams-Moulton or Runge-Kutta methods. Some of the calculations are summarized in Figures 8 and 9, which compare System 2 with and without inert species present to System 1. Even though calculations were not carried to reaction equilibrium in all cases, some differences between the reaction systems are evident.

Figure 8 shows the comparison between the two reaction systems at 800 K. The addition of the one reaction involving k₇ and k₉ to System 1 without inert species produces a reduction of about one order of magnitude or greater in CH₃I concentration for times between 10 to 10⁷ sec. The variation in HI between the two cases is less pronounced during this same time interval. The results for System 2 without inert species were not taken to reaction equilibrium. However, they do tend to indicate very little or possibly no peak in the HI and CH₃I concentration. This absence of peak is observed for System 2 with inert species present, a case in which the kinetic calculations are complete. In this latter case HI and CH₃I
reach equilibrium concentrations in a short time and are significantly higher for reaction times up to 10^4 sec than those calculated for Systems 1 and 2 with no inert species.

At 1000 K, as shown in Figure 9, CH$_3$I in System 1 with no inert species peaks at about the same concentration as it did at 800 K but then drops almost three orders of magnitude to an equilibrium concentration two orders of magnitude less than that at 800 K. In the case of System 2 without inert species, for which the calculations are for short reaction time only, the CH$_3$I is reduced by at least two orders of magnitude in comparison with System 1 for times ranging from 1 to 10 sec, while the HI concentrations are almost identical from 10$^{-2}$ to 10 sec. Increasing the reaction system pressure by the additions of inert species to System 2 produces a CH$_3$I concentration that is initially higher than that for both System 1 and 2 with no inert species present. At about 2 sec, the CH$_3$I concentration for System 2 with inert species present crosses over the CH$_3$I curve for System 1 and appears to be bending toward its equilibrium value without showing any definite peaking tendency. The inert species also increase the HI formation for reaction times up to 100 sec at which time its concentration is approximately equivalent to its equilibrium value. In general, it appears that the addition of the radical reactions $k_7$ and $k_8$ to reaction System 1 results in the elimination of or a significant reduction in the magnitude of the CH$_3$I peak at both 800 and 1000 K. The presence of the inert species in the cases studied appears to decrease the reaction time necessary to attain equilibrium.

The results of homogeneous kinetics calculations based on System 1, the simple reaction involving CH$_4$ and I$_2$, show nonequilibrium CH$_3$I concentrations which are higher than the concentrations attained at
equilibrium. The overshoot in the CH$_3$I can be more than two orders of magnitude greater than the equilibrium values at temperatures of 800 and 1000 K, with the maximum difference being at the higher temperature. The CH$_3$I concentrations that are higher than equilibrium occur for reaction times between about 1 min and 1 hr. This places the CH$_3$I peak at a point in time where it could be a factor in many of the experiments where CH$_3$I concentrations above those expected at equilibrium are observed. Thus CH$_3$I concentrations at the levels observed experimentally can be reproduced by this simple calculational model, indicating the possibility that the high CH$_3$I concentration observed experimentally could be nonequilibrium concentrations produced at high temperatures and then frozen in at low temperatures.

RADIATION INDUCED FORMATION OF METHYL IODIDE

There has been very little work on the radiation induced formation of methyl iodide under conditions pertinent to postulated reactor accident conditions except those of TANG and CASTLEMAN [14]. The experiments described here were undertaken to provide data on the formation of methyl iodide in a radiation field over a range of temperatures and in the presence of water. All experiments were conducted in the gas phase in sealed glass vials in a $^{60}$Co source. Methane and iodine were the reactants in all cases except where methyl iodide decomposition was being investigated. Product methyl iodide was measured by gas chromatography and, in the case of methyl iodide decomposition, product iodine was determined spectrophotometrically. Details of the experimental procedures have been reported elsewhere [6].

In the experiments summarized here, total doses ranged up to $5 \times 10^7$ rad and dose rates ranged between $9.0 \times 10^5$ and $7.1 \times 10^6$ rad per hour, methane:iodine mole ratios ranged from 10:1 to 500:1 and steam:methane mole ratios up to 4:1 were used. The irradiations were performed at temperatures from 50 to 350 C.

Reaction to produce CH$_3$I from CH$_4$ and I$_2$ proceeds smoothly to high conversions of iodine when methane is in excess. Typical results are shown in Figure 10 for experiments at 100 C and a dose rate of $3.2 \times 10^5$ rad/hr. The G-value for CH$_3$I production changed somewhat with reactant ratio, reaching a maximum of $G$(CH$_3$I) = 4.4 with a CH$_4$:I$_2$ mole ratio of about 300. The high conversions are not unexpected since in all cases methane is in excess. As long as iodine remains (a well known radical scavenger) to react with methyl radicals formed by irradiation of methane, the yield of methyl iodide should increase and its rate of formation should be directly proportional to the rate of methyl radical formation. Over the range of dose rates used in these experiments, the G-value for methyl iodide formation is independent of dose rate.

Under the conditions used in this investigation it is expected that the radiation induced formation of methyl iodide would be independent of temperature. As discussed in the previous section, the thermal reaction between methane and iodine becomes quite slow below about 600K. The radiation induced formation of methyl radicals from methane is independent of temperature and the scavenging of those radicals by iodine requires little or no activation energy. The rate of formation of CH$_3$I from CH$_4$ and I$_2$ in a radiation field at some fixed dose rate would be expected to remain constant until the rate of the thermal reaction exceeds that of the radiation induced reaction. The temperature at which the thermal reaction begins to predominate will be proportional to the dose rate. Data from about 30 irradiation experiments are summarized in Figure 11 which shows that at a dose rate of $3.2 \times 10^5$ rad/hr the rate of CH$_3$I formation remains constant up to a temperature of about 550 K whereupon the rate of formation increases.
FIG. 10. Radiation conversion of methane-iodine to methyl iodide at 100°С and various reaction ratios.

FIG. 11. Summary of radiation runs for CH₃I from CH₄ and I₂ at several temperatures and 6 x 10⁸ rad.
markedly with increasing temperature. All of these experiments were at a total dose of $6.0 \times 10^5$ rad utilizing a 90 cm$^3$ sealed reaction vessel initially containing 350 mm CH$_4$ and 5 mg of I$_2$ for a mole ratio CH$_4$:I$_2 = 87$. Below 275 C (548 K) the thermal reaction is insignificant and above 350 C (623 K) the radiation reaction is insignificant compared to the rate of the thermal reaction. Between these limits there is apparently a synergistic effect between radiation and heat as indicated by the following data:

1. Conversion of iodine to methyl iodide during 18 hrs. of irradiation at 275 C = 1.9 percent.
2. Conversion of iodine to methyl iodide during 18 hrs. without irradiation at 325 C = 4.3 percent.
3. Conversion of iodine to methyl iodide during 18 hrs. of irradiation at 325 C = 15 percent.

If the radiation-induced reaction rate remained constant between 275 and 350 C as it does below 275 C, the expected conversion would be the sum of the radiation and thermally induced reactions, or about 6.2 percent. The observed conversion is significantly higher than this, however. The reason for this effect is not known.

The effect of steam or steam-air mixtures on the reaction between CH$_4$ and I$_2$ is quite pronounced, as shown in Figure 12 at 100 C. The presence of oxygen leads to a significant decrease in the rate of formation of methyl iodide. Oxygen is known to act as a free radical scavenger so this effect is not surprising. When water alone is present but at a concentration less than that of methane, it has little, if any, effect. When water is in excess, however, the effect is pronounced and leads to an increase in the rate of methyl iodide production, i.e., $G(CH_3$I) = 5.5.

![FIG. 12. Effect of saturated steam and steam-oxygen on radiation conversion of 100.1 mole ratio methane:iodine to methyl iodide.](image_url)
The fact that excess water increases the yield of methyl iodide is interesting since in this case most of the energy is absorbed initially by the water. The increase in methyl iodide then implies some transfer of absorbed energy from the water to the CH₄:I₂ system. This could be transfer of energy directly from H₂O to CH₄ similar to the well-known rare gas sensitization sometimes observed in gas systems or perhaps some ion-molecule reaction leading to eventual methyl radical formation. Also, hydrogen and hydroxyl radicals are formed by irradiation of water and if some of these should abstract hydrogen from methane, methyl radicals would be formed in excess of those expected from direct irradiation of methane. Any such increase in methyl radical production would be expected to lead to increased methyl iodide formation.

The effect of water on the radiolytic decomposition of methyl iodide is to decrease the rate, as has been shown previously by CASTLEMAN [14]. Typical results obtained at 150°C and dose rate of 3.2 x 10⁵ rad/hr are shown in Figure 13. The decomposition in the presence of steam is seen to be consistently less than in the absence of steam. Also the rate of decomposition is decreasing with increasing dose even though only a few percent of the CH₃I has been consumed. This is consistent with the high conversions to methyl iodide observed in the previous experiments and indicates that in the presence of a radiation field the steady-state CH₃I concentration can be a high fraction of the total iodine concentration.

FIG. 13. Radiation decomposition of methyl iodide in the presence and absence of steam at 150°C.
Although no detailed studies were made to determine the mechanism, the main direct-radiation-initiated reactions expect to be of importance are:

\[ \text{CH}_4 \xrightarrow{k_f} \text{CH}_3 + \text{H} \]

and

\[ \text{CH}_3\text{I} \xrightarrow{k_d} \text{CH}_3 + \text{I} \]

Although there will be some direct radiolysis of the iodine, it will never be more than a few percent of the effect in the methane since most of the energy is absorbed by the methane under the condition of excess methane used in this study. Under these conditions the radiation-induced rates of formation and decomposition of methyl iodide are about equal. The G-value for formation is about 5.5 and the G-value for decomposition is about 6 in steam atmospheres. It is then expected that the same reaction steps involved in the thermal reaction of methane and iodine would be important in the radiation reactions even though the temperatures are different.

Under the conditions of the experiment and the previous calculations, an almost constant concentration of methyl radicals would be expected from the radiation interaction with methane. Since \( k_2 \) is much larger than \( k_4 \), and the rate of formation of \( \text{CH}_3 \) is larger than \( \text{I} \), \( \text{CH}_3\text{I} \) will form rapidly as long as there is significant iodine present. Also, \( k_1 \) is small compared to \( k_3 \), and with an essentially constant supply of \( \text{CH}_3 \), it is likely that \( \text{CH}_3\text{I} \) would be favored over \( \text{HI} \) in this simplified view. Although \( k_4 \) and \( k_f \) are of the same order of magnitude, the excess of \( \text{CH}_4 \) over \( \text{CH}_3\text{I} \) will keep the radiation decomposition of methyl iodide from being a major factor in the overall reaction, at least until almost all of the iodine is converted to iodide.

Although this is an oversimplified mechanism, it agrees qualitatively with the experiments presented above. Starting with methane and iodine, the conversion of iodine to methyl iodide is linear with dose at a given dose rate. High conversions to \( \text{CH}_3\text{I} \) are achieved and methyl iodide is favored over hydrogen iodide as a product under the conditions used in this study. Also, when methyl iodide is initially the only reactant, decomposition does not precede very far before deviations from linearity are observed at a constant dose rate. That is, with only a small conversion of the iodine in the reactant (\( \text{CH}_3\text{I} \)) to molecular iodine (\( \text{I}_2 \)), deviations from the simple radiation decomposition of methyl iodide are manifest. That is in qualitative agreement with the simple mechanistic picture discussed above.

CONCLUSIONS

If we can assume that \( \text{CH}_4 \) is present at a concentration of \( 4 \times 10^{-8} \) g mole per liter and that steam is about \( 3 \times 10^{-2} \) g mole per liter, then from Figures 8 and 9 one would expect the \( \text{CH}_3\text{I} \) coming from the core to be near equilibrium at a concentration below \( 10^{-12} \) g mole per liter. As can be seen in Figure 9, the methyl iodide at 1000 K is near equilibrium at about 100 sec. In general, the temperatures within the core are well above 1000 K and the higher temperature would lead to lower methyl iodide equilibrium concentrations as well as more rapid equilibrium. Also the higher concentration of inert species in a postulated accident situation would lead to more rapid equilibration.
The iodine concentration may be several orders of magnitude higher in the postulated accident situation than covered in the kinetic calculations. Equilibrium calculations, however, with iodine concentrations of the order of $10^{-6}$ g mole per liter show maximum CH$_3$I concentrations of the order of $10^{-18}$ g mole per liter at 1000 K dropping to about $10^{-20}$ g mole per liter at 1500 K. The CH$_3$I concentration at the core exit is expected to be quite low, therefore.

As the steam leaves the core and flows through the plenum system the gas cools rapidly shifting the equilibrium in favor of CH$_3$I. The hot steam exiting from the core may have a low CH$_3$I concentration but relatively high levels of methyl radicals and iodine atoms. As the gas is cooling in the plenum region, the kinetics probably can be represented by the reactions described earlier for which CH$_3$I concentrations higher than equilibrium can be predicted under some conditions. Although the calculations indicate that 55 seconds in the plenum system would not be long enough to reach peak or approach equilibrium CH$_3$I concentrations, in the postulated accident situation the iodine concentration could be several orders of magnitude higher than used in the calculations and the pressure could also be higher. Both of these factors would probably lead to significant decreases in the time to reach a peak CH$_3$I concentration or to attain equilibrium. As the gas continues to cool the reactions will become quite slow and concentrations will become essentially static.

However, it must be remembered that the gas in the plenum carries its own radiation source with it. As the gas cools the thermal reactions will become slower but the radiation reactions will not be slowed in the same manner and could lead to higher rather than lower methyl iodide concentrations. As discussed above, after about 30 sec. the gas in the plenum is cooling rapidly and has reached a temperature at which the radiation induced reactions can begin to compete. As shown in the experiments, the radiation conversion of iodine to methyl iodide could be linear with dose rate over a wide range at high dose rates. Since dose rates in the plenum gas could reach levels at least three orders of magnitude higher than used in the experiments [6], several percent of the iodine could be converted to methyl iodide in times of the order of one minute. Thus, at later times in the plenum and throughout the containment regions the radiation induced reactions could well be the predominant factor in methyl iodide production. In the experiments discussed above, iodine availability tended to be a limiting factor due to the excess of methane present. In some postulated accident situations, however, the availability of organic compounds, more specifically methyl radicals, may limit methyl iodide production. However, within the limits set by reactant availability, it is expected that the radiation induced conversion of iodine to methyl iodide will occur rapidly. Several percent of the iodine could be converted to methyl iodide in the plenum region and because the back reaction is not favored this concentration would be maintained or increased in the volume of the containment vessel.

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DISCUSSION

J.G. WILHELM: The results now available show that the fraction of methyl iodide depends on many factors. To test charcoal filters and interpret results in the light of safety analyses, we have to assume a value for the percentage of methyl iodide formed under MCA conditions.
What do you suggest as a reasonable amount of methyl iodide likely to reach the iodine filter plant in water-cooled reactors?

J. F. KIRCHER: I can, of course, only make a guess, but I would expect an amount of the order of 10-20%. I certainly would not expect a larger amount.

C. PELLETIER: Have you any opinion as to whether methyl iodide will remain as methyl iodide once released to the natural environment?

J. F. KIRCHER: I have no idea.

R. E. HOLMES (Chairman): Conditions in the United Kingdom's AGRs are ideal for the formation of methyl iodide. This situation is realized and treatment plants have been developed using potassium iodide and cryonic impregnated carbons to remove the methyl iodide. Persons interested should refer to the work of R. D. Collins of the UKAEA (3rd Int. Conf. peaceful Uses atom. Energy (Proc. Conf. Geneva, 1964) 13, UN, New York (1964) 69; Int. Symp. Fission Product Release and Transport under Accident Conditions, Oak Ridge, 1965, CONF-650407, 2, 830)

W. SCHIKARSKI: Is the methyl iodide present in airborne organic compounds, on which many biological organisms depend, sufficient to deliver the necessary concentration of methane, etc. to produce the amount of methyl iodide observed in experiments?

J. F. KIRCHER: Yes, there are sufficient organic compounds in the atmosphere; in particular there is enough methane to produce the required concentration of methyl iodide. The concentration of methane used in most of the calculations reported in our paper is based on the amount of methane present in the standard atmosphere. Moreover the measurements by Adams et al. (Ref. [3] of the paper) confirm that the amount of organic compounds of various types in typical reactor buildings is as high as, or higher than, expected for the standard atmosphere. If these values are indicative of organic concentrations within the reactor, then iodide production will not be limited by lack of organic components. However, we do not actually know the concentration of organic compounds in the reactor. This information is certainly needed in order to put calculations on a sounder basis.
GENERAL DISCUSSION

J. G. WILHELM: In testing alternative materials for iodine filters we have found that we run into discussion with the people at reactor stations as to the amount of elemental and particulate iodine and its penetrating forms (mostly in the form of methyl iodide) expected. The importance of this question is enhanced by the fact that most iodine filters are still designed with a type of charcoal which is not impregnated for the retention of methyl iodide, so that the removal efficiency of an iodine filter system will depend on the ratio of methyl iodide to total iodine you expect under MCA conditions. Now, looking over the literature we can find for this ratio every value between $10^{-5}$ % and 30 to 50%. Normally the people who are interested in meeting the standards required for their filter system pick the lower values, however, some have selected the higher ones. I do not think the matter is as obscure as all that and it should be possible to agree on a single value which we could use until more data becomes available. For example, I like to recall the manner in which the fission-product release values were obtained for halogens, rare gases and so on. When these values were published in the United States ten or fifteen years ago, very approximate numbers were picked like 50% for halogens, 100% for rare gases, and so on, and these numbers are accepted till experimental work or experience show that other numbers should be substituted for them. In point of fact, most of these old numbers have been changed very little as yet. It seems to me that this pragmatic approach is a very good approach because when these numbers are based on some experience which can be discussed, they are very helpful to the people responsible for reactor safety. I feel internationally agreed values are urgently needed, otherwise whenever you test an iodine filter, you encounter the same discussion. Moreover, in reactor safety calculations it does not make a big difference if you have 1 or 2 or 3% — mostly it's a question of the order of magnitude which you should assume for a reactor accident. On the other hand, I think we should definitely make a distinction between water-cooled reactors and gas-cooled reactors. So I would like to hear if people could suggest what numbers seem to be reasonable in these two cases for the amount of methyl iodide, considering the total amount of iodine reaching the filter system after an accident of the MCA type.

R. E. HOLMES (Chairman): Thank you Dr. Wilhelm. An appeal then, as I understand it, from a participant from the Federal Republic of Germany that we might try to agree on a design figure for safety evaluation based on the percentage of organic compounds of iodine released in maximum credible accidents. First of all, let us restrict it to water-cooled reactors. Are there any United States participants who would like to make initial comments on this?

G. BURLEY: We have done a pseudo-theoretical calculation of the maximum amount of organic iodide (in the total iodine released) which has been produced by conversion of elemental iodine, taking into consideration the several mechanisms which could occur — conversion in the fuel (which is very small), gas-phase conversion in the hot cell (with radiation and high-temperature conditions), conversion in the containment (where essentially you have ambient conditions) and conversion by adsorption of...
elemental iodine on surfaces (conversion to methyl iodide and subsequent desorption). We were interested in getting figures which could be considered feasible from the regulatory standpoint, so we are using the maximum figures, and the maximum conversion of the inorganic iodide to organic iodide for a pressurized water reactor over something like a ten- or twenty-day period seems to be up in the 8 - 10% range. In one sense this is somewhat unrealistic because we are not considering competing reactions and other things, so it's probably high, but for the moment it might be a good starting point.

Also, there are two ways of looking at the problem. One is the purely theoretical. The other one is to look at laboratory experiments, but unfortunately there are no laboratory experiments which I feel have duplicated simultaneously all the conditions which one might observe under post-accident conditions. Most of the numbers published vary from considerably under 1% to about 5%. Then there are a very few numbers in the 5 - 10% bracket and several which are higher than 10% ranging up to 40 and 50%. Well, looking at things realistically, I have satisfied myself that just about all the numbers over 10% can be eliminated as inapplicable to the conditions we are interested in. High numbers are obtained, as you mentioned yesterday, for CO₂-cooled reactors, where you have optimum conditions for methyl iodide formation. You can also get very high conversion under conditions where you have a very small amount of iodine in the air, a large fraction of that would be converted to the organic form, but again these are not the conditions we are interested in. We are interested in the conditions as defined in the relevant United States recommendations (document TID 14844, issued in 1962), which specify that 25% of the core inventory reaches the containment and is available for leakage. So we have a fairly sizable iodine inventory for a 3000-MW plant — it comes out to somewhere around 3 or 4 kg of iodine (total). On this basis we feel that nothing much over 10% would be possible — probably 5%, but to be on the safe side, I feel at the moment that 10% might be a good number to start with.

R.E. HOLMES (Chairman): Mr. Burley, you mentioned some cases of over 10% with reference to gas-cooled reactors. Are there any cases which you have not yet been able to explain where you have found values of over 10% in water reactors?

G. BURLEY: There are none that we have not been able to explain. A figure of about 15 - 17% was obtained by Castleman and his group at Brookhaven about a year ago, and we discussed this at length and came to the conclusion that his iodine concentration per unit volume was considerably lower than what we would observe under post-accident conditions. So this, we feel, is an unrealistically high number.

R.E. HOLMES (Chairman): In other words these were not typical conditions. Now can I put the question to Dr. Wilhelm — does that give you a satisfactory answer?

J.G. WILHELM: Well, just by accident and quite independently, I also picked the 10% figure for my iodine filter testing. I did so by checking through all the numbers that I could find in the literature, also taking into account some practical considerations. If you take the highest value as 30%, then you know that at 10% your maximum error in that direction is a factor of 3. Now, in safety work a factor of 3 is not a big factor: we all know what a lot of assumption goes into such an MCA model. If on the other hand the error lies in the other direction, then if we go down
by a factor of 3 from 10% we reach 3%, which many people will also find acceptable. So the value of 10% seems a good intermediate value, whether one arrives at it by the scientific approach followed by Dr. Burley’s group or by the not so scientific approach we ourselves adopted.

R.E. HOLMES (Chairman): I think it is worth pursuing this point for a moment. I would like to ask how valid we feel this figure of 10% will really be. Have we established, or have we any views on, whether there is any one significant major contributor towards the organic iodides? For example, is the major contributor contaminant in fuel manufacture? If so, are we in a position where some changes in manufacture could lead to changes in the methyl iodide level? In other words, could any figure which we may agree upon here in good faith as a reasonable figure suddenly become invalid because of a change in some process which we had not even considered, as lying outside our control? I should therefore like to ask if there are any views from the floor on whether there is any one dominant process leading to organic iodides under these conditions.

W. SCHIKARSKI: I believe that the fuel element, particularly under MCA conditions, is not the primary location of methyl iodide generation because temperatures and the radiation field are so high — I refer to the work of Castleman — that methyl iodide would decompose pyrolytically and by irradiation. I think most of the American experiments on reactor safety and containment showed that the place where methyl iodide will form is in the containment, i.e. far from the core. If you have a transient-type accident, the U₂ will be melted down in a shorter time than the cladding, because the heat must first be transported to the outside. Inside the can the temperature is so high that no methyl iodide could exist, and the radiation field is also so high that — taking into consideration Castleman’s number — the methyl iodide will be totally decomposed. On the other hand, the further you go from the fuel element, the more surfaces with ordinary contaminants become available, moreover, the temperature will drop so that steam or water will be present. All these factors conducive to the conversion to methyl iodide will come more and more into the picture. So I think it is outside the core that most methyl iodide will be generated, relatively little in the fuel element itself.

R.E. HOLMES (Chairman): Yes, thank you. I was quoting that as an example, really — with a view to getting other people’s views on whether or not we were in enough control over the conditions which lead to methyl iodide to feel confident. Has anyone anything to say on this?

P.J. LINDER: In this connection I have heard it suggested that the type of residues in the cleaning system for the primary circuit can influence the contribution of organic compounds in the containment after an accident.

A.H. PETERS: First of all I would like to say that generally we feel that the methyl radical mechanism or the methane source is the primary contributor to the formation of methyl iodide. We agree with the German view that we can expect the fraction conversion of the iodine into methyl iodide to be insignificant in the water reactor. Now yesterday we heard a paper by Dr. Kircher where he indicated that in the transition zone of the plenum you can theoretically calculate relatively high conversions, and this I think was the basis of his number of 30%. I would like to point out, though, that those calculations neglect methyl water reactions which contribute steam and which favour conversion to HI and decrease con-
version to methyl iodide. Moreover, when you try in your best judgement to appraise the conditions you might have during an accident, it seems extremely unlikely that all the conditions Dr. Kircher was assuming — in respect of steam generation, iodine generation and methyl iodide generation — could be simultaneously fulfilled in a high-temperature field where the radiation source is of the order of $10^6$ - $10^{10}$ rads per hour per thousand MW of thermal power. We feel that if steam were generated on this scale, core melt-down would result. So this generally led to the work which we reported two years ago in the general literature, where we tried to go through the whole train of events. There is other information available today that should be factored into this analysis, but this only supports our view that it is in the containment building itself that the major fraction of conversion occurs, and here again the environmental conditions are very important.

So obviously I am in a position where I feel the relevant figure is certainly far less than 10% — I think I could say that from my own personal views I feel it is less than 1%, even for conditions where the residence times in these facilities are quite long. And my basis for this is that invariably, in all the experiments that have been run in this country where an attempt was made to simulate accident conditions in these so-called confinement test facilities, the concentration of iodine in the facility was 10-30, sometimes even 40 times lower than what you would expect, assuming a 50% release of iodine from the core during an MCA type of accident. Now the lower the concentration, the higher should be the percentage conversion to methyl iodide. So if all these things are taken into account, I think it can be said that in almost all the American literature — except where there was a deliberate attempt to add methane to the test, as in one run by George Parker at Oak Ridge — the fraction converted to methyl iodide is very small. Recent experiments, I think, confirm that: for example, Parker has just recently reported two results — one was 0.3% and the other 0.03%.

D. A. NITTI: In view of what I've been hearing I was wondering whether the percentage of methyl iodide in the fuel or in the atmosphere is the right way to attack the problem. Maybe we should be talking in terms of a certain number of milligrams of methyl iodide per cm$^3$ or something of this nature since the value does seem to depend upon the total amount of iodine which is released or the concentration of iodine that happens to be present during these testing periods.

A.H. PETERS: Are you suggesting that we should speak in all these accident analyses in terms of a total mass of individual products and then follow the analysis beyond that point?

D. A. NITTI: Since the percentage seems to change with the total amount present — in other words, as the amount present is increased the relative percentage of methyl iodide formation is decreased — I was wondering whether we would get a better correlation of the data if we spoke in terms of the absolute concentration of the methyl iodide rather than percentage of the total iodine present.

A.H. PETERS: I would generally agree. When we did this work we had a very difficult time in straightening out some of the data quoted in the literature because the authors sometimes failed to identify what their concentrations meant. Quite frequently you'll find that in a test where the concentration is really low, the conversion to methyl iodide is pro-
portionately high but in terms of the fraction of the total iodine inventory, it's a very small number.

R.E. HOLMES (Chairman): I personally think that clarifies the situation.

G. BURLEY: Yes, I think that everyone will agree that as you decrease the iodine concentration the percentage of organic iodide might increase. However, that's not the problem we're facing. We are facing the problem of what is the maximum quantity of organic iodide which might be generated and the right way to look at it, I feel, is to proceed on the basis of a 25% release of the total amount of iodine available, if we then determine the maximum percentage of that which can be converted to the organic iodide, that will probably give us the maximum amount we are looking for.

A.H. PETERS: The trouble about arriving at so-called maximum numbers is that you can arrive at a whole spectrum of numbers, depending on the accident and how you define your conditions. So we get right back to the same question again, what is a reasonable upper limit to use, and on this we obviously have an equally broad spectrum of opinion.

R.E. HOLMES (Chairman): It is a pity there are no Canadian participants present to tell us whether they have any relevant experience on a slightly different type of water-reactor system.

J.G. WILHELM: I think we should not only look at the concentration of iodine in the containment, but also at the concentration of organic compounds which can react with iodine to form methyl iodide. If you have an MCA type of accident and burn paint, insulation material, and so on, you not only increase your iodine concentration, you also greatly increase your organic reaction partner, too. And I feel that in most containment experiments this organic reaction partner was not available in the form it could be under MCA conditions.

A.H. PETERS: This is in support of the Chairman's point earlier and of course the amount of additional organics that could be added will vary widely from application to application. All I will say is, as regards paints, that generally the temperatures in the containment building are mild from this standpoint and there are numerous paints available on the market today that will withstand the sort of conditions that occur, moreover, there have been some experiments run by Battelle at Hanford using organic paints in their confinement facility. But of course there may be other sources of organics too.

R.E. HOLMES (Chairman): Well, I think we have an answer for Dr. Wilhelm. There seems to be general agreement that for water reactors under MCA conditions, 10% would appear to be an upper-limit figure, together with a large measure of support for the view that this is possibly an order of magnitude in excess of what in reality might well occur.

Now I would like to elaborate the point I made yesterday, that in the United Kingdom with an advanced gas-cooled reactor we have optimum conditions for the production of methyl iodide: we have a CO₂ coolant and high radiation, the coolant is dosed with methane (to inhibit the graphite oxidation) and this methane itself breaks down radiolytically to produce water. This represents, I think, just about the optimum conditions and we reckon that any iodine released might well be converted to methyl iodide. We do test our treatment plants on methyl iodide and I think you
will be interested to know that a fairly big plant — rated for CO₂ at 5 tons
an hour — tested with methyl iodide alone has shown a measured efficiency
of 99.8% removal. So I wonder in fact whether this is a real problem.
We are possibly a little bit uncertain of the percentage of methyl iodide,
but does it really matter? Are we in areas where we have plant difficulties
in removal or are we not?

H. ISBIN: I thought I detected in the previous sessions some under­
current of feeling regarding a continuing need for identification of all the
constituents involving iodine. Is the emphasis which is now being given
at this special session to methyl iodide a rejection of the arguments ad­
vanced, say, by Barry in his paper? Are you sure you really know all
the constituents of iodine that are formed?

R.E. HOLMES (Chairman): This is a very valid point. No, I don't
think there is any formal intention, certainly not on my part, to reject
this viewpoint. This is a completely informal session and we were really
hoping it would build up as it went along. Certainly I'm not aware of any
formal rejection of the other organic forms. But this is undoubtedly a
valid point.

A PARTICIPANT: As far as the methyl iodide fraction is concerned,
I think there is fairly good evidence, mainly from the mass-spectrometry
techniques, that most of what is trapped by the charcoal beds is methyl
iodide, so while there may be 1% or even 10% of other constituents, methyl
iodide is still the major constituent at that moment. As to whether there
really is a problem with methyl iodide, I still feel there is, as it were, a
dual problem, under the conditions we have in a water reactor, and the
problem is this: Are charcoals, impregnated or not impregnated, efficient
for the removal of organic iodides under extremely high relative humidity
and temperature conditions? And is the alternative proposed method for
removing elemental iodine, namely sprays with reactive additives, equally
efficient for the removal of methyl iodide? In other words the reason why
we are concerned with the percentage of methyl iodide is simply that methyl
iodide may not be trapped very efficiently.

F.O. CARTAN: In reply to the comment you just made that methyl
iodide may be the principal species you see in charcoal beds, this seems,
in view of some recent data we have, to be in question. It may in fact be
a minor constituent and much of what in the literature, especially at very
low iodine levels, is called methyl iodide may not be methyl iodide at all,
so the problems that we are tangling with may be somewhat unreal.

A PARTICIPANT: I think I've seen numbers as low as 50% retention
on charcoal for methyl iodide under conditions of high humidity. If you
assume that 5% of the initial iodine is methyl iodide and that the filter
efficiency is 50% for methyl and 90 or 99%, I forget which, for the elemental
iodine and that there is no efficiency for spray removal of the methyl iodide
but that there is an effective decay constant for spray removal (about
13 hours⁻¹), then about 50% of your dose is due to this 5% methyl iodide.

J.G. WILHELM: Two points are important in determining how much
methyl iodide we will have. One is that a lot of filter plants use unimpreg­
nated charcoal, which is not able to remove methyl iodide under high humi­
dity conditions. For a lot of plant people the question therefore arises
whether to discard this charcoal and buy new filter elements or whether
to use the existing elements to capacity. And this depends on the amount
of methyl iodide one expects. One can very easily approach this 99% re­
moval efficiency for elementary iodine with a well-designed filter, there is no problem here because the stay time one needs for this is very short. If one now assumes 1% of the iodine is in the form of methyl iodide one can still carry on with the existing filters. If one assumes 10%, one has to discard one's filter. It is as simple as that.

The other point is, we know that you can overload your charcoal, that is you can give it too much methyl iodide. For example, in England Taylor and Taylor found out that for a certain type of English charcoal one should not exceed 100 micrograms methyl iodide per gram of charcoal. In other words one needs to know how much methyl iodide will stick to the charcoal, and thus how much one can assume will be converted in the worst case.

I should add that generally, if one constructs one's filter properly, the size of the filter is dependent on the stay time, in other words with a big enough stay time it will withstand all the methyl iodide it can get. That means that the amount of charcoal is relatively large compared to the amount of total iodine you can expect on the charcoal.

A.H. PETERS: I would like to revert to the relative humidity problem. I think all of us have neglected one important factor in determining the relative humidity and that is the heat generation within the carbon bed from the beta and gamma radioactivity from the absorbed radioiodines. I'll give you a typical set of conditions for the Savannah River reactors as represented by the high-flux demonstration charge we ran about three years ago. The thermal power level reached was about 1000 MW and the reactors were maintained in the on-line condition. If we take a time zero to a time when the iodine is essentially all released into the confinement system following an accident where we have generated quite a sizeable amount of steam, we have a 100% saturated condition in what we call the process room. Then after running a heat transfer analysis and self-absorption analysis on the carbon beds, we find that at 30 minutes the relative humidity is decreased to approximately 50% just on the basis of a 100% self-absorption of the beta activity and 40% self-absorption of the gamma activity (in this case the beta activity is a substantial fraction, about 40%, of the total heat generation). So for any sizeable reactors, depending upon the actual mass of carbon one had in the system, on the air flow, on the design and so on, the relative humidity tends to decrease, the point being that if the methyl iodide is generated outside the reactor vessel and there is a time-delay between the formation of methyl iodide and the iodine, you will have a much drier situation on the carbon beds. Of course, if the methyl iodide comes out simultaneously with the iodine then you get a change in relative humidity from 100 to 50% over a 30-minute period.

J.G. WILHELM: Well, we discussed these things in connection with the German Obrigheim reactor, a 300-MW(e) reactor, and one really can have all different kinds of conditions. The worst combination would be to have first the steam and then the iodine, so that the steam will condense in your charcoal. So one really has to make a very careful safety analysis for each type of reactor. This being so, I think it is inaccurate to say the influence of relative humidity is over-estimated. In certain cases it is very great. For this reason we in Germany are thinking more in terms of deep-bed filters with a bed depth of 50 cm, though I must add that at Obrigheim we have especially difficult conditions.
because we have a stack 60 metres high while the surrounding hills are 200 metres high. We can't take any risk in this case.

J. L. KOVACH: I would like to bring up one point concerning these calculations of what happens in the containment after release. I would like you to remember that the heat absorption of water is very high, so this idea, that whenever you hit any carbon with steam you are going to get condensation, won't work. The Δt is very high on immediate absorption, so you do have the possibility of condensation in the carbon systems later, certainly not initially when you introduce the water.

The second point I would like to mention is there are a number of reactors today with impregnated charcoal systems, you must keep in mind the amount of iodine in some of these systems when you start calculating the relative concentrations of methyl iodide and iodine. Some of these carbon systems contain literally tons of iodine, and your figure for the elemental iodine concentration becomes so high that the ratio reaches quite astronomical numbers.

J. G. WILHELM: With that heat capacity, I know what you mean. The fact remains that whenever you test the removal efficiency of charcoal, you really notice how quickly you can get condensation on your charcoal. With very slight temperature changes you definitely see the water on the surface of the charcoal though it will disappear after a short time when you run at a slightly higher temperature with 100% relative humidity. In fact, the main problem in testing charcoal in conditions of high relative humidity is to avoid condensation, and this being so, it seems only too likely it will occur in an actual reactor accident.

J. L. KOVACH: Most of the tests done on methyl iodide used carbon which is presaturated, so that at the point when the methyl iodide was introduced, the carbon was already in equilibrium with the steam air under high relative humidity conditions.

J. BRION: I would like to mention a point about the measurement of methyl iodide. I think most measurements are done with gas-chromatographic technique, and I would like to ask if the experimenters have noticed some difficulty about this technique. We have noticed that from the measurement itself, one can produce methyl iodide from pure iodine.

R. E. HOLMES (Chairman): Yes, I think we have all experienced this. Would anyone else like to comment?

If not, I feel we have reached the point in this informal discussion where we are beginning to impinge upon other meetings. I think we have this evening got a pretty general measure of agreement, as I summarized it, as far as MCA conditions in water-cooled reactors are concerned. Do I understand correctly that that summary also represents the general American view, if there is such a thing?

G. BURLEY: I don't think I can enunciate a general American view at this point, as what I have said is a purely personal opinion and I'm not sure that as a result of the very limited discussion we have had here anybody would be prepared to go on record as favouring a specific number. I think the discussion has served a useful purpose, outlining the positions taken by responsible people in different countries in looking at the same problem. I think that is all we really wanted to do.

R. E. HOLMES (Chairman): Personally, I agree. There is no intention of making a formal statement. I just wanted to make sure we all understood each other.
D.A. NITTI: Dr. Holmes, with regard to your summary, I think we ought to have a clear statement of what we mean by this figure of 10%. 10% of what? I think it would also be helpful if Dr. Burley could elaborate a little bit on the results of his pseudo-theoretical study that broke the methyl iodide formation into four phases and tell us if he broke down the amount of methyl iodide that he anticipated from each phase, since much of it might come in this 24-day period when the iodine is, so to say, dormant in the containment vessel.

G. BURLEY: By 10% we mean 10% of the iodine in the containment available for leakage, and under the United States regulations this is 25% of the core inventory at the time of the accident. So the 10% comes down to 2.5% of the core inventory iodine when converted to methyl iodide.

To arrive at the figure of 25%, I may add, it is assumed that 50% is released and 50% of that is plated out prior to reaching the containment.

H.H. Van Den BERGH: Up to now we have been talking about water-cooled reactors. I wonder if we have time to go into the gas-cooled reactors, or is it a little late now?

R.E. HOLMES (Chairman): Well, as far as we are concerned, with the advanced gas-cooled reactor, we recognize, as I indicated, that we have a high percentage of methyl iodide that would be produced if elemental iodine were released into the coolant. Nevertheless, we feel that our design problems are rather less severe than those with the water reactor system in that we have proven plant design with high removal efficiency for these compounds.

A.H. PETERS: Would you tell us what you normally use as a design basis for the fraction that is methyl iodide?

R.E. HOLMES (Chairman): We assume that 100% of the fraction that is released into the gas circuit is converted to methyl iodide.

J.L. KOVACH: I believe you are probably talking of the carbon dioxide-cooled, methane-doped system while Mr. Van den Bergh is talking about the helium-cooled reactor. Is this right?

R.E. HOLMES (Chairman): Yes.

H.H. Van Den BERGH: The thing I would like to ask is whether anybody has any idea what numbers could be used for helium-cooled, high-temperature reactors (with vented containment).

G. BURLEY: In a helium-cooled reactor you have taken away most of your sources of organic contaminants, so the iodine is there in the circulating coolant and the amount of conversion, as I see it, is strictly limited by the conversion of any organic contaminant to the methyl form. In other words, we have a two-step process and the amount of organic iodide is probably quite low, certainly nothing of the order that we face in the water-cooled reactor.

R.E. HOLMES (Chairman): I also feel that the systems of gas clean-up and gas processing in the helium-cooled reactors essentially solve the problem, but this is perhaps a design aspect. I think any sort of more detailed statement on high-temperature reactors is more pertinent to the next symposium we attend than to this.
FILTRATION: DESIGN, DEVELOPMENT, COST

(Session III)
ENVIRONMENTAL PROPERTIES
AND INSTALLATION
REQUIREMENTS OF HEPA FILTERS*

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Abstract

ENVIRONMENTAL PROPERTIES AND INSTALLATION OF HEPA FILTERS. The ability of HEPA (i.e. 'absolute') filters to withstand severe environmental conditions is often critical to reliable operation of a contaminated exhaust system. This paper discusses findings related to the installation, mechanical strength, and the heat, moisture, and corrosion resistance of HEPA filters determined during the course of the filter development program of the USAEC Division of Operational Safety. As a result of these findings, wood-cased filter units are recommended in preference to steel-cased filter units wherever possible. Wood-cased filter units should have rabbeted casing joints, not butt joints. The limiting temperature for continuous exposure of HEPA filters to hot air is 400°F, above this temperature the tensile strength of the media drops sharply, to as little as 50% of the room-temperature tensile strength at 500°F. Fibre fracture and fibre loss occur at temperatures in excess of about 550°F. The limiting temperature of the assembled filter element is actually determined by the sealant used between the casing and the frame and, for wood-cased units, the casing material. Plywood is good for continuous exposure at temperatures up to 300°F for periods up to 48 hours, and up to 200°F for indefinite exposure (i.e. weeks or months). Steel is good for any temperature within the useful operating range of the media, although damage may be caused by differential expansion between the casing and the filter pack. Volatilization and reduction in shear strength of adhesives limits continuous operating temperatures to 250-350°F for periods up to 48 hours, and 200-275°F for indefinite exposure (according to adhesive used in manufacture). Steel-cased units with special sealants may withstand substantially higher continuous operating temperatures but in most cases are unable to meet the requirements of Underwriter's Laboratories Standard UL-586 for fire and hot (750°F) air.

Resistance of the filter element to flexure, vibration damage, 'working' of casing joints, gasket relaxation, and casing damage under abnormal pressure loadings is in large part a function of the mounting frame or fixture in which the filter is installed. Critical aspects of mounting frame and fixture design are structural rigidity, the method of joining individual frame members and the method of sealing the frame or fixture into the filter housing (all-weld construction and sealing preferred), the tolerances on dimensions, flatness, alignment, and surface finish of gasket seating surfaces, rigidity of filter clamping devices, and uniformity and degree of compression of filter gaskets in the frame or fixture. Recommendations on each of these factors are presented.

The properties of high-efficiency particulate air (HEPA) filters that are usually of concern to the designer are its particle collection efficiency, airflow capacity, and pressure drop. Of equal importance, however, is the ability of the filters to withstand the rigors of handling, shipping, installation, and service conditions. Failure to install the filters properly or to consider all operational limitations of the particular filter construction can compromise the best intentioned designs, particularly where the filters will or could be exposed to severe environmental conditions. The ability of filters to withstand such conditions during system malfunction is often a critical requirement in nuclear applications.

The United States Atomic Energy Commission (USAEC) has been conducting an extensive air filter development program for many years, and some better

* Research sponsored by the US Atomic Energy Commission under contract with Union Carbide Corporation
known results of this program include the development of fiber glass media, the fire-resistant filter, and the Underwriters' Laboratories Standard UL-586 [1]. Much of the work of this program has been unstructured and many developments have gone unreported. Some of these developments related to heat resistance, moisture resistance, and mechanical properties of HEPA filters are summarized in this paper.

The typical construction of steel-framed and wood-framed open-face HEPA filters used in the United States is shown in Fig. 1. The filter pack is formed by pleating a continuous web of fiber glass paper back and forth over corrugated aluminum or asbestos-paper separators. The separators give strength to the pack and provide air passages between the pleats. The filter pack is then sealed into a wood or steel frame usually with an elastomeric adhesive. Ceramic and non-adherent packed-fiber sealants are used in some filters intended for very high temperature service. Where filters are to be exposed to severe environmental conditions, it is essential that the designer be aware of the operating limitations of the particular filter construction selected. The high-temperature, moisture, and mechanical properties of the various fire-resistant filter constructions presently available in this country are summarized in the following discussion.

![STEEL-CASED HEPA FILTER](image)

![WOOD-CASED HEPA FILTER](image)

**FIG. 1.** Typical construction of steel-framed and wood-framed open-face HEPA filters used in the USA.
High Temperature Properties

The limiting service temperature of HEPA filters ranges from about 200 to 400°F, depending upon the media and the materials used to construct complete filter units and the period of exposure. Where reduced tensile strength of the filter medium and decreased efficiency can be tolerated, the service temperature may be considerably higher.

Fiber Glass Media

A section of a thermo-gravimetric balance chart of the heating cycle for a specimen of fiber glass HEPA filter paper is shown in Fig. 2. The sloping line on the right shows the temperature, and the S-curve on the left shows the change in the weight of the specimen. This chart covers a time period of about 8 to 10 min. After the moisture was driven off during the first few minutes of the run, the specimen lost approximately 5% of its weight as the organic binder was burned out, as shown by the S-curve.

Binder burnout was accompanied by a rapid decrease in the tensile strength of the paper to about 50 or 55% of the value at room temperature, as shown in Fig. 3. As the temperature was increased further, self-welding of the fibers apparently took place until the tensile strength increased to about 70% of the room-temperature value at 800°F. Above this temperature, fiber softening apparently took place with a corresponding decrease in tensile strength. Binder burnout, with the resultant decrease in tensile strength of the medium, is a time-temperature effect, as may be seen by comparing the 5-min heating curve with the 2-hour heating curve shown in Fig. 4. Although the data shown in Figs. 3 and 4 represent only a single grade of paper, the data are probably representative of the changes that take place in almost any fiber glass filter paper.
An electron photomicrograph of the same fiber glass paper in its as-received condition is shown in Fig. 5. The translucent areas between fibers are the binder. Examination showed that most of the binder was on the outer surfaces of the paper and that relatively little was in the center. Specimens heated for a period of 1 hour at temperatures of 600°F, 752°F, and 960°F were examined under the electron microscope to determine the effect of heating on the fibers. Some evidence of broken fibers, probably caused by contraction and expansion of the binder, is apparent in the specimen heated at a temperature of 600°F, as is shown in Fig. 6. Extensive damage took place in the specimen heated at a temperature of 752°F, as is evidenced by the large number of fragmented, broken, and melted fibers shown in Fig. 7. When heated at a temperature of 960°F, large areas were found to contain only broken, melted, and distorted fibers, as shown in Fig. 8. The progressive increase in the amount of open area shown in Figs. 5 through 8 indicates that there was considerable loss of fiber. Although no penetration tests were made on the specimens after heating, it is probable that this fiber loss was accompanied by some decrease in filter efficiency.

Complete Filter Unit

The service temperature for complete filter units is usually limited by materials of construction other than the media. Both asbestos-paper and alu-
The temperature-limiting material in the complete filter unit is usually the sealant between the filter pack and the filter frame. The limiting service temperatures for steel-framed fire-resistant HEPA filters made with elastomeric adhesives that have been approved for USAEC installations are given in Table I. Filters with these sealants have met the requirements for heat resistance of the U. S. National Bureau of Standards and of UL Standard 586 [1]. The limiting temperatures given in Table I are based on data furnished by the adhesive manufacturers. Since the shear strength of elastomeric adhesives at a temperature of 300°F may be as little as 1% of the room-temperature value, the recommended temperature limits should be used with caution for high air resistance applications at temperatures above 200°F.

For higher temperature applications, ceramic sealants or a mechanical seal of tightly packed glass or asbestos fibers may be used. However, ceramic sealants are extremely fragile, and the filter must be handled, shipped, and installed with the utmost care if it is to meet the specified efficiency. Ceramic sealants are also subject to cracking caused by differential expansion between the steel frame and the filter pack. Cracking of
FIG. 5. Electron photomicrograph of fibre glass paper in as-received condition.

FIG. 6. Electron photomicrograph of fibre glass paper after heating for 1 hour at a temperature of 600°F.
FIG. 7. Electron photomicrograph of fibre glass paper after heating for 1 hour at a temperature of 725°F.

FIG. 8. Electron photomicrograph of fibre glass paper after heating for 1 hour at a temperature of 960°F.
Table I
Recommended Limiting Service Temperatures for Steel-Framed Fire-Resistant HEPA Filter Units Sealed With Elastomeric Adhesives

<table>
<thead>
<tr>
<th>Sealant Used</th>
<th>Temperature to Which Filter Was Exposed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Up to 10 Min&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>HT-30-FR&lt;sup&gt;b&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
<tr>
<td>Z-743&lt;sup&gt;c&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
<tr>
<td>EC-2155&lt;sup&gt;d&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
<tr>
<td>Polyurethane&lt;sup&gt;e&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
<tr>
<td>Cemen-TAC&lt;sup&gt;f&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
</tbody>
</table>

<sup>a</sup> Some reduction in efficiency may occur after 5 min of exposure.
<sup>b</sup> Goodyear.
<sup>c</sup> Pittsburgh Plate Glass.
<sup>d</sup> Minnesota Mining and Manufacturing (3M).
<sup>e</sup> Proprietary formulation of Flanders Filters, Inc.
<sup>f</sup> Tallon Adhesives, Grades NB-38A, -38B, and -38C.

Table II
Recommended Limiting Service Temperatures for Wood-Framed Fire-Resistant HEPA Filter Units<sup>a</sup>

<table>
<thead>
<tr>
<th>Frame Material</th>
<th>Temperature to Which Filter Was Exposed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Up to 10 Min</td>
</tr>
<tr>
<td>3/4-in. thick plywood&lt;sup&gt;c&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
<tr>
<td>3/4-in. wood particle board&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>750°F</td>
</tr>
</tbody>
</table>

<sup>a</sup> Subject to sealant limitations given in Table I.
<sup>b</sup> Maximum temperature of 120°F where relative humidity is 75% or higher.
<sup>c</sup> Exterior grade fire-retardent treated.
<sup>d</sup> Minimum density = 45 lb/ft³.

The sealant results in leaks and a decrease in filter efficiency. Experience with packed fiber filters has not been good. These filters nearly always have steel frames and there often is a problem of corner joint leakage. There is also some question about the efficiency of such filters at operating temperature because of differential expansion between the filter frame and the filter pack. The 24-in. side of a 1000-cfm filter expands nearly 5/64 in. with an increase in temperature from room temperature to 600°F. With only a mechanical seal between the frame and filter pack, this expansion may result in leaks and reduced efficiency at operating temperature.

Where operating conditions permit, the use of filters with wood frames is preferred to those with steel frames. However, the use of wood frames is...
limited by operating temperatures, and the recommended service temperatures are given in Table XI. These recommendations are based on information furnished by the Forest Products Laboratory of the U. S. Forestry Services. [2]

The heat resistance of gaskets is sometimes questioned. Under the operating conditions of a HEPA filter it has been found that a highly compressed sponge neoprene gasket will retain a reliable seal to temperatures of several hundred degrees Fahrenheit. However, lightly compressed neoprene gaskets degrade rapidly at high temperature. Certain silicone rubbers are suitable for use up to the design operating temperature limit of the material, but they will delaminate at temperatures of only a few degrees above this design limit. Fiber glass mat gaskets have been used for some high temperature applications, but their use is not generally recommended because of their extreme fragility and nonelastic character. These gaskets are usually unable to meet the penetration criteria of the remainder of the filter unit (0.03% maximum for 0.3-micron-diameter particles) even at room temperature and under maximum compression.

**Moisture Properties**

Rigorous moisture tests of HEPA filters made by several organizations have shown that properly built units can withstand severe moisture loading for long periods of time without failure. In tests made at the USAEC Hanford facility, wood-framed HEPA filters were exposed to a supersaturated steam-air environment at flow rates of 1000 cfm for periods of up to 3 hours. [3] In tests made at the USAEC Savannah River Laboratory, steel-framed HEPA filters were exposed to similar environments for periods of up to 10 days. [4] In both instances, many of the filters tested showed no significant deterioration as a result of the tests. However, both tests showed a wide variation in the ability of different makes of filters to withstand such severe moisture conditions.

The important factors in moisture resistance are the wet tensile strength of the media, which is related to rupture of the media under high overpressure, and its water repellency, which is related to plugging of the filter that produces high overpressure. Tests of the type made at Hanford and Savannah River are very expensive and cannot be performed on a routine basis, particularly by the average user. Therefore, the U. S. Army Edgewood Arsenal and the USAEC are developing a test to demonstrate the capability of various filter constructions to withstand high moisture loading. After being conditioned for 24 hours at a temperature of 95°F and a relative humidity of 95%, samples taken from the manufacturer's production line are subjected for 15 min to an airflow that will produce a pressure drop of 10 in. of water across the filter. The air flowing during the test is conditioned to a temperature of 95°F and a relative humidity of 95 to 100%. Sensible moisture is injected in the form of water spray at the rate of 1 1/4 lb/min per 1000 cfm of rated filter capacity. The acceptance criteria is the ability of the wet filter to meet the 99.97% collection efficiency requirement at both rated flow and 20% of rated flow upon completion of the test.

The results of preliminary tests of this type made on a number of filter units rated as moisture resistant by their manufacturers are shown in Fig. 9. The filters were DOP tested periodically, and for qualification of a given manufacturer's model, four units of the model must meet the acceptance requirement. Each line in Fig. 9 represents the worst results in tests of four filter units of the same manufacturer and A-1 and A-2 are two models from the same manufacturer. It may be seen from Fig. 9 that those models
that were unable to meet the 30-min exposure test have been identified within the first 15 min of the test. When this test is perfected, filters from each manufacturer will be tested and the results will be tabulated and made available to users in the form of a Federal Qualified Products List.

The test results shown in Fig. 9 are representative of filters with both steel and plywood frames. However, operating experience indicates that moisture infiltration into the fibers of plywood frames, with subsequent failure of the bond between the elastomeric sealant and the frame, is possible after extended exposure (40 to 50 days) to humid (80 to 100% relative humidity) air at temperatures around 150°F. These conditions are regarded as extremely severe for plywood by the Forest Products Laboratory. [2] For this reason, a limiting service temperature of 120°F is recommended when filters with plywood frames are to be exposed to air with a relative humidity of 90% or more for long periods of time. Wood particle board is not recommended for filter frames where high moisture loading is expected. Accelerated moisture exposure tests performed on both wood particle board and plywood showed that even the best grades of particle board tested swelled many times more than an equivalent exterior grade plywood, as shown in Fig. 10. Some grades of particle board fell apart during the first 5 min of the test. Since all of the elastomeric sealants listed in Table I are moisture resistant, filters with steel frames that have been qualified by the testing procedure described in the preceding paragraphs should be suitable for use over the full temperature range of the sealant even in air with a relative humidity of 100%.

**Mechanical Properties**

The resistance of a HEPA filter to vibration, pulsation, shock, and other mechanical forces that tend to deteriorate the filter in service is a function of the filter unit itself, of the mounting frame or fixture, and of the manner in which the filter is mounted.
Mechanical Strength of Filter Unit

Other factors being equal, wood-framed filter units are preferred to steel-framed units. The properly constructed wood frame has greater rigidity, superior vibration damping characteristics, and greater corner strength than a steel frame. Common practice in radioactive exhaust service is to compress filter gaskets to 80% or more. Using a Grade SCE-43 (ASTM Standard D1056-62T) [5] closed-cell neoprene gasket, this amount of compression requires a clamping force of at least 18 psi or a total clamping load of at least 1250 lb to reliably seal a filter unit with dimensions of 24 x 24 x 11 1/2 in. Because its moment of inertia is nearly 20 times that of a steel frame, the wood frame is much better able to withstand such clamping loads without damage.

The corner strength of a filter unit is reflected by its resistance to "racking" or skewing when subjected to a force couple, as shown in Fig. 11. The racking strength of a filter with a properly constructed wood frame is double that of an equivalent filter with a steel frame, as shown in Fig. 12. This is based on a wood frame with double-nailed rabbeted corners, as shown in the corner detail in Fig. 1. A filter unit with butt corners tested in the same manner had only 20% of the corner strength of the unit with rabbeted corners. Racking forces, which are frequently encountered during handling, shipping, and installation of filters, can damage the seal between the filter pack and the frame and could damage the filter paper itself if severe enough. The corner weakness of filters with face dimensions greater than 24 in. and depths of one-half the minimum face dimension or less is also illustrated in Fig. 12.

The weakness of very large filter units is illustrated by their poor resistance to shock. An extrapolation of the data presented by Anderson and Anderson at the 9th Air Cleaning Conference (6) is illustrated in Fig. 13. Since shock pressures of 1 psi or higher could be experienced under shipping...
FIG. 11. Force couple applied to HEPA filter causing racking of frame.

FIG. 12. Corner strength of HEPA filters as a function of filter size and construction.
or handling conditions, filter units with face dimensions larger than 24 by 24 in. are not recommended for nuclear applications. Even use of 24 X 24 X 5 7/8-in. filters is questionable from the standpoint of mechanical strength, as may be seen in both Figs. 12 and 13.

Mechanical Strength of Mounting Fixtures

A little over two years ago, the design problems in the application of high-efficiency air filters were investigated by A. B. Fuller and the author. The outcome of that investigation will be an engineering manual entitled "Design and Construction of High-Efficiency Air Filtration Systems for Nuclear Applications". The ability of HEPA filters to withstand for long periods of time the vibration, pressure, and environmental conditions often encountered in radioactive exhaust systems was found to be a function of the (1) structural rigidity of the mounting fixture; (2) method of joining individual members of the fixture; (3) method of sealing the mounting fixture into the filter housing; (4) tolerances on dimensions, flatness, alignment, and the finish of the filter seating surface; (4) rigidity of filter clamping devices; and the (6) degree, and uniformity of filter gasket compression.

It was concluded that the maximum permissible deflection of any member of the filter mounting fixture should be 1/16 inch in 6 feet. This is comparable with the maximum permissible deflection value of 0.1% of member length that was independently arrived at by users and designers of clean room filter systems. To allow a factor of safety that will prevent damage to the fixture in the event of shock loading, this deflection is specified under a pressure loading of 1.5 times the maximum dirty-filter pressure drop. Assuming a uniformly loaded simply supported steel (36,000 psi yield strength) beam with 2-in. spacing between filter units, the moment of inertia required to meet this criterion can be found by using Eq. 1.
where

\[ I = \frac{\Delta p L}{1.59 \times 10^5}, \tag{1} \]

I = moment of inertia, in.²,
\( \Delta p \) = maximum dirty-filter pressure drop, in. of water,
L = length of member, in.

The length of the member, L, is that of the shortest major member of the fixture. For example, in a mounting fixture holding twelve 1000-cfm filters in a 3 by 4 array with 2-in. spacing between filter units, the member length

\[ L = 3(24) + 4(2) = 80 \text{ in.} \]

The 2 in. spacing between filters is recommended to allow adequate finger space for handling. Knowing the value of I, suitable structural members can be selected by direct reference to a handbook of properties of structural shapes, such as the AISC Manual of Steel Construction [7]

To ensure a reliable seal between individual members of the mounting fixture and between the mounting fixture and the filter housing, all welded construction of the fixture and a seal weld between the fixture and the housing are recommended. Because of manufacturing tolerances and unavoidable defects in the gasket seating surfaces of production-line filter units, adherence to very tight tolerances in the fabrication and erection of mounting fixtures is essential. The recommended tolerances are given in Table III.

For reliable operation under severe conditions, filter units must be clamped into the mounting fixture with enough pressure for the gasket to maintain a reliable seal in spite of any manufacturing deficiencies in the filter unit, construction deficiencies in the mounting fixture, and vibration, pulsation, flexure, shock, overpressure, and widely varying conditions

<table>
<thead>
<tr>
<th>Table III</th>
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</thead>
<tbody>
<tr>
<td><strong>Recommended Construction Tolerances for HEPA Filter Mounting Fixtures</strong></td>
</tr>
<tr>
<td><strong>Alignment</strong></td>
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<td></td>
</tr>
<tr>
<td><strong>Flatness</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Dimensions</strong></td>
</tr>
<tr>
<td><strong>Surface finish</strong></td>
</tr>
</tbody>
</table>
of temperature and humidity that may be encountered in service. The major factors involved in the design of filter clamping devices are magnitude and uniformity of gasket pressure. Experience in both contaminated exhaust and clean-room applications has shown that flat closed-cell neoprene sponge gaskets, Grade SCE-43 (ASTM D-1056) [5], give the most satisfactory service. [8] Gaskets that are too soft take excessive compression set at even light compression, and gaskets that are too hard require such heavy clamping forces to provide a reliable seal that there is risk of damaging the filter frame. For 1/4-in.-thick gaskets, a compression of at least 80% is recommended for a long-lived reliable seal. This requires very rigid clamping. Bolt and nut clamping arrangements are usually used in USAEC operations, usually with a stainless steel bolt and brass or bronze nut to eliminate corrosion and galling problems. It is desirable to clamp each filter unit individually rather than to use the same bolt or clip to hold two or more units. Where no pressure distribution frame is provided, one bolt is required for every 12 in. of filter perimeter to ensure uniform gasket loading. This means that eight bolts are required for a filter unit with face dimensions of 24 by 24 in. Where a pressure distribution frame is provided, as shown in Fig. 14, one bolt per side is sufficient. Minimum recommended bolt size for 1000 cfm (24 x 24 x 11 1/2 in.) filters is 1/2-in. diameter; 5/8-inch bolts are used in many installations.

Because of the superior vibration-damping characteristics of wood when compared with steel, wood-framed filters are recommended for applications where high sound or vibration levels are expected, other factors being equal. Where sound or vibration exposure is to continue for a period of hours or days, an elastomeric sealant between the filter pack and the frame is essential. Tests made by the USAEC's Sandia Laboratory showed that steel-frame filters with packed-fiber sealant are degraded under exposure to high acoustic levels. Although the filters tested did not fail (the criterion of failure was a

![Fig. 14. Filter mounting fixture for individual clamping arrangement with pressure distribution frame.](image-url)
decrease in filtration efficiency), there was extensive loss of sealant after a period of 80 min and the filters probably would have failed had the tests been continued another 30 to 40 min. [9] Accelerometers mounted on the filter frame and on the mounting fixture showed a vibration response in the filter 10 times higher than that in the mounting fixture. The response in the filter would probably have been lower had wood-frame filters been used and had the filters been clamped more tightly to the mounting fixture. [10]

Thus, the application of HEPA filters, where they will be exposed to severe environmental conditions, often involves a trade off of filter properties. In selecting a filter for a particular application, the designer must consider the environmental limitations of the filter unit and the design for the installation.

Acknowledgments

In presenting this paper, I wish to acknowledge the assistance of L. J Brady, W. R. Laing, and T. E. Willmarth of the ORNL Analytical Chemistry Division in relation to high-temperature properties of fiber glass media, D. E Engleman of the American Air Filter Company and R. T. Goulet of the Cambridge Filter Corporation in relation to the racking strength of filter units, and G. Smith and G. A. Xenakis of Edgewood Arsenal in relation to moisture tests of HEPA filters.

References

[10] Personal communication with E. J. Buksa of Sandia Corp.
DISCUSSION

W. HEYSE: You stated that the photomicrographs of heated filter media showed a progressive increase in open area, indicating considerable loss of fibre. Can you draw such a conclusion when the samples selected differ for each photomicrograph?

C. A. BURCHSTED: Eight samples were examined after each heating cycle (room temperature, 600, 750, 950°F) and all series showed some progressive deterioration.

W. HEYSE: What was the weight per unit area for each photomicrograph sample? It must be infinitely small for you to achieve resolution of individual fibres.

C. A. BURCHSTED: I do not know the weights, but samples were obviously small.

H. ISBIN: Recognizing that wood-framed filter units may have better mechanical properties than steel frames, but that wood frames are not recommended for exposures where high moisture loading is expected, what type do you recommend for use in nuclear power reactors?

C. A. BURCHSTED: Steel frame units for post-accident clean-up systems; wood frame units for other purposes.

H. ISBIN: Do I understand correctly from your paper that the pressure shock loading of a filter should be limited to 1½ times the maximum dirty-filter pressure drop?

C. A. BURCHSTED: No. The shock-overpressure resistance of a 24 X 24 X 11½ inch unit may be as much as 2 lb/in² (see Anderson, 9th USAEC Air Cleaning Conf.). The recommendation is for mounting-frame design. A frame designed for 1/16 inch deflection in 6 feet, under 1½ X dirty-filter pressure drop, should withstand 2-2.5 lb/in² shock without exceeding the elastic limit of 36 000 lb/in² yield steel.
RECLAMATION OF A PARTIALLY PLUGGED GLASS FIBRE VENTILATION FILTER AT THE HANFORD PUREX NUCLEAR FUELS REPROCESSING PLANT *

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Abstract

RECLAMATION OF A PARTIALLY PLUGGED GLASS FIBRE VENTILATION FILTER AT THE HANFORD PUREX NUCLEAR FUELS REPROCESSING PLANT. Canyon ventilation air from the Hanford Purex Nuclear Fuels Reprocessing plant is exhausted through a filter system before being released to the atmosphere. The filter installation consists of a bulk-particulate removing, glass fibre fore-filter, and a fine-particulate removing, high efficiency, glass fibre after-filter. The original filter installation was built in 1955 during plant construction and operated satisfactorily until early 1964 when the fore-filter indicated a loss of capacity because of particulate loading. Construction of a new filter installation was started immediately and it was put into operation in 1965. When plugging of the original filter became evident, a program was initiated to define the cause of the problem and to develop, if possible, a way to reclaim the filter without damaging it. Samples of filter entrance air indicated a large percentage of the particulate to be crystalline ammonium nitrate. Core samples of the fore-filter glass fibre bed showed a predominantly ammonium nitrate loading confined to the inlet side of the bed. In a laboratory unit, an ammonium nitrate loading was shown to displace and disperse in the glass fibre bed, with resulting reduced pressure drop for a given air flow, by passing highly humidified air through the glass fibre bed. Based on the laboratory studies the partially plugged original filter, which had been removed from operation, was treated for reclamation using a small flow of highly humidified air through the fore-filter. The results of the reclamation treatment were satisfactory and it was possible to return the original filter installation to service handling the entire exhaust ventilation flow. The filter was reclaimed at a cost of $15 000; the filter replacement cost $750 000. While the reclaimed filter again developed a high pressure drop after five months of service and is not now in service, it remains useful as an emergency back-up to the replacement filter.

1. Introduction

The Purex Plant at the Hanford Works was designed to process low enrichment uranium fuels using the Purex Process as discussed in earlier meetings[1]. It is a canyon type building approximately 1000 feet long, 61 feet wide, and 104 feet high. It contains fourteen individual cells of varying size to remotely contain the process equipment.

The containment of airborne radioactivity in the Purex Plant is accomplished by systematically adjusting the static pressure throughout the building. The ventilation air flows from the zones of the least contamination toward the highly contaminated process cells. Prior to discharge to the atmosphere via a tall stack, the air is filtered through an underground glass fiber filter. The original filter operated successfully from plant startup in late 1955 until March of 1964. At that time

excessive differential pressures appeared across the fore filter which, in turn, reduced the total air flow of the system to marginal values. A new glass fiber filter was constructed to ensure operating continuity of the Purex Plant and a program to define and correct the high differential pressure across the original filter was initiated.

This paper describes the original glass fiber filter, the cause of the high differential pressure across it, the development work conducted in support of its reclamation, and the humidification of the ventilation air to reclaim the partially plugged filter.

2. Facility Description

The Purex Plant is used to chemically reprocess the nuclear fuels of the Hanford plutonium production complex. A solvent extraction process is used to remove radionuclides and inert impurities and isolate uranium, plutonium, and neptunium. The process is based on the extraction of uranium, plutonium, and neptunium from aqueous nitric acid solution into organic tributyl phosphate-normal paraffin hydrocarbon mixed solvent. Radionuclides and inert contaminants are relatively unextractable.

The high radioactivity associated with the nuclear fuel requires that massive concrete shielding be placed between processing equipment and operating personnel. The processes are operated remotely, i.e., the basic operations including maintenance are done from remote

FIG. 1. Hanford Purex canyon.
FIG 2 Process area ventilation system
FIG. 3. 291-A filter No. 1.
stations with no direct observation or contact between personnel and equipment. The processing equipment is within concrete shielded cells below concrete cover blocks. The cells are within the concrete walled Purex Building canyon. Changes in processing equipment are accomplished by removing the cell cover blocks and working within the cells with a traveling bridge crane. The crane operator sits in a shielded cab behind a concrete parapet and views the crane movements through periscope optics. Figure 1 shows the Purex canyon, the crane and the processing cells.

The Purex canyon is ventilated by drawing air into the canyon, down through the processing cells, and into the air tunnel. The supplied ventilation air is heated, filtered, and washed before going to the canyon. The exhaust air from the air tunnel is drawn through a fibrous glass filter to remove radioactive particulate material before being discharged to the atmosphere. Exhaust fans pull the air out of the canyon through the filter and discharge this air to the stack. The ventilation scheme is shown in Figure 2. The supply air normally is 80,000 cfm (cubic feet per minute) and the exhaust ventilation air 120,000 cfm. The 40,000 cfm of air not supplied comes from in-leakage via the process lines and the railroad tunnel door.

The original ventilation filter is depicted in Figure 3. It is enclosed below grade in a concrete housing 80 ft. by 50 ft. by 15 ft. and is divided into two areas with one containing a fore-filter and the other an after-filter. The fore-filter is the larger and removes most of the particulates from the incoming exhaust air. The after-filter removes additional particulate matter which passes the fore-filter. Air enters the filter through the intake duct and flows over the top, down through, and out beneath the fore-filter bed. The air then flows across beneath the inlet side of the after-filter, up through the frames of the after-filter units, and finally across the outlet duct.

The fore-filter is divided into three bays. Each of these bays contains free-packed Owens-Corning Fiberglas\(^R_1\), Type 115 K, retained by upper and lower stainless steel screens. With the free-packed glass fibers the desired density gradient is achieved by the weight of the media. As originally installed the bed media density varied from 0.7 lb/ft\(^3\) (pound per cubic foot) at the top to 3.3 lb/ft\(^3\) at the bottom. There is approximately 37,000 pounds of fibrous glass filter media in the fore-filter. The fore-filter collection efficiency was designed for 92.0 percent removal of all particles 0.7 micron in diameter or greater. The fore-filter has 2,500 ft\(^2\) of flow area and a 50 ft/min. air velocity through the bed at 126,000 cfm designed capacity.

The after-filter is made up of 132 American Air Filter Company's Deep-Bed filter units. Each unit is packed with 1/2 in. No. 25 FG Filterdown\(^R_2\) and 1/2 in. of No. 50 FG Filterdown. The density of the No. 25 media is 1.4 lb/ft\(^3\) and the No. 50 media is 1.2 lb/ft\(^3\). The units consist of five wedge-shaped pockets supported in a grid on frames. There is 6,600 ft\(^2\) of area in the after-filter and an air velocity of 20 ft/min. through the media at designed capacity. The collection efficiency of the after-filter is 98.8 percent for all particles 0.7 micron in diameter or greater, giving an over-all filter collection efficiency of 99.9 percent.

\(^R_1\) Registered Trade Name, Owens-Corning Glass Co., Toledo, Ohio

\(^R_2\) Registered Trade Name, American Filter Co., Louisville, Kentucky
3. Filter Plugging Problem

From 1955 to 1964, the differential pressure across the fore-filter slowly rose from a 3.0 in., w.g. (water gauge), to 4.4 in., w.g., at a nominal air flow of 125,000 cfm. The differential pressure across the after-filter remained relatively constant at 2.1 in., w.g. During a one-week period in the latter part of March, 1964, the differential pressure on the fore-filter increased to 7.0 in., w.g., with a resulting decrease in total air flow to 110,000 cfm. The rate of rise of the differential pressure across the filter increased until a rise of 1.5 in. per day was observed.

It was first thought that the increasing pressure drop and decreasing flow were caused by excessive moisture in the filter. Humidity measurements were first taken with a sling psychrometer, later, data were obtained from a Cloud-Cup apparatus. A continuous Foxboro Dew Cell R3 was then installed upstream and downstream of the filter. All data collected indicated that the relative humidity did not exceed 51 percent and most of the time it was below 30 percent. At these relative humidities, the accumulation of water was considered improbable.

Aliquot samples of the influent air were taken to determine particle loading and size. During the initial period of the rapid rise of the differential pressure of the fore-filter dust loadings as high as 200 milligrams per 1000 cubic feet of air were measured. This deposition rate was ten times greater than the estimated average rate of solid deposition on the filter and one hundred times greater than the probable rate of deposition from atmospheric solids alone. A spectrographic analysis of the collected sample indicated that a large fraction of the solids was ammonium nitrate.

Several core samples, 4 in. in diameter by 24 in. long, were taken of the glass fibers in the fore-filter. The core was made up of four readily distinguishable parts. Photograph 1 shows a view of the longitudinal axis of the core with the crust lying in the foreground; photograph 2 gives a head-on view of the surface crust, and photograph 3 gives a view of the four parts with (A) being the crust; (B) the gray dirt; (C) the white powder; and (D) the glass fibers. The crust and gray dirt were 44–53 percent ammonium nitrate, 8–11 percent iron; 7–12 percent silicon dioxide; 5–9 percent water, and 3–6 percent organic material. The white powder was greater than 85 percent ammonium nitrate.

An intensive sampling program was undertaken to determine the source of the ammonia or ammonium ion. Two chemicals — sulfamic acid, NH₂SO₃H, and hydrazine, N₂H₂ used in the Purex Process — are a possible source of ammonia. Samples of the atmospheres of all the tanks, both in acidic and basic conditions, indicated that these chemicals were not emitting ammonia to the atmosphere.

Simultaneously with the tank sampling program, the integrity of another part of the processing system containing a known source of ammonia was investigated. The removal of the aluminum jackets from the uranium fuel elements with sodium nitrate and sodium hydroxide in the dissolver vessels evolves copious quantities of ammonia. This ammonia is removed from the dissolver off-gas by

R3 Registered Trade Name, Foxboro Co., Foxboro, Massachusetts
PHOTOGRAPH 1. Filter core – longitudinal axis.

PHOTOGRAPH 2. Filter core – surface crust.
a scrubber and the dilute ammonium hydroxide formed in the scrubber is routed to an underground disposal site called a crib. The hydraulics of the piping system used to route the dilute ammonium hydroxide to the crib were such that the pipe from each of the three dissolvers had to be vented via a stand pipe to the cell atmosphere. A small differential pressure was found to exist across the three cells and ammonia was being evacuated into the ventilation air via this route.

4. Development Work

Development work was initiated at the Pacific Northwest Laboratories of Battelle Memorial Institute (PNL) to establish methods for filter reclamation. Since ammonium nitrate is known to be deliquescent, humidified air was drawn through the core sample of glass fibers in the Analytical Hot Cells at PNL. When the relative humidity remained below 65 percent, no dissolution or rearrangement of the crust was observed. When the relative humidity of the air was 75 to 90 percent, approximately 45 percent of the crust was dissolved. These data encouraged a pilot plant scale demonstration of removing the crust by adjusting the humidity of the purge air.

The demonstration equipment was a small scale model of the actual filter as shown in Figure 4[6]. The fore-filter consisted of a 5-3/4 in. ID tower of clear plastic pipe. Two and one-half pounds of 115K Fiberglas were loaded into the pipe from the top. The bottom layers of Fiberglas were compressed more than the top layers to simulate compression of the actual filter due to its own weight. The glass fibers were held in place by packing supports that were fabricated from 1 in. mesh screen. The 11-in. free space above the packing was left open to the atmosphere to provide an air inlet to the filter. The final clean-up filter was 8-3/4 in. in diameter and consisted of two, 1/2-in. thick layers of AA Fiberglas compressed to
FIG. 4. Pilot model of filter.
1/2 in. thickness between packing supports. The filter was installed in a 10-in. ID clear plastic pipe to allow visual observation of the clean-up layer. Associated pressure taps, vacuum jet, steam supply, etc., as shown in Figure 4 were supplied.

A synthetic dust was used to load the filter. As shown in Figure 4, the composition was 81.4 percent NH$_4$NO$_3$ and 18.6 percent sand. All dust was passed through a 200-mesh screen. A total of 519 grams was loaded onto the filter by dispersal of the dust in the incoming air. The differential pressure across the fore-filter increased from 2.9 in., w.g., to 5.05 in., w.g., and the differential pressure across the after-filter remained unchanged at 1.1 in., w.g. After the addition of the dust, a gray colored dust layer completely covered the filter. The layer varied between 1/4 and 3/4 in., and appeared to penetrate the filter approximately 4 in.

The relative humidity of the air entering the filter was then varied by adjusting a steam bleed. At relative humidities below 60 percent there was no apparent change in the crust of dust on top of the filter or the differential pressure. At a relative humidity of 60-65 percent at a dry bulb of 73 F the differential pressure decreased from 5.05 in., w.g., to 4.48 in., w.g., in a two-hour period. Damp areas began to appear on thin spots in the dust layer and particles of ammonium nitrate on the side walls above the Fiberglas began to dissolve. At 85-95 percent relative humidity at a dry bulb of 73 F the differential pressure decreased to 3.45 in., w.g., within three hours and remained at this level.

The remaining dust layer had the appearance of damp brown dirt and had the consistency of damp sand. The surface was very irregular and had a maximum thickness of 1/4-in. The dark brown color of the dust layer, as compared to the original gray color, indicated that a considerable portion of the ammonium nitrate had dissolved and flowed downward into the Fiberglas. No change occurred in the differential pressure across the filter below the top 6 in. No change in the differential pressure or appearance of the final clean-up layer occurred.

The remaining dust layer was dried by regulating the incoming air to 15 percent relative humidity. A light brown, dry crust appeared with several cracks and small holes. The differential pressure increased from this drying from 3.45 to 3.49 in., w.g.

Supplemental solids with the same chemical composition as those previously used were added to the fore-filter to obtain information on the effect of adding solids on top of the crust and additional information on humidity effects. Two hundred fifty seven grams of dust were loaded into the filter through a 200-mesh screen. The dust was added in four increments. After each of the first three increments, the relative humidity of the inlet air was raised and maintained for 10 to 15 minutes in the range of 90 to 100 percent. The short periods of high humidity and drying were enough to cause the dust to form a crust. Immediately after the humidity was raised, the pressure drop would decrease and the drying periods did not change the differential pressure. After addition of the final dust increment the layer of solids was approximately 3/4 in. deep and there were no visible holes or openings. The differential pressure rose from 3.49 in., w.g., to 20.15 in., w.g., during the four loadings.
The relative humidity was raised and maintained for 21 hours in the range of 80 to 90 percent. After two hours the differential pressure had decreased from 20.15 in., w.g., to 10.5 in., w.g. After eighteen hours the differential pressure was down to 8.0 in., w.g. The dust layer was damp and had the consistency of damp sand. The thickness varied from about 1/4 in. to 1/2 in. and several cracks and small holes were visible. The top of the dust layer was dark brown in color, denoting that the ammonium nitrate had migrated downward. After twenty-one hours the differential pressure had fallen to 7.6 in., w.g., with no change in the appearance of the dust layer. These observations suggest that once adequate passages are opened there is little intimate contact between the humid air and the major portion of the dust layer. As a result, further pressure drop reduction and solids removal occur very slowly or stop altogether. After the twenty-one hours at high humidity the filter was dried for two hours and the differential pressure increased to 8.1 in., w.g.

The filter was then washed with seven water washes and was dried for at least one hour after each wash. Details of the washes are shown in Table I. The differential pressure was reduced from 8.1 to 3.15 in., w.g., and 71 percent of the ammonium nitrate was flushed from the fore-filter. At the flow rates employed water addition was just a slow drip so the inlet line was moved manually to allow water to drop over the entire surface. Clear water started draining out of the bottom of the filter approximately 7 minutes after each wash began. The water always drained out along the wall in the same spot during each wash. The water formed a puddle at the bottom of the free space below the fore-filter, and then flowed through the discharge line to the chamber below the cleanup filter. No water entrainment to or wetting of the cleanup filter was observed and the differential pressure across the unit remained unchanged at 1.1 in., w.g.

The first wash rapidly dissolved several 1/4 to 1/2 in. diameter holes through the crust and removed about 30 percent of the crust. Fiberglas was visible through the holes and appeared to be free of ammonium nitrate and sand while the filter was wet. The differential pressure decreased from 8.1 in., w.g., to 3.55 in., w.g. During the one-hour drying cycle after the first wash the differential pressure across the filter increased from 3.55 in., w.g., to 7.30 in., w.g. Additional drying for 16 hours caused no further change. This was the first occurrence of a significant differential pressure increase during a drying cycle. Inspection of the filter showed that the Fiberglas at the bottom of the holes in the crust was completely covered with a thin, hard crust of white ammonium nitrate. Dissolution, possibly as a result of entrained water in the air, is required to produce a sudden differential pressure increase during a drying cycle.

After the fourth wash the entire crust was gone. No solids were visible on top of the Fiberglas but sand was visible about 1/2 inch below the top. During the drying cycles after these washes only a slight pressure drop increase occurred and no white crust was observed. These washes removed 59 percent of the ammonium nitrate and the only downward movement of the insoluble material was along the channel followed by the water.

Three additional washes were carried out with higher flow rates to further study the removal of ammonium nitrate and the movement of the insoluble materials. These washes removed an additional 12 per-
<table>
<thead>
<tr>
<th>Wash Increment</th>
<th>Flow Rate, ml/min</th>
<th>Addition Time, min</th>
<th>Volume Added, cm³</th>
<th>Volume Out, cm³</th>
<th>NH₄NO₃ Removed, g</th>
<th>% of Total</th>
<th>ΔP Across Fore Filter, ln., w.g.</th>
<th>ΔP Across Filter Wet</th>
<th>ΔP After Drying</th>
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<td>17.9</td>
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<td>250</td>
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<td>Total</td>
<td>3.5</td>
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<td>2</td>
<td>17.9</td>
<td>14</td>
<td>250</td>
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<td>3</td>
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<td>250</td>
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<td>four washes</td>
<td>3.2</td>
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<tr>
<td>4</td>
<td>17.9</td>
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<td></td>
<td>71.3</td>
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</tr>
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</table>
cent of the ammonium nitrate and a very slight trace of fine insoluble material was visible at the bottom of the filter along the water channels. No changes occurred in the differential pressure across the portion of the fore-filter below the top 6 in.

No change occurred in the appearance or differential pressure of the final cleanup filter during the washing. This observation is of considerable significance since previous experience has indicated that wetting of this type of filter causes holes to appear in the filtering media.

The data from the PNL development program indicated that air with a relative humidity of 60 percent or greater would dissolve a portion of the crust which was causing the high differential pressure across the fore-filter. This dissolution would reduce the differential pressure and would allow the filter to operate for an unknown period of time. Water washing would do a more thorough job of removing the crust and if the air velocity through the fore-filter was 45 ft/min or less no water entrainment will be transported to the after-filter.

5. Filter Reclamation

Based on the laboratory development work the plugged Purex Plant ventilation filter was reclaimed by passing air with a relative humidity of 80 to 90 percent through the fore-filter bed. Previously a temporary by-pass duct leading directly to the after-filter had been

![Filter reclamation flowsheet](image-url)
placed around the fore-filter to maintain adequate air flow for plant safety during the time required for designing and constructing the second ventilation filter. This by-pass ductwork was used to return the highly humidified air to the main air stream as shown in Figure 5. Ten thousand cfm or eight percent of the total air flow was humidified by steam injection at a rate of 500 lb/hr., routed through the original filter, and returned to the main air stream, \(^{14}\) which was exhausted through the second ventilation filter.

The fore-filter was initially treated with humidified air for four weeks. Prior to treating the filter the differential pressure was greater than 20 in., w.g., at an air flow of 115,000 cfm and after the four-week treatment the differential pressure was 7.7 in., w.g. After satisfactory operation for two weeks, the filter was again removed from service and the humid air treatment was resumed to increase the effectiveness of ammonium nitrate crust removal. Humid air was passed through the filter for three weeks. At the conclusion of this humidifying period, full air flow was routed to the filter with a resultant differential pressure of 7.5 in., w.g.

6. Post Operation

The original canyon ventilation filter was returned to service on September 25, 1967. Initially the total air flow through the filter was measured as 115, 000 cfm and the pressure drop across the fore-filter and after-filter was 5.4 and 2.1 in., w.g., respectively. During the succeeding 12 weeks the air flow through the filter gradually decreased to 113, 000 cfm at a pressure drop of 5.6 and 2.1 in., w.g., respectively. During the next 7 weeks the flow decreased and fluctuated between 106,000 cfm and 110,000 cfm. The filter differential pressures remained essentially unchanged, although some fluctuations were noted.\(^{18}\)

On January 6, 1968, a significant downward trend in flow started, and continued until February 12, at which time the filter flow had reduced to 92,000 cfm. During the same period the fore-filter differential pressure increased to 6.2 in., w.g., and the after-filter differential pressure decreased to 1.8 in., w.g. By March 9, 1968, the air flow had decreased to 83,000 cfm and the differential pressures were 6.8 and 1.6 in., w.g., respectively. Although no problems of contamination control were associated with the reduced air flow, the filter was removed from service as an operational unit. It remains available as an emergency back-up for the replacement unit.

7. Cost Analysis

The reclamation program to extend the life of the original filter was a financial success as shown below. The net savings for reclaiming the filter amounted to $24,000 based on the beneficial use of the filter for an additional five months. Subsequent additional use will, of course, add to the savings.
8. Future Effort

The development work indicated that a more satisfactory crust removal could be obtained by contacting the deposited solids with water. Previous operating experiences with the types of glass fibers in the after-filter have indicated that these fibers must remain dry at all times to remain effective as filter media. Additional studies and a satisfactory safety analysis will have to be completed before washing of the fore-filter will be attempted.

Preliminary planning also has been done on the physical removal of the fore-filter fibers. The control of airborne contamination during the actual removal would be very difficult and additional decontamination of the structure walls with liquids would probably have to be done before a re-packing operation could commence.

REFERENCES


DISCUSSION

J. D. JOUBERT: Did you measure the efficiency of the filters after the increase in differential pressure?

W. C. SCHMIDT: Yes, indirectly. We constantly monitor the radioactivity released to the atmosphere through the tall stack. Within slight variations, we did not find that the amount of radioactivity passing the filter was appreciably different before and after reclamation of the filter. Since the processing activities which contribute to the radioactivity found in the ventilation air were always the same, it is fair to assume that the amount of radioactivity entering the filter was constant, and the amount passing the filter was measured as constant, so that the filtration efficiency was not affected by the reclamation.

H. ISBIN: In view of the importance attached to the filter, did you assess the safety implications of operating the plant with the known deposition of NH₄NO₃ in the filter?

W. C. SCHMIDT: Yes, there is a USAEC document stating that the critical mass of ammonium nitrate is in the range of many tons. For this reason, we do not believe that any explosion hazard exists.

R. I. NEWMAN: The paper gives overall efficiency of the filters as 99.9% for 0.7-micron particles. What is the efficiency for 0.3-micron particles and what is the efficiency of removal of activity from the air?

W. C. SCHMIDT: We have not measured the efficiency for 0.3-micron particles.

99% of the activity is removed from the air. This is measured by using upstream and downstream aliquot samples of air from the ventilation filter system.
THE APPLICATION OF PLASTIC FIBRE HEPA FILTERS TO THE TREATMENT OF AIRBORNE RADIOACTIVE WASTES

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THE APPLICATION OF PLASTIC FIBRE HEPA FILTERS TO THE TREATMENT OF AIRBORNE RADIOACTIVE WASTES. HEPA filters used to separate airborne radioactive wastes must not be inflammable. This particular safety requirement is met with almost ideally by HEPA filters made of glassfibre. Plastic-fibre filters are inflammable, and therefore they appear to be unsuitable for the purpose from a safety standpoint. While glass-fibre filters are rather bulky when disposed of, plastic-fibre filters can be reduced to tiny lumps by the use of suitable solvents. Filter frame and filter layer are moulded together using identical plastic material. The use of solvents and the application of subsequent evaporation techniques will reduce the bulk of the radioactive waste to a minimum. The plastic-fibre filter layer also offers a method of recovering valuable radioactive components. Safety requirements, however, make it compulsory to combine plastic-fibre filters with glass-fibre filters of the HEPA type. Several applications will be demonstrated and the results discussed.

As is well known, HEPA filters are made of fibres of asbestos, cellulose, glass, plastics, ceramic materials or blends thereof. During the past 15 years HEPA filters with plastic-fibre filter media have been used in Europe to an ever increasing extent. Besides their use in clean rooms and clean work benches they are naturally also used for filtering contaminated radioactive exhaust air from nuclear reactors and isotope laboratories. The most commonly used plastic HEPA filter material is made of polystyrene fibre. These particular filters are traded under the name MICROSORBAN.

PRODUCTION OF PLASTIC-FIBRE FILTER MEDIA

Plastic fibres are manufactured by forcing molten plastic material or a solution of plastics in a volatile solvent through jets. Anderson [1] has made a number of different filter media in the US Naval Research Laboratories using a molten plastic material. The polystyrene fibre material discussed here is processed by the application of the second technique: Chlorinated hydrocarbons such as methylene-chloride and trichlorethylene are primarily used as solvent. Acetone too is a good solvent for polystyrene. The solution usually consists of approx. 1 kg (2 lb) of polystyrene and 4-10 litres (1-2 gal) of solvents. The blend is pumped under pressure through jets into a tunnel which is ventilated...
FIG. 1. Microphotograph of MICROSORBAN polystyrene filaments.
at an air velocity of less than 1 m/sec (3 ft/sec). The tunnel temperature is approx. 50°C (122°F). Whilst the solvent evaporates under the above operating conditions, the plastic filter material remains in the form of finest fibres. These fibres in turn are collected on a slowly moving device. It is possible to recover the solvents from the exhaust air with activated carbon, thereby increasing the economical features of the process. As the chlorinated hydrocarbons are insoluble in water, the recovery process is relatively simple and economical.

To mention some of the difficulties, let me only point out that the air stream must be guided most accurately at all times. The fact that the orifices constantly disturb the air stream makes this task highly complicated. Experience shows that the change from a small plant to a large production unit involves problems which usually cannot be foreseen on a basis of the experience gathered with the small unit. The selection of the jets and of a suitable solution ratio govern the production of fibres with diameters ranging between 0.5 and 1.5 μm. The advantages of this production process are evident because the filaments collected on the collecting device are available in the form of useful filter media. They require none of the many processes known to us from the paper industry. Whilst the manufacture of paper requires a multitude of processes, the plastic filament filter layers are ready for immediate use. To illustrate this I would compare these with very fine cobwebs, piled in a layer.

The thickness of these plastic filter layers is simply determined by allowing more or less collecting time. In addition to the adjustment of the filter layer thickness, it is easy to produce any desired filter diameter. This particular process produces filter layers with any desired efficiency rate. A special supporting skeleton is not required because the filaments are extremely pliable and virtually unbreakable. Figure 1 is a microphotograph of filaments made of polystyrene and traded under the name MICROSORBAN.

TECHNICAL DATA

Figure 2 is a graphical presentation of several MICROSORBAN materials with different layer thicknesses and varying fibre diameters. These filters were subjected to a DOP test. The velocities varied between 7.1 and 217 cm/s and the penetration was between 8.3 and 0.01%. Similar data were obtained on the basis of a paraffin oil test. This latter was specified by the Dust Research Institute of the Trade Corporatives at Bonn [2]. It should be mentioned that the penetration limit is 0.3%, which can be considered the limit of the instruments used. Higher efficiency rates cannot be obtained by this particular method. Another method prescribed by the preliminary directives of the Research Institute is based on the use of radioactively contaminated natural atmospheric dusts with a diameter of less than 0.3 μm. This method resulted in a penetration of less than 0.01%. To determine the lowest penetration value, a special test method is applied.

The test uses a paraffin oil mist with a maximum particle size distribution of 0.3 to 0.4 μm. A commercial smoke generator described by the above-mentioned laboratory is used to produce the smoke [3]. The smoke concentration is approx. 10 million particles (>0.3 μm) in 3 litres of air. When measuring the concentration on the clean side of the HEPA filter with a
Royco Particle Counter, the amount of particles found in top-quality MICROSORBAN filters for an air volume of 3 litres is 1-10. This means that penetration rates of 0.0001% can be measured.

The data are reproducible. Figure 3 shows the pressure loss at the filter layer in relation to air volume and air velocity. These measurements coincide with those of Winkel [4] at Bonn, Germany. The low pressure loss is one of the outstanding characteristics of this filter medium. When compared to most of the other HEPA filter media, the plastic filament layer is without any binding agent. You will appreciate that all filter layers of glass fibre or asbestos cellulose are made like paper. The plastic filaments do not require such a process. The striking difference lies in the fact that they do not require any binder. They have a very fluffy structure. This explains why the service life of MICROSORBAN filter media is extremely favourable. Even when used for filtering the waste
FIG. 3. $\Delta p$ in relation to face velocity for some air filter media.

Air of the radiochemical laboratories (e.g. Farbwerke Hoechst) the service life of suitable layers is approximately 4 years. The mechanical strength of plastic polystyrene filament filter media is extraordinarily high. When used for filtering radioactive exhaust air it does not matter if some of the particles of the filter medium enter the air stream. This must, however, be avoided under all circumstances where a clean air supply is desired. Most of the glass-fibre and asbestos-cellulose filter media which we investigated emitted a larger number of particles into the air stream even after 8 or 10 hours of use. It has been proved that polystyrene filter media emitted practically no particles into the air stream. This is understandable considering the fact that the glass fibres are extremely brittle. If they are not handled carefully enough they will soon show a great many holes. By contrast, plastic filaments are extremely pliable and soft. These characteristics explain why they will not release the minute fibres that enter the air stream. This has been ascertained by a 0.3-μm sensitive Royco Particle Counter on the clean-air side of the HEPA filter [5].

APPLICATION TECHNIQUE

The polystyrene-based filter layers described are available in a variety of dimensions. The flat filter material is used for measuring purposes. But round cartridges and pads of the smallest and largest sizes are also available. It is unnecessary to explain how to install these because they are used and installed in the same way as all other filter media in filter banks or appropriate housings. To repeat: the main advantage of this filter layer is its extremely high resistance to mechanical damage. The material is soft and pliable. It is nearly Impossible to damage when installing in the filter frame. Another most important advantage lies in the solubility of the plastic filter layer with suitable solvents. Here is a possibility of reducing radioactive waste to the smallest conceivable minimum volume. Keeping in mind the high population density of Europe, this factor should not be underestimated.

The advantages of such soluble filter layers for certain types of dust are known. The known disadvantage is the low temperature resistance, which is limited to approx. 80°C (176°F) for polystyrene. Many air ducts
in radioactive laboratories are of PVC or other plastic material. In such cases the temperature resistance of the filter would just about match the duct material. If, however, emergency situations or fire regulations require higher temperature resistances, it would be necessary to install a non-combustible glass-fibre filter behind the polystyrene filter. In practical application, this glass-fibre filter would never be directly exposed to radioactive air since the polystyrene filter in front of it would retain all the radioactive dust.

Conventional HEPA filters are usually mounted in a wooden frame, whereas polystyrene-fibre filters are moulded into frames of the same material. This is the best possible method of avoiding leaks. In addition thereto, filter media and filter frames are equally soluble.

Anderson [6, 7] has observed that HEPA filters made of PVC fibres have a lower efficiency rate in an electrical field or under radioactive irradiation. We measured the efficiency rate of radioactively contaminated polystyrene HEPA filters and found that there was no measurable efficiency drop.

Experience shows that HEPA filters made of polystyrene fibres are useful for special applications where they are superior to filter media made of other materials.

REFERENCES


DISCUSSION

C. A. BURCHSTED: What is the ignition temperature of the fine polystyrene fibres?

R. E. KRATTLE: Probably about 120°C. There is no difference between the ignition temperatures of normal polystyrene and polystyrene in fibre form.

L. F. FRANZEN: What have you observed regarding the radiation stability of polystyrene fibres? I expect that it is inferior to that of the glass fibres.

R. E. KRATTLE: Under normal operating conditions, we did not observe a decrease in the efficiency of HEPA filters (polystyrene-type) or a change in the fibre surface.
DESIGN AND OPERATION OF A LARGE SAND BED FOR AIR FILTRATION*

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Abstract

DESIGN AND OPERATION OF A LARGE SAND BED FOR AIR FILTRATION. Large sand beds to filter exhaust air from radiochemical separation plants have performed satisfactorily for 13 years at the Savannah River Plant. The beds are 100 X 240 X 8 feet deep and are made from layers of sized sands and gravels. Activity penetrates only to the smallest-mesh (30-60) sand; about 1000 curies of gamma activity is estimated to be in the bed. Filtering efficiency has remained at 99%. Resistance to air flow has increased in the beds throughout the years of operation. Some increased pressure drop resulted from groundwater leaking into the sand. Air flows have generally been maintained in excess of 115,000 ft³/min. Filter differential pressures currently are in the range of 8 to 10 inches of water.

INTRODUCTION

Two chemical separations facilities at the Savannah River Plant (SRP) are used to separate and purify the products of the SRP reactors. These processes are 1) recovery of unconsumed uranium, 2) separation of plutonium, and 3) separation of special isotopes. Operations are carried out in two large fuel reprocessing “canyon” buildings, located in F and H Areas. Figure 1 shows a cross section of the reprocessing building, and that portion of the exhaust air system that goes to the sand filter. The initial steps of the separations process are performed in the hot canyon, steps involving lower radiation levels are in the warm canyon.

Separate air supply and exhaust systems are provided for the canyons, the center sections (occupied by personnel), and the plutonium finishing areas. Exhaust air from the canyons goes through a sand filter to remove particulate radioactivity and then to a 200-foot stack. Part of the air from the center sections goes directly to high-efficiency filters and then to the stack, the other part passes through process areas and combines with the canyon air. Vessels in the canyons are ventilated by a process vessel vent system that exhausts through a dehumidifier, heater and fiberglass filter before entering the sand filter. Air from the plutonium finishing areas is triple filtered through high-efficiency filters and part is exhausted directly, the remainder enters the sand filter for additional activity removal.

SUMMARY

Large sand beds, one each for F and H Areas, have satisfactorily filtered exhaust air for 13 years. Filtering efficiency has remained greater than 99% with acceptable increases in differential pressure.

* Information in this article was developed during the course of work under Contract AT (07-2)-1 with the US Atomic Energy Commission.
Activity has penetrated only to the smallest mesh (30-50) sand, about 1000 curies of gamma activity is estimated to be in the bed. Filtering efficiency has gradually improved, probably because dust accumulation has created a finer filter medium. Air flow has ranged from 100,000 to 130,000 cubic feet per minute throughout the years of operation. Filter differential pressures have increased slightly because of dust accumulation and occasionally because of water inleakage.

SAND FILTER DESIGN

The sand filters are 100 feet wide, 240 feet long, and 8 feet deep. Only the roof section is above ground level, and it is supported by columns that extend through the filter bed. The sides are waterproofed concrete. General construction of a filter is shown in figure 2.

The bed is made from layers of sands and gravels in graduated sizes. The largest rocks (1-1/4" to 3" diameter) are supported on special tiles (shown in detail on figure 2) which distribute the air from 12 tunnels connecting to the main supply tunnel. Progressing from the...
bottom to top, the air passes through layers of successively smaller particle-size until the primary filter medium (30-50 mesh sand, 3 feet deep) is reached. Coarser sand and gravel top the bed to prevent loss of sand through entrainment. Air passes through exit ports into an exhaust tunnel and then to a 200-foot stack. A filter bypass tunnel is provided, but has never been used. Sumps are provided in the supply and exhaust tunnels to collect any condensed moisture.

OPERATING EXPERIENCE

The sand filter in F Area has been in continuous operation since 1954 and in H Area since 1955 at a nearly constant superficial velocity of 4.7 ft/min.

Operation and Problems

There have been variations in air flow rates from about 100,000 to 130,000 cu ft/min which are attributed to changes in differential pressure. Figure 3 shows the change in
differential pressure through the F Area filter since 1960. Increased differential pressure is attributed to two causes: 1) ground water inleakage which may have resulted in some permanent compaction of the bed, and 2) dust accumulation.

A relatively abrupt increase in pressure drop across the filter in F Area prompted comprehensive investigation in 1966-1967. Flow measurements were refined, pressure differentials checked, and dew point instruments employed to determine moisture content. Excessive moisture was indicated, so the filter was inspected. Cracks were found in the concrete side walls above the bed (above the 1/4 inch gravel) through which ground water could enter, and stains on the walls indicated that seepage had occurred. The bed had settled about 3 inches. Earth was excavated from around the walls and all cracks were repaired, the space was not backfilled, thus preventing further inleakage. An effort was made to dry the sand by heating the incoming air, but the temperature attainable was limited by process restrictions in the separations plant. About 15% less pressure drop was realized in several months. A plot of the time versus flow per inch of differential pressure, figure 4, shows the recovery in 1968 after drying.

Sampling of the filter input air indicated dust accumulates at about 2 lb/day routinely, the dust may well function as a filter aid. Dust is present because some escapes the canyon inlet air filters, over the years it has accumulated on process equipment. Higher dust loading rates to the sand filter occur when extensive equipment movement disturbs the dust deposits in the canyon and when other special work is performed, e.g., in the exit air tunnels. Slow deterioration of concrete also contributes. No steps have been taken to change the dust accumulation rate.

Radioactivity Filtration

Radiation from the gamma emitters deposited in the sand is measured routinely by inserting an ion chamber into monitor tubes which pass through the bed. A typical radiation survey is shown in figure 5. Intensity has ranged to twice that shown. The intensity varies with cooling time and type of material processed as well as processing rate.

---

*FIG. 5. Typical radiation intensity in a sand filter.*
The air entering and leaving the filter is monitored constantly to determine the input and output of radioactivity. Annual input of gamma emitters is about 1000 to 2000 curies. Gamma pulse height analyses indicate that the emitters are fission product Ce, Ru, and Zr-Nb. The nuclides present will vary depending upon the material being processed. Figures 6 and 7 show activity input and leakage for nonvolatile beta and alpha emitters from 1962 through 1967. These data indicate that the filter efficiency improves with time. The relation between input and leakage of the nonvolatile beta emitters better emphasizes the filtration improvement, figure 8 illustrates this with two years' data selected to show best correlation. Release is a
function of two variables, filter inventory and instantaneous input. High instantaneous input gives a lower percentage release while high inventory gives a more constant release. This indicates that inventory is the prime contributor to activity release.

Figure 8 further indicates that data from an operating filter should not be used for predicting the release from a new filter. A new filter should be tested for release and, if necessary, steps taken to improve filtration before active operation begins.

**DISCUSSION**

C. CHEEVER: Were the individual sand grains regular or irregular in shape?

G. H. SYKES: We only washed the sand; we did not shape it. I assume that the grains were irregular.

C. CHEEVER: Have you any recommendations for improving the efficiency of new sand-bed filters?

G. H. SYKES: I think they should be pre-loaded with dust.

R. I. NEWMAN: Why were only some of the exit-gas streams passed through the filters and on what basis was your selection made? Has any study been made of relative costs (initial and operating) of sand versus HEPA glass filters?

G. H. SYKES: Regarding the exit gases, some of those which do not pass through the filters show merely trace levels of contaminants; in any case, they do pass through other filters. In another case, air from the plutonium finishing areas is passed through separate, high-efficiency filters three times. Air from work areas occupied by personnel also has an extremely low activity not necessitating sand filtration. Air is not passed through the sand filters unless this is really necessary, since lower air velocities and volumes mean better filtration.

I do not know of any comparison of filter costs.

H. A. MOREWITZ: How did you decide on the number and thicknesses of the sand layers, type of medium, etc. in order to predict that they would perform the functions allotted to them?

G. H. SYKES: Our filter was constructed many years ago and I do not know all details of the design studies. Du Pont had already constructed a filter at Hanford, based on data in its possession, and I believe that our filter was based to a large extent on the design of this one.
THE ECONOMICS OF SOME TYPES OF ABSOLUTE FILTERS

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Abstract

THE ECONOMICS OF SOME TYPES OF ABSOLUTE FILTERS. The cost of air-cleaning filters is determined by the purchase price of the filter and its mean life. If filter changes are not caused by a high level of activity, the increase in pressure drop will make a filter change necessary. In the latter case the dust-holding capacity of the filter determines the interval between changes. A number of different filters have been compared in this respect using atmospheric aerosols and a significant difference in cost has been observed.

INTRODUCTION

The cost of air-cleaning filters is determined by the purchase price of the filter and its mean life. Different factors influence the purchase price of a filter, primarily the efficiency and the pressure drop. These data can be specified and tested according to official codes. The life of a filter depends on one of two factors, either the activity level of the dust in the filter or the amount of dust accumulated in it. If the radiation from the filter is allowed to rise to a high level, handling becomes too complicated and is in fact impossible without special shielding arrangements. Thus, the filter has to be changed before an acceptable level is exceeded. The increase in pressure drop up to this point may still be rather insignificant. On the other hand, if the dust collected in the filter has a low specific activity or if the activity is mainly alpha and beta radiation, the radiation problem will be of secondary importance and the increase in pressure drop, caused by the dust collected in the filter, will be the limiting factor which determines the life of the filter. It is, however, very difficult to get relevant information on the dust-holding capacity of filters. First of all, it must be stated that the dust-holding capacity must be expressed as a function of the increase in pressure drop of a filter at a given air flow through the filter. A single figure saying that the filter can accumulate a certain amount of dust does not mean anything. Secondly, the type of dust used for determination of the accumulation characteristic has to be specified, but even so the situation is not satisfactory as the results obtained with different dust types cannot easily be interpreted and compared with the dust in the actual plant.

Sometimes some information is available on the relation between the dust layer and the pressure drop for a small piece of filter paper of the same sort as the large filters. To produce a large filter area on a limited face area, the filter paper is folded and forms several deep channels where the air can enter and leave the surface of the filter paper. It is obvious that there is an optimum area of filter paper that can be accommodated inside a given filter unit size. Irrespective of the dust-holding capacity,
the pressure drop of the clean filter will have a minimum for a certain filter paper area. For a standard size of absolute filter, 610 X 610 X 290 mm (24 X 24 X 12 in), the filter area in commercially available filters is normally 20 times the face area. If the distances between the folds are short the channels are so narrow that they rapidly become clogged by the dust and give an increased pressure drop, which is much greater than the corresponding increase that would have been obtained if the dust had been evenly distributed over the filter paper surface.

To compare the operation costs for different types of filters, an attempt was made to calculate the total cost, assuming that the accumulating capacity was proportional to the nominal filter area. To verify this assumption and to find out if the folding technique and other effects would influence the result, a long-term test was performed.

TEST PERFORMANCE

Four filters were operated for one year under as identical conditions as possible. Figure 1 illustrates the arrangement which was located in a large hall. The air inlet of the hall ventilation was installed 5 m above ground level. In this way large particles were separated from the air, both outside and inside the hall, and thus the filters were exposed to a normal atmospheric aerosol. Every inlet duct was provided with an orifice to measure the air flow and made in accordance with the Swedish codes for flow-rate measurements. The flow rate was adjusted with a throttle valve after each filter. The ducts were checked for leakage between the orifice and the filter.

The data for the tested filters is given in Table I. The efficiency data is based upon the factory tests. Before our test the filters were checked for damage by means of an aerosol test. The filters were also weighed before the test after they had been dried at 50°C for three days.

The air flow through each filter was adjusted to 1700 m³/h at the start of the test and was then checked and adjusted every week for one year. The actual pressure drop was recorded after each flow-rate adjustment. In this way, the same flow of air passed through every filter and they were exposed to the same amount of dust.
TABLE I. DATA FOR THE TESTED FILTERS

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Rated capacity (m(^3)/h)</th>
<th>Initial pressure drop (mm wg)</th>
<th>Total filter area (m(^2))</th>
<th>Efficiency before test (DOP %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1500</td>
<td>21</td>
<td>35</td>
<td>99.98</td>
</tr>
<tr>
<td>B</td>
<td>1700</td>
<td>25</td>
<td>25</td>
<td>99.97</td>
</tr>
<tr>
<td>C</td>
<td>1850</td>
<td>25</td>
<td>21</td>
<td>99.97</td>
</tr>
<tr>
<td>D</td>
<td>1700</td>
<td>25</td>
<td>21</td>
<td>99.97</td>
</tr>
</tbody>
</table>

TEST RESULTS

The increase in pressure drop is shown in Fig. 2. The irregular shape of the curves illustrates how the dust concentration varied during the year. During April and May the dust concentration was obviously high. Roads get dry and dusty after the snow melts and flower pollen flies around. During the vacation period in July, the activity at the Studsvik research establishment is low which could explain the almost constant pressure drop during that month.

The ventilation plant has to be designed to overcome the maximum pressure drop of the dirty filter. One often designs for a degree of dust accumulation corresponding to a doubling of the initial pressure drop. As absolute filters usually have an original pressure drop of 25 mm wg (1 in.), most plants at Studsvik can accept a maximum pressure drop of
TABLE II. LIFETIMES OF THE TESTED FILTERS

<table>
<thead>
<tr>
<th>Filter</th>
<th>Lifetime (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>360</td>
</tr>
<tr>
<td>B</td>
<td>195</td>
</tr>
<tr>
<td>C</td>
<td>330</td>
</tr>
<tr>
<td>D</td>
<td>320</td>
</tr>
</tbody>
</table>

50 mm wg (2 in.). With this maximum acceptable pressure drop of 50 mm wg, the respective lifetimes of the tested filters are as given in Table II.

At the end of the test, the filters were dried and weighed, and the dust collected in the filters was determined. The pressure drop of the filter B grew too high for the test arrangement before the end of the test period, so the test run of that filter was interrupted before the others. As indicated in Table III, the other three filters collected roughly the same amount of dust.

TABLE III. AMOUNT OF DUST COLLECTED BY THE FILTERS

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Efficiency after test (DOP %)</th>
<th>Test period (d)</th>
<th>Dust accumulated in the filter (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>98.2</td>
<td>372</td>
<td>0.70</td>
</tr>
<tr>
<td>B</td>
<td>98.0</td>
<td>254</td>
<td>0.45</td>
</tr>
<tr>
<td>C</td>
<td>100.0</td>
<td>372</td>
<td>0.72</td>
</tr>
<tr>
<td>D</td>
<td>100.0</td>
<td>372</td>
<td>0.70</td>
</tr>
</tbody>
</table>

ECONOMY

The purchase price for filters may vary from time to time. But at a specific time with valid market prices, the choice between different filters must be made on the basis of valid offers and available technical information. A first attempt can be made, assuming that the filter life is proportional to the filter paper areas listed in Table I. The prices are given in Table IV.

If the filter costs are compared with respect to the measured filter life, as given in Table II, the cost relation will be as shown in Table V.

The test runs have revealed that filters C and D are most economic and A and B not at all favourable, contrary to what might have been expected from Table IV, when only considering the filter area. The relative purchase price per area of filter paper and operating costs for the four filters are illustrated in Fig.3.
TABLE IV. RELATIVE COST OF FILTERS BASED ON FILTER PAPER AREA

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Purchase price (Sw.Cr.)</th>
<th>Price per area of filter paper (Sw.Cr./m²)</th>
<th>Relative price D = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>630 -</td>
<td>18 -</td>
<td>0.85</td>
</tr>
<tr>
<td>B</td>
<td>520 -</td>
<td>20 80</td>
<td>0.98</td>
</tr>
<tr>
<td>C</td>
<td>455 -</td>
<td>21 70</td>
<td>1.02</td>
</tr>
<tr>
<td>D</td>
<td>445 -</td>
<td>21 20</td>
<td>1.00</td>
</tr>
</tbody>
</table>

TABLE V. RELATIVE COST OF FILTERS BASED ON FILTER LIFETIME

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Purchase price (Sw.Cr.)</th>
<th>Operation time (d)</th>
<th>Charge per day (Sw.Cr./d)</th>
<th>Relative charge D = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>630 -</td>
<td>360</td>
<td>1 75</td>
<td>1.26</td>
</tr>
<tr>
<td>B</td>
<td>520 -</td>
<td>195</td>
<td>2 67</td>
<td>1.92</td>
</tr>
<tr>
<td>C</td>
<td>455 -</td>
<td>330</td>
<td>1 38</td>
<td>0.99</td>
</tr>
<tr>
<td>D</td>
<td>445 -</td>
<td>320</td>
<td>1 39</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Relative values

D=1

FIG. 3. Comparison of costs for different types of filters.
CONCLUSION

From the results of the test related in this report it is obvious that the choice of a filter cannot be based only on its purchase price, even if the price is corrected for total filter paper area per unit. Relevant data about the dust load carrying properties of the filter are needed. These data are not easily obtainable from the manufacturers of the filters, and even if such information is available, it is difficult to compare data from different suppliers. Laboratory tests with filter paper samples only do not give satisfactory information.

These tests comparing four filter types have shown a significant difference between the lifetimes of filters exposed to the actual atmospheric aerosol. Even if the characteristics of the dust in most plants are different, the test performed may be capable of indicating good or bad dust accumulation properties. A realistic standard method for testing the dust capacity of a complete absolute filter is desirable, both from user's and producer's points of view.

DISCUSSION

J. BRION: Where did you obtain the units you tested?

P. J. LINDER: Filter A was European; filters B and C were American and filter D was Swedish. We deliberately identified the filters by letter only, in order not to involve the makers.

J. BRION: I asked the question because we carried out similar tests, with French, British and American filter elements, using the same concentrations as you, i.e. \( \sim 0.05 \text{ mg/m}^3 \), and fully agree with your general conclusions.

K. T. THOMAS: What media were used in the various types of filter tested?

P. J. LINDER: They were all of the glass-fibre type and all were high-efficiency, particulate, air filters with good humidity resistance.
OCTENNIAL HISTORY OF THE DEVELOPMENT AND QUALITY OF HIGH-EFFICIENCY FILTERS FOR THE US ATOMIC ENERGY PROGRAM

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Abstract

OCTENNIAL HISTORY OF THE DEVELOPMENT AND QUALITY OF HIGH-EFFICIENCY FILTERS FOR THE US ATOMIC ENERGY PROGRAM. Two facilities are operated for the US Atomic Energy Commission in its program to ensure the uniform quality of commercially manufactured high-efficiency particulate filters. The filter-testing program was started in January 1960 after it was realized that the commercial fire-resistant product incorporated deficiencies of manufacture. The record of testing for quality assurance by the two facilities and an analysis of factors governing the quality of filters are presented. The analysis is complemented with a description of efforts, made in the course of the filter testing, to improve the design of the filter for efficiency and reliability.

The fire-resistant (HEPA) filter of 1959 was inadequate. The inadequacy of the filter, now judged by reflection, was brought about by the intensive accelerated efforts to replace and preclude, wherever possible in the US atomic energy program, use of filters made of combustible materials. This desire for fire resistance of filters has proliferated widely among other members of the international atomic energy family. The intensive AEC effort caused US industry to produce filters of fire-resistant design but without the opportunity for development of manufacturing technology adequate for ensuring reliability of the filter. The state of the fire-resistant filter today is in sharp contrast to the 1959 filter. The testing program, coupled with a program for continuing improvement of the filter, has resulted in the effective removal of radioactive aerosols at atomic energy installations on a consistent and dependable basis.

Introduction

Two related programs to assure the quality of filters and to develop better filters for US atomic energy installations are continuing into their ninth year. The programs grew out of an acknowledgment that the Atomic Energy Commission had a responsibility to prevent atmospheric pollution from nuclear plants and laboratories. The AEC's use of quality assurance facilities to verify the high order of integrity routinely required for filters and its support of filter improvement confirm the conscientious manner in which this responsibility is being discharged. The Division of Operational Safety of the Atomic Energy Commission coordinates the operation of these programs.

Filter combustibility

Filters containing a combustible cellulose-asbestos filter medium were used at atomic energy locations until 1956. The filter medium had been introduced into gas mask canisters by Germany in World War II. [1] Cellulosic fibers predominated over asbestos fibers in the composition, therefore the medium was highly susceptible to ignition. Moreover, combustion of the filter can produce a backflash similar to that illustrated in Figure 1. This stems from an explosive concentration of carbon monoxide given off by the combustion process and pocketed immediately downstream when the filter is operated at low air flow. Backflash occurs when the fire penetrates the filter to contact the explosive concentration of carbon monoxide.
FIG. 1. Demonstration of explosion possible in ignition of carbon monoxide effluent of burning cellulose-asbestos filter.

FIG. 2. Linear crack perpendicular to pleats of filter. Common sign of failure in early fire-resistant model.
Although the combustibility of the cellulose-asbestos filter was useful for incineration to recover scarce fissile material, involvement of the filter in incidental fires, which interfered with the operation of atomic energy plants, precipitated a demand for filters more resistant to ignition. A suitable filter medium, made of glass fibers, had been available since 1951 but the technology for its fabrication into a fire-resistant filter had not been developed completely. The filter then produced was deficient.

Facilities for quality assurance of filters

The poor quality of this fire-resistant filter became known in 1959 and the information has been documented fully in reports to earlier air cleaning conferences sponsored by the Atomic Energy Commission. [2,3] Figure 2 shows the degradation in a section of a filter fabricated at that time. Following the realization that fire-resistant filters supplied commercially could not be operated with the high degree of efficiency that AEC had specified routinely for a number of years, two filter testing facilities were established in January 1960 to verify filter quality.

Testing facility equipment

The two filter testing facilities are located at Oak Ridge, Tennessee, and at Richland, Washington. Each facility is equipped basically with three penetrometers which measure filtration by generation and detection of a homogeneous aerosol of dioctyl phthalate. A small penetrometer, indicating in metric units, has an air flow capacity of 100 litres per minute to test items such as filter paper and gas mask canisters. The largest of the three

![FIG. 3. Model Q107 dioctyl phthalate penetrometer for testing larger high-efficiency filters.](image-url)
penetrometers will accommodate filters with air flows to a range of 1250 cubic feet per minute. A photograph of the larger instrument may be seen in Figure 3.

UL label

Manufacturers of these filters likewise employ penetrometers using dioctyl phthalate aerosol. When a filter has been fabricated, it is given the dioctyl phthalate test by the manufacturer and the results of the test are marked on the frame of the filter as illustrated in Figure 4. Results of tests by the testing facility also appear in this photograph together with the "UL" label of Underwriters' Laboratories, Inc. The appearance of the "UL" label on the filter frame signifies that the design of the filter conforms to the requirements of the standard UL 586 for fire resistance. [4] This standard was introduced in 1964, to provide surveillance of filter fire resistance at the manufacturing level, and the standard has been revised on two occasions in keeping with increasingly stringent requirements for a better filter. The AEC has recommended that fire-resistant filters for the U. S. atomic energy program conform to this standard. [5]

Sequence of quality assurance operations

Purchasers of filters for the atomic energy program stipulate that filters be delivered by the manufacturer to one of the two filter testing facilities. Here they are subjected individually to inspection, measurement of resistance to air flow, and to penetration of dioctyl phthalate through the filter. Filters rated at an air flow capacity of 500 cubic feet per minute,

FIG. 4. Tests marked on filter frame by manufacturer (centre) and testing facility (upper left). UL label (upper centre).
and larger filters, are enclosed while under test so that any points of leakage through the frame of the filter will be detected. In addition, filters of these sizes are given a second dioctyl phthalate test with the air flow reduced to 20 percent of the flow for which the filter is rated. This detects small leaks that occur only when the aerosol is delivered to the filter at reduced flow, a phenomenon first reported in 1945. [6]

Following these tests, acceptable filters are shipped to the purchaser. Unacceptable filters are returned to the manufacturer or destroyed, in accordance with standing instructions from manufacturers. The testing facility also sends to the purchaser a report of all tests and of the disposition of unacceptable filters.

**Improvement of filter quality**

When testing facilities were commissioned in 1960, filters purchased earlier and then in storage at atomic energy program locations were removed and tested. Figure 5 indicates that only 51 percent of these filters were found in acceptable condition. For comparison, Figure 5 shows also that an average of 95 percent of newly purchased filters were accepted in the eight years following.

Unacceptable filters for the eight-year period, actually 49 filters per thousand, are categorized by basis of rejection in Table I. The low incidence of shipping damage listed in the table is a tribute to the packaging by manufacturers of the filters. The information provided in Table I has been compiled from the very complete records maintained by the filter testing facilities. Tests of approximately 100,000 new filters have been recorded. The data are highly representative of the excellent quality of filters currently available from commercial sources in the United States.

![FIG. 5. Percentage of acceptable filters purchased in periods prior to, and during operation of filter testing facilities.](image)
TABLE I. REJECTION OF NEW FILTERS BY TESTING FACILITIES IN 8-YEAR PERIOD 1960-1967

<table>
<thead>
<tr>
<th>Cause</th>
<th>Average no. of rejections per 1000 filters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shipping damage</td>
<td>3</td>
</tr>
<tr>
<td>High resistance</td>
<td>11</td>
</tr>
<tr>
<td>Excessive penetration</td>
<td>17</td>
</tr>
<tr>
<td>Manufacturing deficiency</td>
<td>18</td>
</tr>
<tr>
<td>Total</td>
<td>49</td>
</tr>
</tbody>
</table>

Cooperative program for filter improvement

This commendable record of filter quality was difficult to attain. When filter testing facilities were established, a parallel program of cooperation was started with all segments of the filter industry. From the level of an incompletely developed technology for the manufacture of a fire-resistant filter, the patient and conscientious cooperation of the purchaser and the filter industry through many tedious steps has resulted in the filter supplied today. [7] One example of the cooperation is illustrated in Figure 6. This apparatus is operated intermittently at an AEC site to test prototype filters against heat and flame. The test subjects in the photograph are filters that contained newly developed components intended to offer a more efficient, a stronger, or a more economical filter. Fundamentally, however, the filter must exhibit a minimum level of fire resistance, and the test apparatus is operated to determine this.

An additional example of the cooperative program was an informal conference held August 25, 1968, at New York City. The conference was one of a number of such meetings devoted to the improvement of filters. Participants included suppliers of filter fibers, media makers, filter manufacturers, researchers, specification writers, and government representatives.

The cooperative program knows no national boundary, for conferees came also from government and industry of other member states of the IAEA. There are further improvements to be made in filters and the cooperative program will be extended wherever a mutual interest exists to provide a better filter. The proceedings of this informal conference will be summarized at the Tenth AEC Air Cleaning Conference of August 28, 1968, also at New York City.

Increasing volume of filters

Within the past four years, the AEC has decommissioned seven production reactors. These reactors have required a significant quantity of filters. As a result of this, a decline should have been expected in the volume of filters purchased and shipped to filter testing facilities. The converse is true, as indicated in Figure 7, which shows an increase in the index of annual volume of filters tested over the eight-year period. More filters are being used at existing locations and this is evidence of the awareness in the U. S. atomic energy program to prevent nuclear contamination of the atmosphere.
FIG. 6. Apparatus, partly disassembled, for test of filters against heat and flame. Filters tested shown left of centre.

FIG. 7. Index of filters required annually by US atomic energy program.
REFERENCES


DISCUSSION

M. TOMŠIČ: What tests have you carried out on the filters as installed and what is the possibility of damage during installation? I am thinking particularly of the filters in ventilation systems which are not used under normal conditions, but are called on only to mitigate the consequences of accidents.

H. GILBERT: In-place testing is a common procedure in US installations and in view of the stringent regulations, we believe our filter systems are trustworthy.

L. F. FRANZEN: Table I of your paper indicates four categories of cause for the rejection of filters. Could you elaborate on these categories?

H. GILBERT: "Manufacturing deficiencies" include such items as loose gaskets or other faults obvious upon inspection and not necessitating DOP tests. "Excessive penetration" relates to the penetration of DOP through the filter. "High resistance" means resistance to air flow.

L. F. FRANZEN: Does much damage occur during shipment from the testing facility to the purchaser?

H. GILBERT: I have no data for that, but judging by the number of complaints received, there must be very little damage.
SEPARATEUR A PULVERISATION ELECTROSTATIQUE

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Abstract — Résumé

L'efficacité d'un séparateur est d'autant meilleure que, pour un aérosol donné, le nombre ou la masse des particules captées sera plus grand. On définit généralement la qualité d'un dépoussiéreur par son rendement massique \( \eta_m \), ce qui est à notre avis regrettable. En effet, cette définition ne tient compte pratiquement que des particules de dimensions super-microniques et il en résulte que le rendement des dépoussiéreurs industriels est rarement inférieur à 99,99%. Si l'efficacité des appareils est aussi élevée on ne comprend pas pourquoi il est nécessaire de faire des recherches dans ce domaine et pourquoi les particules micro-niques ou sub-microniques ne sont pas captées.

Cependant il est évident que le rendement d'un séparateur peut être de 99,99% et qu'aucune particule micronique, et a fortiori sub-micronique, ne soit captée, et que la coloration de la fumée soit la même avant et après un dépoussiéreur ayant un rendement massique supérieur à 99%.
L'efficacité d'un collecteur élémentaire sera d'autant meilleure que la grandeur caractérisant la déviation de la trajectoire de la particule solide par rapport à celle de la particule fluide sera grande vis-à-vis des dimensions du dépoussiéreur. Au moyen de champs extérieurs appropriés et en diminuant les dimensions du dépoussiéreur élémentaire - venturi-scrubber, filtres en tissu - on peut augmenter le rapport déviation caractéristique-dimensions du collecteur élémentaire. Cependant, d'une part il est très difficile de pulvériser très finement un liquide, et d'autre part, par suite des phénomènes d'évaporation et de leur faible inertie, les particules liquides sont d'autant plus difficilement captées que leurs dimensions sont plus petites. Dans les filtres en tissu, les collecteurs élémentaires sont fixes, mais dans ce cas, la perte de charge du séparateur est très importante.

Il résulte de ces différentes remarques que la séparation de particules microniques ou sub-microniques du gaz vecteur est un problème très difficile à résoudre.

A la suite des résultats obtenus par l'auteur dans sa thèse de doctorat [1], il a été mis au point un nouveau type de dépoussiéreur et un nouveau type de séparateur à gaz.

a) Dépoussiéreur proposé

De l'eau ou tout autre réactif liquide est pulvérisé mécaniquement et électrostatiquement dans l'axe d'un cylindre métallique relié à la terre. L'eau est portée à une haute tension continue ou alternative. L'expérience montre que l'eau est d'autant mieux pulvérisée que la tension appliquée est plus élevée et que les gouttelettes sont chargées électriquement du même signe que la tension appliquée. La pulvérisation est meilleure dans le cas où la tension appliquée est alternative. Les micro-gouttelettes jouent le rôle de micro-collecteurs comme dans un scrubber.

FIG. 1. Schéma de l'appareil.
classique, mais, par suite de leur charge importante, elles peuvent capter plus facilement les particules d'aérosol et, dans le cas d'une tension appliquée continue, ces micro-collecteurs peuvent être captés aisément au moyen d'un électrostatique classique. Il a été montré expérimentalement [2] que l'efficacité de l'appareil proposé ne dépend pas de la charge initiale de l'aérosol, ce qui laisse supposer que les particules d'aérosol sont captées principalement sous l'action des forces images et non des forces coulombiennes.

La figure 1 montre le schéma de l'appareil. Les figures 2, 3 et 4 permettent de comparer l'efficacité numérique de l'appareil proposé.
FIG. 4. Rendement du dépoussiéreur en fonction de la tension pour différentes valeurs du débit d'eau. Vitesse de l'air 4 m/sec, rayon des particules: 0,5 µm, concentration de l'aérosol < 50 particules/cm³.

avec celle d'une cellule Cottrell (sans pulvérisation d'eau) et d'un laveur classique (tension appliquée nulle) [3]. Les aérosols utilisés sont des aérosols mono-dispersés obtenus par la méthode de Sinclair-La Mer. Afin d'éliminer les grosses particules, celles-ci sont captées à l'entrée du dépoussiéreur au moyen d'un préfiltre.

b) Séparateur de gaz proposé

L'auteur a montré que, lorsqu'on injecte des particules d'aérosol dans la zone couronne d'une cellule Cottrell, celles-ci acquièrent une charge beaucoup plus importante que ne le prévoit la loi de Pauthemer ou de White et que, quel que soit le signe de la tension appliquée, les particules sont captées par l'électrode périphérique. Dans le cas de capture de gaz, une des principales difficultés est d'augmenter la surface d'échange gaz-réactif, soit en utilisant un lit fluidisé, soit en pulverisant le réactif en solution [4]. Dans la méthode du lit fluidisé, d'une part la perte de charge est très importante et d'autre part il peut y avoir entraînement de particules constituant le lit fluidisé. Comme dans le cas d'un laveur, les micro-gouttelettes de réactif sont d'autant plus difficiles à capter que leurs dimensions sont plus petites.

Dans l'appareil proposé, un aérosol constitué de particules de quelques microns de réactif obtenu par des méthodes classiques (condensation) est directement injecté après formation à travers une buse portée à un potentiel électrique continu ionisant. Par suite de leurs dimensions, les particules captent aisément les gaz réagissant avec elles. Très fortement chargées, les particules sont captées pratiquement instantanément à l'aide d'une cellule Cottrell suivant immédiatement l'injecteur. Une étude comparable à celle effectuée pour le dépoussiéreur sera publiée prochainement. Le gaz utilisé est de l'anhydride sulfureux et le réactif du carbonate disodique.

Initialement nous avions tenté de pulvériser mécaniquement et électriquement une solution aqueuse de carbonate disodique, mais la formation d'acide sulfurique conduit à un amoncèlage très rapidement.
REFERENCES


DISCUSSION

J. A. GIESEKE: What were the sizes of the drops formed and to what extent were the drops charged?
J. D. JOUBERT: Droplet size depends on several parameters. For any given liquid, the main factors are injection pressure, nozzle size and the strength and sign of the voltage applied. For our operating conditions (injection pressure, 5 kg/cm²; continuous voltage applied, 30 000 V) the distribution curve is found to have two peaks, i.e. the aerosol comprises, in fact, two water droplet aerosols, one consisting of fairly large droplets (a few tenths of a millimetre) and the other of minute particles (a few microns). Unfortunately, we were unable to establish percentage values for these two aerosols and thus the electrical charge acquired by each type of droplet.

I would like to add an important statement. As you may have noted, the yield of the system for various flows is rather low and I have often been criticized for working at such low yields. We used mono-disperse aerosols and tested the apparatus by injecting the aerosol directly into our dust-extractor. For somewhat complicated reasons, we used two dust-extractors in series. The numerical, or mass, yield of the first unit was of the order of 99%; that of the second, identical, extractor was about 30%. A few large particles were sufficient to raise the yield of the first unit from 30 to 99%.

R. E. KRATEL: Did you use pure (demineralized) water or ordinary water?
J. D. JOUBERT: At the beginning of our experiments we used demineralized water, but later – and during the work reported on here – we used ordinary water for financial reasons. We observed no appreciable difference, especially as regards the spray, which – if I remember correctly – conflicts with Zebel's results. This disagreement may be due to the difference in experimental conditions. In Zebel's experiments spraying was purely electrostatic.
TESTING HIGH-EFFICIENCY FILTERS
(Session IV, Part 1)
Chairman  P. J. LINDER
REVIEW OF INSPECTION AND TESTING OF INSTALLED HIGH-EFFICIENCY PARTICULATE AIR FILTERS AT ORNL*

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Abstract

REVIEW OF INSPECTION AND TESTING OF INSTALLED HIGH-EFFICIENCY PARTICULATE AIR FILTERS AT ORNL. High-efficiency filters are indispensable elements in the contamination control programs of most atomic energy installations. These filters, if in good condition, will remove 0.3-μm particles from an air stream with an efficiency of 99.97% minimum. In the United States it is standard procedure to measure the efficiency of new filters by determining the efficiency with which they remove a 0.3-μm particle diameter monodisperse aerosol of DOP from an air stream. This test is used by filter manufacturers and other quality assurance laboratories. The use of pretested high-efficiency filters alone does not ensure that the system in which they are installed will have a comparable efficiency. Experience has clearly demonstrated that systems should be assumed to be inefficient until an in-place test shows the contrary to be true.

Routine in-place testing of high-efficiency filter systems was initiated at Oak Ridge National Laboratory in mid-1962. The in-place test method adopted by the Laboratory is patterned after the standard test used to measure the efficiency of new filter units. The principal difference is that the DOP aerosol used for the in-place test is polydisperse with an average particle diameter slightly larger than 0.3 μm. Though the basic in-place test has remained unchanged, six years of experience has resulted in refinement and standardization of techniques which permit wider application of the in-place test and more economical testing. To facilitate the in-place testing of all ORNL high-efficiency filter systems, as required by Laboratory policy, a computer program was instituted in mid-1965. This program provides automatic advance notification to cognizant management and operating personnel when systems are scheduled for test. Similarly, test results are reported automatically.

The paper discusses (1) the computer program; (2) present practice at ORNL with regard to in-place testing policy, techniques, and equipment, and (3) the effect that six years of in-place testing has had on the overall problem of contamination control.

1. INTRODUCTION

In most atomic energy installations HEPA (High-Efficiency Particulate Air) filters are used in ventilation exhaust or off-gas systems and constitute the primary means of preventing the release of radioactive particulate material to the atmosphere. HEPA filters are also used to provide air, extremely low in particulate material, to work areas, such as clean benches or clean rooms. These filters, if in good condition, will remove 0.3-micron particles from an air stream with a minimum efficiency of 99.97%; however, our experience with filter systems at ORNL and at other sites indicates clearly that systems containing these filters should be assumed to be inefficient unless an in-place test shows otherwise.

Table 1 presents the results of the first in-place efficiency test of 487 different systems. The term "first-

* Operated by Union Carbide Corporation for the US Atomic Energy Commission.
Table 1 Results of the First In Situ Test of 487 Systems Employing High-Efficiency Filters

<table>
<thead>
<tr>
<th>Range of Efficiency (%)</th>
<th>Size Category 1 Systems Containing 1 or 2 Filters per Bank</th>
<th>Size Category 2 Systems Containing 3 or more Filters per Bank</th>
<th>All Systems Size Categories 1 &amp; 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number</td>
<td>Percent</td>
<td>Number</td>
</tr>
<tr>
<td>100.00 - 99.97</td>
<td>335</td>
<td>76.6</td>
<td>15</td>
</tr>
<tr>
<td>99.97 - 99.95</td>
<td>8</td>
<td>1.8</td>
<td>4</td>
</tr>
<tr>
<td>99.95 - 99.90</td>
<td>17</td>
<td>3.9</td>
<td>4</td>
</tr>
<tr>
<td>99.90 - 99.0</td>
<td>30</td>
<td>6.9</td>
<td>20</td>
</tr>
<tr>
<td>99.0 - 95.0</td>
<td>29</td>
<td>6.6</td>
<td>4</td>
</tr>
<tr>
<td>95.0 - 90.0</td>
<td>7</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td>90.0 - 80</td>
<td>4</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>80.0 - 0</td>
<td>7</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>437</td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>
"test" is intended to mean the first in-place test of the particular system and bears no relation to the age of the installation or the length of time the particular filters were in service prior to the test. It is apparent from the data that small systems containing one or two filters give a higher "first-test" efficiency than larger systems. In only a few cases (a fraction of 1%) was low efficiency related to chemical attack of the filters or the function of the system. The significant causes of leakage were:

1. Improper sealing between filter and frame:
   a. loose hold-down clamps,
   b. damaged gaskets,
   c. foreign material between gasket and frame,
   d. rough or warped surfaces on the filter mounting frame,
   e. insufficient number of hold-down devices or devices incorrectly positioned;

2. Defective filter medium:
   a. punctured due to careless handling at time of installation,
   b. sagged due to incorrect installation, that is, pleats horizontal instead of vertical;

3. Defects in filter frame and housing:
   a. unwelded joints at corners and sides of frames,
   b. absence of a frame member between two adjacent filters,
   c. no provisions for clamping filter to frame (the designer apparently believed that the pressure drop across the filter would provide an adequate gasket-seating force).

The minimum acceptable system efficiency at ORNL is 99.95%. As shown in Table 1, approximately 25% of the first 487 systems tested failed to meet this requirement on the "first-test."

As a result of system repair and modification plus improvement in filter handling and installation methods, the failure rate has decreased markedly. Only 7% of the 3145 routine system tests conducted during the last two years yielded results below the Laboratory's minimum efficiency requirements. In most instances it was possible to repair the systems promptly and retest with acceptable results.

2. BACKGROUND

Historically, high-efficiency filter papers were developed during World War II for use in gas masks and for other military purposes. When the paper was first used in gas masks by the Chemical Warfare Service, it was classified and not available for commercial applications. In 1946 the USAEC became interested in the potential uses of such papers and initiated a major development program. In 1950 the
filter medium was declassified. Since then, high-efficiency particulate filters have come to be widely used in both the nuclear and nonnuclear industries. During the early years of commercial availability, quality was taken for granted by users.

Discussions at an air-cleaning seminar at Harvard University in 1957 cast doubt on the presumed uniform high quality of filters being supplied to atomic energy installations. As a result, the AEC in cooperation with the Army Chemical Center at Edgewood Arsenal in Maryland tested random samples from filter stocks of atomic energy plants. The survey disclosed that a significant percentage of the filters were unsatisfactory for several reasons. Subsequently, in 1959, the AEC established two Quality-Assurance Stations to inspect and test high-efficiency filters for participants in the atomic energy program. The testing service is still available and now is also offered to private users by special arrangement at nominal cost. The stations measure filtration efficiency by installing the filter to be tested in a rig and confronting it with a flowing aerosol of di (2-ethylhexyl) phthalate, also called dioctyl-phthalate or DOP. The aerosol is thermally generated from liquid DOP in such a manner that it is essentially monodisperse with a 0.3-micron particle diameter. The concentration of the aerosol is measured, before and after the air is filtered, by a photometric light-scattering technique and efficiency is calculated from the two concentration values.

Oak Ridge National Laboratory has participated in the AEC Quality-Assurance Program since the time of its inception. All filters purchased by the Laboratory are inspected at the Quality-Assurance Station. Although the quality of the filters improved significantly, shipping and handling damage continued to be a problem. Consequently, in 1960 ORNL embarked on an exploratory program to find a suitable method of checking the efficiency of new filters upon receipt and prior to stocking.

As a result of the investigation, the Laboratory adopted a test method similar to the test employed by the AEC Quality-Assurance Stations. A portable air-operated DOP aerosol generator (Figure 1) of the type developed by the Naval Research Laboratory,[1] was substituted for the more expensive (and stationary) thermal generators used by the Quality-Assurance Stations. Photometric light-scattering equipment for measuring the concentration of the aerosol was available commercially.

Fundamentally, the efficiency test, shown schematically in Figure 2, consists of discharging a polydisperse aerosol of DOP into the air intake, measuring with the photometer the concentration of the aerosol in samples removed from the duct before and after the filter, and calculating filtration efficiency from the two concentration values.

It is important to recognize that the Laboratory's testing program was intended to supplement, rather than replace, the testing service offered by the AEC Quality-Assurance Station. The monodisperse aerosol with 0.3-micron particle diameter used by the AEC Quality-Assurance Stations is suitable for establishing the quality of the filter medium as well as for detecting leakage through punctures, tears, and other defects. The polydisperse aerosol produced by the air-
FIG. 1. Air-operated DOP aerosol generator.

FIG. 2. Measuring filtration efficiency with polydisperse DOP aerosol.
operated generators is most useful for determining the effect of leakage paths through which it can pass without undergoing significant alteration in particle size distribution. The quality of papers now being used in the manufacture of HEPA filters is such that performance tests of filter units with the two types of aerosol correlate very well when compared on the basis of total penetration.

As of March, 1961, the Inspection Engineering Department of ORNL checked all new high-efficiency filters prior to stocking; however, this practice was discontinued shortly after the Oak Ridge Gaseous Diffusion Plant became an AEC Quality-Assurance Station in January 1963. Due to the proximity of ORGDP to ORNL, repeating the inspection of individual filters before stocking was no longer warranted. In recent years improvements in filter construction and packaging plus more restrictive shipping specifications have done much to eliminate shipping damage to filters.

The efficiency of a filtration system depends not only on the quality and condition of the filters but also on the integrity of the installation as a whole. It is axiomatic that, to achieve efficient filtration, sound filters must be properly installed in a structurally adequate system and all significant leakage paths must be eliminated. Realizing this, it was easy to see the need for a practical test which could be applied to measure the overall efficiency of a system with the operational pretested filters in-place.

The test used by ORNL for measuring the efficiency of individual new filters was studied as a possible means of meeting this need. It was found that the method could easily be adapted to in-place testing and that any system, regardless of size, could be tested in situ by manifolding a sufficient number of the air-operated aerosol generators to produce an adequate upstream concentration.

The aerosol is introduced into the system sufficiently ahead of the filters to assure that it is thoroughly mixed with the air stream before reaching the filters. The aerosol concentration in representative samples of the unfiltered and the filtered air is then measured as shown in Figure 2. The system filtration efficiency may be calculated by

$$E = 100 - 100 \frac{DS}{US}$$

where

- $E =$ efficiency of the system as a percentage,
- $US =$ concentration of the aerosol in the unfiltered air,
- $DS =$ concentration of the aerosol in the filtered air.

In-place testing was begun on a limited scale at ORNL in 1961 and by mid-1962 had become routine. In November 1962 the requirement that all systems containing high-efficiency filters be subjected to periodic in-place tests became a part of the ORNL radiation-safety policy.
3. PRESENT PRACTICE AT ORNL

3.1 General

Although the basic in-place filter test which became routine at ORNL in 1962 has remained unchanged, six years of testing has resulted in several significant developments. A formal policy statement detailing responsibility and requirements for filter systems has been issued within the Laboratory. Testing techniques and equipment have been refined and standardized, permitting wider application of the in-place test and more economical testing. The scheduling of filter tests and the reporting of test results have been placed on a computer program.

3.2 ORNL Filter-Testing Policy

A clear comprehensive statement of policy from responsible management is an invaluable and essential part of an effective filter-testing program. The ORNL policy was first issued as a memorandum from the Safety and Radiation Control Department in November 1962 and later formalized in an Official Laboratory Bulletin. The policy provisions pertinent to this discussion may be summarized as follows:

Research and Operating Divisions are responsible for employing and maintaining ventilation and air-cleaning systems in compliance with Laboratory requirements for potentially hazardous facilities. They are also responsible for requesting inspection and DOP testing of high-efficiency filter systems.

The Inspection Engineering Department is responsible for conducting periodic inspections and in situ tests of high-efficiency filter systems upon request of the divisions. Any system with an efficiency less than 99.95% is unsatisfactory, and steps must be taken to attain the minimum efficiency, or cause must be shown why a less-efficient system should be accepted.

Frequency of testing will to some degree depend on the system, process, and operating hazard involved; however, as a minimum, testing is required:

1. after each filter change,
2. annually for normal systems and semiannually where corrosive materials are involved, and
3. when the integrity of a system is suspected.

The Inspection Engineering Department must be notified in advance of new filter installations as well as filter changes and is required to witness the installation of the filters. Filter systems must be tested as soon thereafter as possible; new systems must be tested and approved prior to service startup. The results of all tests must be reported in writing to the requester, to the Health Division, and to the Safety and Control Department. The responsibility of having unacceptable systems satisfactorily repaired rests with the division or building manager concerned. The Health
Division and the Safety and Radiation Control Department are responsible for auditing conformance to Laboratory standards. ONRL purchase specifications require new HEPA filter units to be 99.97% efficient in removing 0.3-micron particles from an air stream. Since filters which permit penetration of as much as 0.03% of the test aerosol are acceptable, it seems reasonable to permit a small amount of additional penetration in systems to provide for the condition where a barely acceptable filter is installed in a less-than-perfect housing. In making allowances for this condition, it was also necessary to evaluate potentially hazardous systems and to select a minimum acceptable efficiency which provides the required degree of safety. Accordingly, 99.95% was specified as the minimum acceptable efficiency for systems containing HEPA filters at ORNL. More stringent requirements are applied in special cases when the need is demonstrated by a hazards review. The minimum efficiency value and all other provisions of the Laboratory policy were adopted to meet the needs of the Laboratory, and no additional significance is inferred.

3.3 Computer Program

More than 1400 in-place tests are required annually to test the approximately 750 ORNL high-efficiency filter systems in accordance with the plant policy.

To facilitate the in-place testing of all high-efficiency filter systems, a computer program was prepared and put into effect. The reasons for instituting the program were to

1. to balance the testing work load from month to month,
2. provide automatic advance notification to cognizant divisions and individuals when systems are due to be tested,
3. provide automatic reporting of test results to cognizant divisions and individuals, and
4. permit better surveillance of all systems containing high-efficiency filters.

As an added benefit, the computer program resulted in a substantial reduction in the amount of administrative and clerical time required for reporting test results.

Early in each month, the computer furnishes two reports: one lists the systems scheduled for testing during the following month, while the other lists all systems tested the previous month, giving the dates of the tests and the results. Systems not meeting minimum efficiency requirements or otherwise failing to comply with Laboratory policy are identified on the results report. Also identified are systems tested off-schedule and those in which new filters were installed during the month.

Each quarter a separate report is issued listing all systems which failed to comply with Laboratory policy during the quarter.

Figure 3a shows a facsimile of the cover sheet which accompanies each report, and Figure 3b shows a page from a fictitious test-results report. Except for appropriate
changes in titles and the omission of "Date of Test" and "Test Results" columns in the case of the schedule report, all of the computer reports have the same format.

Test results and other information needed to compile reports are entered on form cards which are then sent to the computer facility, where the cards are key punched and used for computer input. All computer reports are reproduced and given wide distribution within the Laboratory as indicated on the report cover sheet shown in Figure 3a.

A moment's reflection will show that the assignment of responsibility provided for by Laboratory policy, the impersonal method of reporting tests, and the wide distribution of reports can aid materially in achieving filter-testing-program objectives.

3.4 Equipment

The basic equipment required for measuring the efficiency of filter systems consists of (1) generators for producing an aerosol of DOP, (2) photometric equipment for measuring the concentration of the aerosol before and after the filters, (3) a small pump for removing samples from the duct for concentration measurements, and (4) miscellaneous items such as DOP, pressure regulators, sources of compressed air and electric power, sample tubing, fittings, etc. Figure 4 shows a convenient portable arrangement of equipment used for field testing.
### Test Results for ORNL High-Efficiency Particulate Filter Systems Tested During June, 1968

<table>
<thead>
<tr>
<th>System Code/Div.</th>
<th>Building No.</th>
<th>System</th>
<th>Number of Filters</th>
<th>Flow Per Test</th>
<th>Efficiency</th>
<th>Minimum Acceptable Efficiency (Percent)</th>
<th>Date of Test</th>
<th>Test Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1513</td>
<td>CH</td>
<td>W500N</td>
<td>Hood Exhaust, RM.</td>
<td>2</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1514</td>
<td>CH</td>
<td>W500N</td>
<td>Hood Exhaust, RM.</td>
<td>2</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
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<td>CH</td>
<td>W500N</td>
<td>Hood Exhaust, RM.</td>
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<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1601</td>
<td>CH</td>
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<td>Hood Exhaust, RM.</td>
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<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
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<td>W500S</td>
<td>Hood Exhaust, RM.</td>
<td>1</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1603</td>
<td>CH</td>
<td>W500S</td>
<td>Hood Exhaust, RM.</td>
<td>1</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1701</td>
<td>CH</td>
<td>W500S</td>
<td>Hood Exhaust, RM.</td>
<td>2</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1702</td>
<td>CH</td>
<td>W500S</td>
<td>Hood Exhaust, RM.</td>
<td>2</td>
<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
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<td>1707</td>
<td>CH</td>
<td>W500S</td>
<td>Hood Exhaust, RM.</td>
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<td>1000</td>
<td>S</td>
<td></td>
<td>99.95</td>
</tr>
<tr>
<td>1801</td>
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<td>3074</td>
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<td>M</td>
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<td>1000</td>
<td>A</td>
<td></td>
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</tr>
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</table>

FIG. 3b. Sample computer report of filter test results.
The specific kinds and types of the major items used in the ORNL filter testing program have been used without substitution for several years. Initially the selection of these items was based on expediency, availability, and limited investigation of available options; however, the equipment now being used does perform well in the ORNL applications and for that reason will be described in detail in the following discussion.

DOP aerosol generators are commercially available; however, those used at ORNL are of the type developed by the Naval Research Laboratory and were fabricated at relatively low cost in ORNL shops.

A task group under Subcommittee N5.2 of the American Standards Association, now the United States of America Standards Institute (USASI), has prepared and proposed as an American standard a document covering in-place testing of air-cleaning systems. The proposed standard is now undergoing the balloting procedure. The provisions of this document are of interest since they may eventually be cited as requirements by regulatory agencies.

The proposed standard describes an aerosol suitable for in-place filter testing as follows:

"The aerosol for the in-place test shall be generated from liquid dioctyl-phthalate by any method which produces a stable aerosol with the proper reproducible particle-size distribution. The aerosol shall have an average number particle diameter of the order of 0.5 micron. Number-wise, the aerosol shall have 95 percent of the particles less than 1.0 micron diameter. Size determination shall be accomplished by use of
FIG. 5. Small air-operated DOP aerosol generator (one or two nozzles).
a light-scattering impactor technique \cite{1,3,4} and calculated assuming a log-normal distribution by using the standard logarithmic probability plot\cite{5}.

The test aerosol described in the report of the development of the NRL-type generator\cite{1} meets the criteria of this description.

The aerosol generators can be sized to meet the user's needs. At ORNL generators similar to the one shown in

Figure 1 have been built with as many as 12 nozzles. Figure 5 shows a small generator which has proved extremely useful in the Laboratory's testing program. Nozzles of the type shown in the detail view of Figure 5 are used in all ORNL generators.

The instrument used at ORNL for measuring the concentration of DOP aerosol is a "Percent Penetration Meter" which was developed by the Naval Research Laboratory\cite{6}. The NRL instrument is of the photometric light-scattering type and consists of (1) light-scattering chamber, (2) light source, (3) optical systems, (4) photomultiplier, and (5) indicator with display meter as shown schematically in Figure 6. Instruments of this type are sometimes referred to as "photometers" or "forward-light-scattering photometers."

Aerosol samples are passed through the light-scattering chamber and the light scattered forward by particles within the "working" region of the chamber is detected by the photomultiplier tube. The output of the photomultiplier is displayed on a meter. The instrument reading is linearly proportional to changes of concentration.* The linear response of the instrument was established by dilution tests.\cite{2}

*The proposed American Standard, mentioned earlier, requires the use of an instrument having linear response and provides that testing agencies may be required to demonstrate the linearity of their instruments.
Other functional features of the photometer used in the ORNL filter-testing program are described in the following discussion.

It is possible, through the use of a direct-light aperture, which may be covered when not in use, to adjust the instrument to a predetermined sensitivity and thus read aerosol concentration in units of reproducible, albeit arbitrary, size. This feature is useful in testing filter systems when the upstream and downstream sample points are not accessible from the same location, making it necessary to disconnect the instrument between readings. For most tests, however, the use of this feature is optional. The efficiency of systems may be calculated knowing only the relative concentrations of the aerosol in the two samples (see equation in section 2), making it unnecessary to adjust the instrument to any particular sensitivity.

The sensitivity is adjustable over a wide range with no loss of linearity. As a basis for comparing sensitivities one may use the "100% smoke" of the AEC Quality-Assurance Stations. The DOP concentration in this aerosol is approximately 100 micrograms per liter. An NRL instrument which reads full scale (100%) when sampling this aerosol is said to be adjusted to a gain of one. The instruments used at ORNL can be operated at gain or sensitivity settings of four or more.

The ability to operate an instrument at high sensitivity is important in an in-place testing program since it permits the use of lower upstream aerosol concentrations. The result is that, for a given test, less aerosol generating capacity is required, there is less equipment to be moved to the test site, less compressed air is required, and testing costs are correspondingly reduced.

With use, instrument sensitivity gradually drops because the dust and other foreign materials which collect in the sample chamber cause an increase in the stray light reaching the photomultiplier. The increased stray-light signal can be balanced out electrically, but the maximum possible gain setting is simultaneously reduced. The instrument can be restored to full sensitivity by simply cleaning the sample chamber and reblackening its interior surfaces with flat black lacquer and a coating of camphor smoke to reduce reflectivity.

The instrument has three scales, 0-100, 0-1, and 0-0.1. Changing from one scale to another is accomplished by turning a rotary switch; no intermediate adjustment or calibration is required. The scale factor of 1000 between the most sensitive and least sensitive scales plus one intermediate scale makes possible the measurement of filtration efficiency over the entire range with adequate precision.

Maintenance on the instrument, except for cleaning the sample chamber, has been infrequent. It withstands field use well, and when maintenance is required, shelf items may be used for repairs. Mechanical alignment of photometer parts is simple and relatively noncritical.

The instrument has exhibited stable operating characteristics over a sample flow range of 1 to 30 liters per minute. To avoid sample chamber pressure variations, which do affect readings, sample probes should be 3/8-in. outside diameter tubing, and connecting tubing should be 5/16-in. inside diameter gum rubber, preferably no more than 50 ft in length.
The use of valves and threaded or other mechanical connectors in sampling lines ahead of the photometer should be avoided because of their tendency to leak.

In selecting a photometer for in-place DOP testing, the important considerations from the standpoint of performance are: (1) stability, (2) linearity, and (3) sensitivity. On these points the purchaser's requirements should be reflected in his purchase specifications. Sampling pumps should be sized to avoid unnecessary delay in instrument response to changes in aerosol concentration when using sample lines of maximum length. Those used at ORNL have a pumping capacity of approximately one cubic foot per minute.

3.5 Testing Techniques

When the overall filtration efficiency of a system is to be measured by the basic in-place test described in Sect. 2, the samples of the filtered and unfiltered aerosol must be representative of the aerosol in the system duct. It is sometimes necessary to induce mixing artificially by means of baffles, fans, or other devices so that the samples are representative. Frequently, a representative downstream sample can be withdrawn after the system fan as shown in

FIG. 7. Filter system requiring injection of DOP aerosol at two locations.
Figure 2. A less desirable but acceptable method for determining downstream aerosol concentration is a multiple sampling and averaging technique. When this technique is used, the number of samples taken and the sampling pattern selected should assure accuracy within the required limits. There is no satisfactory substitute for adequately mixing the aerosol with the upstream air before it reaches the filters. Unless good mixing does occur, some portions of the system will be exposed to a less rigorous test than others. When in doubt, the adequacy of the mixing should be established by multiple sampling. At ORNL the mixing is considered inadequate if the concentration of any sample varies more than $\pm 5\%$ from the arithmetic mean concentration.

At times it may be necessary to close side streams or to introduce balanced concentrations of aerosol at more than one location to assure confronting the filter bank with a uniform mixture. Figure 7 illustrates a system of this kind. Note that the upstream ducts are sampled separately. The aerosol concentrations in the two ducts are made equal by adjusting the pressure of the compressed air supplied to the generators.

Shielding or other factors may limit access to suitable aerosol injection or sampling locations. Figure 8 illustrates one method of circumventing these limitations. At times
it has proved practical to pass sample lines through the filter mounting frames, being careful to avoid creating leakage paths, and route them inside the duct to suitable locations.

To prepare for testing some systems, such as those serving as exhaust filters for cells containing materials having high-level alpha activity, it is convenient to permanently install in a suitable location a small aerosol generator similar to the one shown in Figure 5. When it is desirable to generate aerosol for filter tests it is only necessary to turn on the compressed air supply to the generator. The generator's DOP supply can be replenished when necessary by forcing the appropriate amount of the liquid through the compressed air supply line under pressure. Such schemes as these are most easily incorporated into systems at the time of construction.

Testing techniques should be selected which will assess the ability of the systems to fulfill their functions. For example, it is the function of the make-up air system shown in Figure 9a to supply filtered air to the cell beyond the

FIG. 9. Total leakage test. (a) filter system having several potential leakage paths: (1) defective filter, (2) gasket seal, (3) unwelded frame joints, (4) bolted flanges, (5) valve shaft seal, and (6) instrument line connections. (b) system rigged for DOP test which will measure overall filtration efficiency.
wall. Aside from the possibility of a faulty filter or gasket seal, there are several other potential leakage paths: (1) unwelded joints in the plenum, (2) bolted flange connections, (3) valve-shaft sealing gland, and (4) instrument line connections. Figure 9b shows the same system suitably rigged for a DOP test which will measure the overall filtration efficiency. The entire column under the temporary shroud is flooded with DOP aerosol which will penetrate any continuous leakage paths which compromise system integrity.

When leakage paths do exist, they can usually be located by inspection. In some cases, however, it is necessary to use a probing technique. The upstream side of the filter bank is exposed to DOP aerosol in the usual manner, or smaller areas may be exposed selectively. In either case a sample probe is passed over the suspected areas, as shown in Figure 10, to detect leakage paths. An extension meter is helpful in walk-in systems since it eliminates the need for frequent communication with persons on the outside. The probing test is a very sensitive one since it samples the aerosol which passes through leakage paths before it is substantially diluted. Leakage paths which have no significant
FIG. 11. Portable exhaust fan used to establish flow in system during DOP test when use of system fan is impractical.

Effect on overall system efficiency can be detected, and it is usually not necessary to eliminate all leakage detected by this method: to attempt to do so could be time consuming and costly. However, in systems serving clean benches and other critical areas, the effort may be justified.

FIG. 12. "Total leakage DOP test for face-mask particulate filter canister."
When it is impractical to use the system exhaust fan during DOP tests, it is sometimes possible to use a portable fan to establish an air flow in the system (see Figure 11). It should be recognized that the filtration efficiency may vary when the flow rate is changed. One reason for this is the "pinhole effect,"[2,7] which results in relatively higher penetrations at reduced flow. The reduced flow also results in lower differential pressure across the filters, which could tend to either improve or adversely affect the gasket seals, depending on the method used for fastening the filters in place.

A disposable sample chamber for the NRL photometer was developed at ORNL.[8] The use of this device (see Figure 4) helps to avoid costly instrument decontamination after testing contaminated systems.

Particulate canister filters for masks and respirators can be tested by the DOP aerosol method. A total-leakage test method which evaluates the unit's ability to seal in the mask or respirator facepiece is best. For such a test, the entire canister and test fixture should be immersed in the DOP aerosol mixture as shown in Figure 12.

4. LONG-RANGE EFFECTS OF IN-PLACE TESTING

Testing filters in-place has brought about numerous changes by focusing attention on system shortcomings. The repair and improvement of operating systems began almost immediately after testing was begun at ORNL in 1961. Design deficiencies became apparent, and designers were called upon to devise modifications to improve system efficiencies. Predictably, system designs improved greatly. Now newly constructed systems at ORNL almost invariably meet efficiency requirements without difficulty. Testing new systems has been made easier by including in their design the features which facilitate DOP testing, namely aerosol-introduction ports, sample ports, and provisions for producing good mixing of aerosol with the air stream.

In many cases review of the filtration requirements of facilities occasioned by DOP testing results has revealed that high-efficiency filters were not needed. Complete removal of filters or replacement of HEPA filters with units of lesser efficiency has resulted in savings in maintenance and testing costs. Approximately 140 ORNL air-handling systems, mostly laboratory fume hoods, room exhaust systems, and inlet air systems, are in this category.

Since 1962 the practice of testing filter systems with DOP aerosol has spread. The test has the tacit approval of the USAEC. The Division of Licensing and Regulation has included in-place testing as part of the prelicensing requirements for reactors, and the Division of Operational Safety has sponsored eight filter-testing workshops to teach the test method to representatives of numerous installations. At the request of the AEC, ORNL has assisted a number of other installations in developing their own testing capability. A variety of documents on in-place testing and related subjects is available in AEC Air Cleaning Conference Proceedings and in experience reports from nuclear installations. A proposed American standard covering in-place testing has been prepared and is undergoing the balloting procedure (see Sect. 3).
A manual sponsored by the AEC and tentatively titled "Design and Construction of High-Efficiency Filter Systems for Nuclear Applications" is being prepared by ORNL Air Handling Design Department and Specifications and Standards Department personnel.

5. CONCLUSION

The use of sound filters alone does not assure that systems in which the filters are installed will be adequate. There is no suitable substitute for a conscientiously applied in-place testing program. Experience at ORNL indicates that such a program has been, and continues to be, a powerful tool in the overall problem of contamination control.

REFERENCES


DISCUSSION

C. PELLETIER: How was the efficiency of 99.95% arrived at?

E. C. PARRISH: The selection of this number was somewhat arbitrary. Since, under our purchase specifications, filters which permit penetration of as much as 0.03% of the test aerosol are acceptable, it seemed reasonable to permit a small amount of additional penetration in systems, to provide
for the condition where a barely acceptable filter is installed in a less-than-perfect housing. It was also necessary to select a minimum efficiency requirement which would provide the required degree of safety. The value 99.95% seemed to meet both requirements.

D. W. BALLARD: Do you use isokinetic sampling for in-place scanning of filter banks and do you include in your testing program air velocity surveys of filters to be used in clean-room or clean-bench installations?

E. C. PARRISH: We do not use isokinetic sampling for our polydisperse DOP test. We have found it is not necessary, since isokinetic sampling and non-isokinetic sampling yield essentially identical results.

We do not make clean-bench tests at ORNL.

R. I. NEWMAN: You state that if a test shows a filter to have an efficiency of less than 99.95%, steps must be taken to attain the minimum efficiency, or cause must be shown why a less efficient system should be accepted. Could you give us some typical examples of conditions which would warrant continued operation with an inefficient filter system?

Is this on a case-by-case basis, or do you possess technical specifications setting forth the basis for departure from standard operating practice?

E. C. PARRISH: There have been no officially authorized relaxations of the efficiency requirements at ORNL to date. However, minimum acceptable efficiency requirements would be based on the total amount of contaminant involved, its concentration, and the allowable release rate. Such cases would be handled on an individual basis.

J. A. GIESEKE: Since particle size can have a pronounced effect on filtration efficiency, what was the mean droplet size formed by the atomizer and what was the distribution of sizes around this mean?

E. C. PARRISH: In Ref. [1] of the paper the aerosol produced by the improved Laskin nozzle is described as having an average particle diameter of approximately 0.7 microns. However, a more recent description of the aerosol, supplied by Dr. Young of the Naval Research Laboratory, is as follows: "The aerosol has an average number particle diameter of the order of 0.35 microns with a maximum standard geometric deviation (σ_g) of 1.5. Numberwise, 95% of the particles are less than 0.7 microns in diameter."

W. L. FAITH: Was the test that showed isokinetic sampling to be unnecessary performed with the mono-disperse aerosol or the poly-disperse aerosol?

E. C. PARRISH: It was done with the poly-disperse aerosol.

J. D. JOUBERT: Are the figures for average aerosol ranges numerical or mass values? They appear to be mass values. If so, do you plan to obtain numerical values later?

E. C. PARRISH: The Naval Research Laboratory's description of the aerosol indicates that the value given is the numerical average. We do not plan any further investigation of the particle size distribution of this aerosol, since we use it principally to detect leakage paths by which it escapes without undergoing significant alteration.
EFFICIENCY TESTING OF THE AIR CLEANING SYSTEM FOR A HIGH TEMPERATURE REACTOR*

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Abstract

EFFICIENCY TESTING OF THE AIR CLEANING SYSTEM FOR A HIGH TEMPERATURE REACTOR. The Los Alamos Ultra High Temperature Reactor Experiment (UHTREX) utilizes a helium-cooled, graphite-moderated reactor, employing refractory fuel elements. Under accident conditions, the effluent that may be released from this reactor requires an air-cleaning system capable of reducing radioactive gas and particulate contaminants to safe levels. Dioctyl phthalate and iodine-131 were used as test aerosols for the HEPA and activated carbon filters, respectively. Methods of aerosol generation and test procedures are detailed for the pre-installation tests of the carbon and in-place testing of the carbon and HEPA filters. The importance of visual inspection of the HEPA filters prior to installation and supervision of filter installation is discussed.

In-place tests indicated desirable design changes which would (1) simplify in-place testing procedures, (2) expedite installation and future changing of the filter, and (3) ensure operation of a more efficient system. Problems encountered during in-place testing, recommendations for the design of similar systems, and acceptance criteria used at LASL are discussed.

I. INTRODUCTION

The Los Alamos Ultra High Temperature Reactor Experiment (UHTREX) is a graphite moderated, helium cooled reactor, designed to operate at very high fuel and exit coolant temperatures. The reactor is to be operated at a thermal power of 3 MW with a coolant temperature of 2400°F. It is designed exclusively for experimental use and to operate for a minimum of three years at maximum design conditions.

Under accident conditions, the effluent that may be released from this reactor requires air cleaning systems capable of reducing radioactive gas and particulate contaminants to safe levels. High Efficiency Particulate Aerosol (HEPA) filters, meeting the requirements of the U.S. Atomic Energy Commission (USAEC), will adequately reduce particulate contaminants to the desired levels. These filters are designed for a minimum collection efficiency of 99.97% when tested with a 0.3-μm dioctyl phthalate (DOP) monodisperse aerosol. Activated carbon filters were selected to remove radioiodine and other radioactive gases that may be present. These filters are the Barnebey-Cheney type 7-FE-A, which are designed and constructed to satisfy specifications outlined in Report DP-778.

The principal structure at the UHTREX complex is the reactor building which includes a gastight secondary containment enclosing the...
reactor vessel, primary reactor coolant system, and other related systems. This building also houses auxiliary equipment, fuel handling systems, utility systems, a control room, staff offices, and minor maintenance laboratories. Four independent exhaust ventilation systems provide appropriate air cleaning for potentially contaminated spaces. These four ventilation systems serve the following areas: (1) secondary containment structure, (2) fuel handling and hot cells, (3) cell operating areas, and (4) change rooms and other areas that might become contaminated during normal operations (Warm Areas). Figure 1 is a simplified schematic drawing of the exhaust ventilation systems.

Ventilation of the secondary containment during normal reactor operations is achieved by either of two parallel in-line blowers which recirculate air through this system. Within the secondary containment, air moves from the regions that are less likely to be contaminated to regions where contamination is more likely, then passes through particulate and carbon filters prior to recirculation. The flow rate provides 15 air changes per hour in the regions where fission products might be released.

The secondary containment exhaust filters are likely to become contaminated should any leaks develop in the reactor coolant systems. Therefore, they are located in a separate shielded pit outside the reactor building. This system is isolated during reactor runs. The filter pit, without the filters in place, is shown in Fig. 2. During normal operation, 9700 cfm of air enters the side of the filter pit, passes downward through a bank of nine HEPA filters, then through a bank of nine activated carbon filters, finally leaving the filter pit through a duct at the bottom. The 18 individual filters are bolted to a removable steel basket which is supported horizontally inside the filter chamber by an integral perimeter flange made of 5 in. channel iron. Figures 3 and 4 show the basket with filters being installed and the basket in the pit. Bypassing of air around the filter basket is prevented by a seal made by the perimeter flange of the basket resting on a gasketed ledge inside the pit. The entire weight of the basket and filters is borne on this gasket, creating a very effective seal. The individual filter gaskets are
FIG. 2. Filter pit.

FIG. 3. Filter pit basket.
compressed against the rigid, smooth frames of the basket and maintained in this compressed state by bolts and flanges (Fig. 3).

In the remaining reactor building ventilation systems, air is not recirculated except for a cooled air supply for the electronic racks in the control room. All supply air passes through preheat coils and roughing and Aerosolve filters. Exhaust air that might be contaminated is passed through HEPA and activated carbon filters and exhausted to a 100 ft stack. Throughout the facility, air moves from areas that are clean toward those areas that might become contaminated.

A second exhaust filter system, serving those areas that may become slightly contaminated (Warm Areas), consists of 20 HEPA filters held in place with the activated carbon filters on a common framework. The upstream HEPA side of this bank is shown in Fig. 5. Problems with this design are discussed later.

A third filter system serves two hot cells, the fuel transfer lock, and the fuel handling cell. Air is exhausted through single HEPA and carbon filters housed in Model C-1, SGN Caisson Units.15
A fourth filter system functions only when the door between the cell operating area and the cells is open. This exhausts through four HEPA filters backed by activated carbon filters and to the stack. When the cell door is not open, exhaust air from the cell operating area passes through the previously described exhaust system serving the Warm Areas.

II. PREINSTALLATION TESTING AND ACCEPTANCE CRITERIA

A. HEPA Filters

All HEPA Filters installed in the UHTREX facility are quality-control tested [6] at Richland, Washington, prior to their shipment to the Los Alamos Scientific Laboratory (LASL). These tests utilize a thermally generated, 0.3 μm monodisperse, DOP aerosol. The minimum acceptable efficiency is 99.97% as measured, using a forward light-scattering photometer and sampling aerosol concentrations upstream and downstream from the test filter. Because a monodisperse aerosol is used, the measurement represents efficiency on either mass or count bases. However, these quality control tests do not ensure that the filters will have the same integrity on reaching their final destination, be-
cause of damage that may occur in transit. For this reason, it is necessary to visually inspect each filter at our receiving warehouse and again immediately prior to installation.

Close supervision of workmen during installation of the filters is necessary to ensure proper mating of the sealing surfaces, adequate compression of the gaskets, and correct filter orientation in the airflow. It also minimizes the possibility of installing a filter into the framework that may be damaged during this final handling phase.

These visual inspections and the supervision during installation have greatly reduced the number of HEPA systems that are unacceptable during their first in-place tests. This, in turn, has greatly reduced the man-hours spent in removing and reinstalling filters and retesting the system.

B. Activated Carbon Filters

The activated carbon filters used in the UHTREX air cleaning system are manufactured by the Barnebey-Cheney Company according to specifications developed at the Savannah River Plant. Each filter contains ~50 lbs of 8-14 mesh, activated coconut shell carbon, with a minimum packing density of 35.0 lbs/ft$^3$. Each filter weighs ~150 lbs. The carbon is held in a pleated configuration, fixing the carbon bed depth at 1 in., and includes baffle plates which minimize settling of the carbon granules. Each filter was visually inspected at LASL to check its structural integrity and gasket condition, then individually tested using iodine-131 as the tracer gas. Similar procedures for testing activated carbon filters have been employed at other facilities.

This test method was selected in preference to using one of the Freon compounds for several reasons: (1) it tests the carbon filter with the contaminant of primary concern during a postulated accident; (2) there are no limitations relative to test velocity, relative humidity, or duration of the test period; and (3) specialized equipment is not required for generating the tracer gas, collecting air samples, and determining concentrations of the tracer in the system being tested.

Sodium iodide-131 is commercially available at a nominal cost and was purchased in 10 to 25 mCi quantities for our test program. Because of its 8-day half-life, it is necessary to prepare for immediate use of the material on receipt from the vendor. Precautions must be observed to prevent contamination of test areas and personnel. Routine radiochemistry procedures sufficed for the quantities involved in our test program. There were no contamination problems.

Figure 6 shows the test system, iodine generator, and upstream air sampler used in quality-control testing.

Elemental iodine-131 was generated by adding 6N sulfuric acid to a solution of sodium nitrite, sodium iodide-131, and nonradioactive sodium iodide (carrier). The solution was heated to accelerate iodine ger-
eration. A Stairmand disc, located in the duct, assured complete mixing of iodine-131 in the airstream. Air samples were obtained using high efficiency glass filter papers followed by an activated charcoal respirator cartridge sampling upstream and downstream from the carbon filter. All samples were gamma counted using a 200-channel gamma analyzer and the 0.36-MeV photopeak used to indicate iodine activity. The ratio of iodine activity on the downstream sampling charcoal cartridge to that on the upstream sampling charcoal cartridge indicated iodine-131 penetration through the carbon filter. Iodine-131 collected on the glass filter paper was assumed to be attached to particulates, and was not used in calculating penetration through the carbon filters. By testing all filters at a flow rate of 540 cfm, and using a minimum 0.5 mCi of iodine-131 in the iodine generator, penetration in excess of 0.01% could be determined. Because of the relatively low activity levels on the downstream samples, counting times of 10 min were necessary to ensure a counting error of <3%.

Forty-four charcoal filters were tested prior to their installation at UHTREX. Filter efficiencies (1-penetration) are summarized in Table I. These results indicate the level of iodine removal that can be expected from filters of this type. All but three had efficiencies in excess of 99.98%, and these three indicated efficiencies >99.96%.

The iodine-131 remaining on the carbon filters tested, presented a minor radiation hazard. After testing, the carbon filters were replaced in their original cartons for temporary storage. At this time, radiation levels of 10 mR/hr could be measured on the outside of each carton.
Supervision during installation of the carbon filters is important. Although filter damage is unlikely, special consideration due to the weight of the filter is necessary to insure proper gasket compression and sealing.

### III. IN-PLACE TESTING

#### A. HEPA Filters

The acceptance criterion for exhaust systems containing HEPA filters at LASL is a minimum efficiency of 99.95% (0.05% penetration) when tested with an air-generated, polydisperse, DOP aerosol. In establishing this criterion, consideration was given to the specifications required by the USAEC for individual HEPA filters when tested with a thermally generated, 0.3 μm monodisperse aerosol. An experimental program was carried out at LASL to compare the efficiency of HEPA filters when tested with these two different aerosols. Results indicated that filter penetration is ~10% greater when using the 0.3 μm monodisperse aerosol.

The aerosol generator for in-place testing is a modification of a design by the Naval Research Laboratory. It is a high capacity, air-operated generator that produces a polydisperse liquid aerosol by atomization of the DOP liquid using compressed air. Figure 7 shows this generator disassembled. When the generator is operated at 25 psi air pressure within the nozzles, the aerosol has a count median diameter of 0.8 μm and a geometric standard deviation of 1.6.

The aerosol detection equipment consists of a forward light-scattering photometer and amplifier combination, and is shown in Fig. 8. An air sample is drawn into the sensing chamber of the photometer, and relative concentrations of DOP upstream and downstream from the filter bank are measured.

The DOP aerosol is injected into the airstream at a point far enough upstream of the filter bank to ensure complete and thorough
FIG. 7. DOP aerosol generator.

FIG. 8.
Light-scattering photometer.
mixing. The concentration (A) of the aerosol upstream of the filter is then determined by passing a sample of this air through the aerosol photometer. The concentration (B) downstream is similarly determined. The efficiency of the system is then indicated by \(1 - \frac{A}{B}\) \(\times 100\). The four systems tested at the UHTREX facility demonstrated the efficiencies noted in Table II.

**TABLE II**

**IN-PLACE HEPA FILTER EFFICIENCIES**

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<thead>
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<th>Exhaust System</th>
<th>Efficiency (%)</th>
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<td>Secondary Containment (Pit)</td>
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<tr>
<td>Warm Areas</td>
<td>99.7</td>
</tr>
<tr>
<td>Fuel Handling and Hot Cells</td>
<td>99.97</td>
</tr>
<tr>
<td>Cell Operating Area</td>
<td>99.97</td>
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</tbody>
</table>

**B. Activated Carbon Filters**

The acceptance criterion for in-place testing the activated carbon filters was set at 99.9% efficiency, and is consistent with previous work reported in the literature. The test procedure permitted measurement of penetrations in excess of 0.1%. This quantity of radioiodine did not pose any special problems relative to handling radioactive materials. Some temporary radiation shielding was required while testing the large filter bank where 25 mCi of iodine-131 was used.

The carbon filters were tested in-place after installation using iodine-131 and following the same techniques and procedures previously outlined in the individual preinstallation testing. The only deviation involved the necessity of generating a greater amount of iodine into the air stream because of the increased volume of air within the system. Results of these tests are summarized in Table III.

**TABLE III**

**IN-PLACE ACTIVATED CARBON FILTER EFFICIENCIES**

<table>
<thead>
<tr>
<th>Exhaust System</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary Containment (Pit)</td>
<td>99.9</td>
</tr>
<tr>
<td>Warm Areas</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Fuel Handling and Hot Cells</td>
<td>&gt; 99.9</td>
</tr>
<tr>
<td>Cell Operating Area</td>
<td>&gt; 99.9</td>
</tr>
</tbody>
</table>
IV. DISCUSSION

Several problems were encountered during in-place testing of these systems. Due to its unusual design, the secondary containment exhaust does not permit probing the downstream side of the filters to detect inadequate gasket seals, damaged filter media, or both. The importance of visual inspection and close supervision during installation into this system is obvious. Initial testing of this system showed some minor leakage (HEPA filter efficiency 99.92%; carbon filter efficiency 99.8%). This necessitated opening the filter pit and removing the framework containing both sets of filters. Fortunately, visual inspection showed that the framework was not centered on the sealing gasket, and when this was corrected the system met specified requirement.

As can be seen in Table II, System No. 2 did not meet the usual criterion for HEPA filters. Because of the carbon filters, the downstream side of this bank could not be thoroughly probed. Repeated corrective measures, such as replacement of apparently defective filters and gasketing modifications, did not bring the system up to an efficiency of 99.95%. However, on reviewing the areas served, and in view of the extremely low potential of radioactive particulates that may be present within these areas, an efficiency of 99.7% was considered to be adequate.

This same system proved to be a major problem in several other respects. Because the HEPA and carbon filters were mounted on a common framework, it was impossible to inspect the downstream side of the HEPA filters or the upstream side of the carbon filters after complete installation. Because of the weight of the carbon filters, we were primarily concerned about obtaining adequate compression of the gaskets on these filters. Therefore, these were installed first to permit visual observation of the upstream side during installation. We then relied on close supervision during installation of the HEPA filters to minimize the possibility of damaging the filter media. The system provided minimal space upstream of the HEPA filters and downstream of the carbon filters. Although the available space was nominally adequate for handling and installation, it did not take into account the fragile nature of the HEPA filters and the difficulty in handling a 150-lb carbon filter.

One disadvantage in testing the carbon filters with iodine-131 is the inability to easily probe the downstream surface while generating the tracer gas. An indication of gross leakage can be measured by monitoring the downstream side of the carbon filters using a beta-gamma radiation survey meter.

V. CONCLUSIONS

Quality control and in-place tests of carbon filters can be carried out using iodine-131 as the tracer gas. This method is relatively simple, requires no special equipment, and provides adequate sensitivity for ventilation systems in excess of 15,000 cfm without handling extremely large quantities of iodine-131.
While all critical systems were satisfactory, the following potential problem areas were pointed out and should be avoided in future designs:

a) Where HEPA and carbon filters are installed in series, space should be provided between the two filter banks to facilitate visual inspections and probing to locate specific points of leakage.

b) Adequate space should be provided to simplify filter installation.

c) Initial designs should include provisions to facilitate: 1) injection of the tracer aerosol or gas, and 2) sampling on both sides of the filter bank.

d) Carbon filters should not be installed so that air flow is vertical. This increases the potential of the carbon settling and channels occurring within the carbon bed.

e) Filters should be attached to the framework on an individual basis. When the filter gaskets are compressed individually, any one filter can be removed without disturbing the seal of the adjacent filters.

REFERENCES

[5] Saint-Gobain Techniques Nouvelles (Mfg), Seine, France.
**DISCUSSION**

O. L. CORDES: Did the little charcoal filter used upstream and downstream of the large charcoal filter being tested contain the same type of charcoal as the large one?

H. J. ETTINGER: Yes. The two charcoals were from different makers, but both were unimpregnated, coconut-shell, activated charcoal.

D. A. NITTI: You do not mention the total mass of stable iodine or the stable iodine concentration and the test period, how do you assure yourself in the in-place test that you have not reached saturation point in the charcoal’s iodine absorption capacity? In other words, how do you assure yourself that the system is not on the verge of break-through at the completion of the in-place test?

H. J. ETTINGER: Basically, there is such a large mass of charcoal that the mass of iodine used in the testing (and probably the total mass of iodine from repeated or periodic testing) could not saturate the charcoal.

R. E. HOLMES: Did you assess the plating-out effect of the elemental iodine used in the test rig? Can you state the contact time between the carbon of the filters and the ventilation air?

H. J. ETTINGER: No attempt was made to estimate wall plate-out of iodine-131. Upstream and downstream samplers were located as close as possible to the test filter. This would minimize any plate-out. Calculations based on the iodine-131 collected by the upstream and downstream air samplers showed that 25-50% of the iodine initially placed in the iodine generator was airborne. A significant amount of iodine remained in the iodine generator.

Contact time in the charcoal is approximately \( \frac{1}{2} \) sec.

C. PELLETIER: How do you know that you had elemental iodine?

H. J. ETTINGER: There are several reasons for believing that no significant quantities of the penetrating forms of iodine (e.g. methyl iodide) are formed and that our test procedure employed elemental iodine. First, the iodine generating technique was employed in the past to evaluate the iodine collection efficiency of charcoal and silver nitrate impregnated filter papers. These impregnated filters, which are only effective when sampling particulate or elemental iodine, were found to be very efficient in sampling the iodine generated. Secondly, the carbon filters tested are not impregnated with KI or ethylenediamine, and if significant quantities of methyl iodide were present, these would penetrate the test filter. All the filters tested showed iodine penetration ranging from 0.01% to 0.04%. Moreover, according to theory, the method used for iodine generation should produce elemental iodine.

L. F. FRANZEN: Could you consider your testing conditions for the carbon filters to be representative for all operating conditions, i.e. normal and accidental ones? Or did you know the retention efficiency of your charcoal as a function of temperature, relative humidity etc., so that you
could limit your investigations to just one point of the retention curve for the charcoal?

H. J. ETTINGER: The MCA postulated for this reactor does not produce severe environmental conditions (i.e., extremely high temperature, high pressure, steam etc.). Therefore, conditions existing during our in-place tests are representative of normal and accident conditions. Since there are no large temperature or humidity variations in the reactor effluent air stream, there is no need to measure in-place efficiency as a function of these variables.

J. G. WILHELM: Was the charcoal in the charcoal filter under test and in the charcoal sampler of the impregnated type? Can you be sure that the iodine in the downstream sampler penetrated the charcoal filter under test through leaks and was not just a part of the iodine test medium in a penetrating chemical form? Otherwise the result of the test may depend more on the quality of the test medium than on the leak-rate of the filter.

H. J. ETTINGER: Neither the test carbon filter nor the sampling charcoal cartridge was impregnated with KI or ethylenediamine. The method used to generate the tracer iodine will produce insignificant quantities of the penetrating forms of iodine (e.g., methyl iodide). This was confirmed by the results of the quality control tests, where 41 of the 44 filters tested showed efficiencies ≥ 99.98%, the remaining 3 filters exhibiting efficiencies ≥ 99.96%. Even the largest iodine penetrations measured during these tests (0.04%) are not significant, considering our criterion of a minimum in-place efficiency of 99.9%. If significant quantities of methyl iodide were produced during the test, your concern would be appropriate.
METHODE SENSIBLE DE MESURE DE L'EFFICACITE DES FILTRES A HAUTE EFFICACITE AU MOYEN D'UN AEROSOL D'URANINE

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Abstract — Résumé

SENSITIVE METHOD OF MEASURING THE EFFECTIVENESS OF HIGH-EFFICIENCY FILTERS BY MEANS OF URANIN AEROSOL. Measurements of the effectiveness of high-efficiency filters are generally not very sensitive because of the very quality of the filters that have to be studied. The fraction of the test aerosol which passes through the filters is very small, and experimenters often have to release heavy concentrations of aerosol upstream in order to get measurable concentrations downstream of the filter — a technique which tends to produce coagulation. The method described in this paper utilizes a test aerosol whose average particle size corresponds to the maximum permeability of the high-efficiency filters. Accordingly the purification factors determined by this method are 10-100 times smaller than those yielded by conventional techniques such as the method using monodispersed DOP. The technique of assaying the samples, based on fluorescence, further increases the sensitivity of the method. The test aerosol concentrations required upstream of the filters are very small (10 µg/m³), and installations of large capacity can be monitored with equipment of comparatively small size and weight. The authors give a detailed description of the method and present results obtained with plane filter samples and filter elements. The results obtained with the new method are compared with those given by monodispersed DOP.

METHODE SENSIBLE DE MESURE DE L'EFFICACITE DES FILTRES A HAUTE EFFICACITE AU MOYEN D'UN AEROSOL D'URANINE. La sensibilité des mesures d'efficacité des filtres à haute efficacité est générale­ment faible du fait même de la qualité des filtres considérés. En effet, la fraction de l'aérosol d'essai qui traverse ces filtres est très réduite et on est souvent conduit à produire de fortes concentrations d'aérosol en amont pour obtenir des concentrations mesurables en aval, ce qui provoque une coagulation. La méthode décrite est caractérisée par un aérosol d'essai dont la dimension moyenne correspond au maximum de per­méabilité des filtres à haute efficacité. Ainsi, les coefficients d'épuration déterminés par cette méthode sont dix à cent fois plus faibles que ceux qui sont déterminés par les méthodes connues telles que la méthode au DOP monodispersé. Le procédé de dosage des prélèvements fondé sur la fluorescence accroît encore la sensi­bilité de la méthode. Les concentrations en aérosol d'essai nécessaires en amont des filtres sont très faibles (10 µg/m³) et le contrôle d'installations à grand débit est possible avec un appareillage de volume et de poids réduits. On donne une description détaillée de la méthode et on présente les résultats obtenus sur des échantillons de filtre plans et sur des éléments filtrants. On établit une comparaison avec quelques résultats obtenus par la méthode au DOP monodispersé.

1 - INTRODUCTION

Il existe de nombreuses méthodes de contrôle des filtres à air, dont le principe général est le suivant : on envoie, en amont du filtre à contrôler, un aérosol d'essai, de caractéristiques déterminées, et on mesure, par un procédé défini, les quantités ou les concentrations de cet aérosol en amont et en aval du filtre. Une méthode est ainsi définie par ses deux éléments : l'aérosol d'essai et le procédé de mesure.

En toute rigueur, on devrait caractériser l'aérosol d'essai par sa natu­re, son spectre de répartition granulométrique, sa concentration, son état.
électrique, etc., mais il est à la fois plus commode et plus précis de définir le générateur d'aérosol et les conditions de son emploi. Cela implique que toutes les conditions assurant la reproductibilité de l'aérosol soient précisées.

De même, on définit le procédé de mesure de l'aérosol en indiquant les dispositifs ou l'instrument utilisés.

Toute la difficulté du contrôle des filtres à haute efficacité réside dans la mesure de la faible quantité d'aérosol d'essai qui les traverse. Pour augmenter cette quantité, on cherche à produire des particules dont la dimension correspond au minimum d'efficacité. Le contrôle de la valeur minimum est d'ailleurs d'un intérêt pratique certain du point de vue de la sécurité des installations. Pour les filtres considérés, la dimension de l'aérosol correspondant à l'efficacité minimum est voisine de 0,1 micron.

Le choix du procédé de mesure est évidemment fondamental pour la sensibilité et la souplesse de la méthode. Avec une mesure instantanée de concentration, on ne peut augmenter la sensibilité qu'en augmentant la concentration d'aérosol en amont du filtre, alors qu'avec une mesure différée sur des prélèvements on peut en outre jouer sur le temps de prélèvement. De la grandeur caractéristique choisie : nombre de particules, masse, couleur, fluorescence, radioactivité, etc., découlent les possibilités de la mesure.

La méthode qui fait l'objet de cet exposé est fondée sur la fluorimétrie, ce qui lui confère une sensibilité particulière. Elle est applicable au contrôle des installations de grand débit comme à la mesure des échantillons au laboratoire sans qu'il soit nécessaire de mettre en œuvre un appareillage volumineux. Le principe en a déjà été exposé [1], [2].

2 - PRINCIPE

L'aérosol d'essai est produit par pulvérisation d'une solution aqueuse d'uranine (fluorescéine sodée, formule brute : $\text{C}_20\text{H}_10\text{O}_5\text{Na}_2$). Après élimination des grosses gouttelettes, au moyen d'un séparateur à inertie, l'aérosol liquide restant est évaporé dans un tube chauffant. On obtient alors un aérosol solide fin qui est injecté en amont du filtre à contrôler. Des prélèvements d'aérosol en amont et en aval de ce filtre sont recueillis sur des filtres plans dont on extrait ensuite l'uranine par lavage. Les solutions obtenues sont finalement titrées par mesure de leur fluorescence.

3 - GENERATION DE L'AÉROSOL D'ESSAI

La figure 1 est un schéma du générateur d'aérosol qui se compose de trois parties : le pulvérisateur, le séparateur et l'évaporateur.

3.1 - Pulvérisateur

La tête de pulvérisation (2), semblable à l' "atomiseur" de Collison, décrit dans la norme BS 2831 [3], comprend huit éjecteurs. Elle est alimentée en air comprimé par le tube coulissant (3). La solution d'uranine est aspirée par le tube (4) et pulvérisée radialement vers les parois du corps (1). Un pare-gouttes (5) arrête les grosses gouttes projetées par l'impact. L'aérosol liquide sort en (6). Le coulissement du tube (3) permet de monter ou descendre la tête de pulvérisation de quelques millimètres. Lorsque la tête est en position basse, le tube (4) est obturé par une pastille de caoutchouc collée au fond du corps et il est possible d'alimenter en air comprimé sans émettre d'aérosol, ce qui est utile, en particulier pour la mise en équilibre thermique de l'évaporateur.
3.2 - Séparateur

Le séparateur, conçu d'après le "centripeter" de HOUNAM [4], comprend deux étages. Chaque étage est principalement constitué d'un corps (9), d'un diaphragme (10) et d'une buse (11). L'aérosol liquide provenant du pulvérisateur traverse à grande vitesse l'orifice du diaphragme (10). Une faible fraction de l'air est admise dans la buse (11). La plus grande partie contournant donc cette buse, du fait de leur inertie, les plus grosses particules ne suivant pas la déviation des filets d'air, sont captées par la buse et recueillies dans le vase décanteur (12). Le courant de captation est filtré en (13) et son débit est limité par le diaphragme (14).

Une couche de matériau hydrophile tapisse intérieurement le corps du séparateur pour fixer les dépôts liquides et éviter la réémission de gouttelettes sous l'action de la turbulence. L'aérosol liquide fin sort en (15).

3.3 - Evaporateur

L'évaporateur est un simple tube chauffant enroulé en solénoïde. La température de sortie de l'aérosol sec est régulée au moyen d'un thermostat.

3.4 - Caractéristiques de fonctionnement du générateur - Présentation

Dans les conditions normales d'emploi, le pulvérisateur est rempli d'une solution aqueuse à 1 % d'uranine et la pression effective d'alimenta-
FIG. 2. Microphotographies de l'aérosol d'uranine.
tion en air est égale à 2 bars. Le débit d'air est alors de 30 litres par minute et le débit de solution est de 40 cm³ par heure. L'analyse granulométrique au centripèteur multi-étage de HOUNAM montre que la proportion en volume des gouttelettes de diamètre supérieur à 1,2 micron (1) est de 30 % avant le séparateur et inférieure à 5 % après. Environ 95 % en masse de l'aérosol est retenu dans le séparateur. Le débit d'aérosol liquide fin est donc de 2 grammes par heure.

Le temps de passage dans l'évaporateur est de 5 secondes et la température de sortie est régulée autour de 130°C. Compte tenu de la concentration de la solution dans le pulvérisateur, le débit massique en aérosol solide après séchage est de 20 mg/h environ, ce qui correspond à une concentration de l'ordre de 10 mg/m³ à la sortie du générateur, avant injection dans le circuit à contrôler.

La figure 2 représente des microphotographies de l'aérosol solide obtenu. Le spectre granulométrique est représenté figure 3 sous la forme d'un histogramme. Les caractéristiques principales de ce spectre sont :
- diamètre moyen (en nombre) : 0,15 μ
- écart type : 0,085 μ
- diamètre moyen en masse : 0,30 μ.

Le pulvérisateur et le séparateur sont assemblés suivant le plan de la figure 4 dans une mallette dont le poids total est de 11 kilogrammes environ. L'évaporateur est contenu dans une mallette semblable.

(1) On considère que la limite de résolution du centripèteur correspond au diamètre de 1,2 μ [4].
4 - PRELEVEMENTS

Le dispositif de prélèvement amont comprend deux porte-filtre en série, le premier contenant un filtre de référence de diamètre 130 mm en papier d'amiante, le deuxième contenant une membrane Millipore de 47 mm en nylon de porosité 1 м (NR WP 04700).

Cette disposition permet à la fois la mesure de la quantité d'aérosol incidente et la mesure de l'efficacité du filtre de référence, cette dernière mesure ayant pour but de contrôler la qualité de l'aérosol d'essai.

Le dispositif de prélèvement aval comprend un seul porte-filtre avec une membrane de nylon. La membrane de nylon a été choisie pour son caractère hydrophile, qui facilite le lavage pour l'extraction de l'uranine, et pour son faible "bruit de fond" en fluorimétrie.

Le débit de prélèvement est de 2,5 à 3 m$^3$/h, ce qui correspond à des vitesses d'air de 7,5 à 9 cm/s à travers le filtre de référence et de 72 à 85 cm/s à travers les membranes de nylon.
5 - MESURES

5.1 - Traitement des prélèvements

La fluorescence de l'uranine dépend du pH (figure 5). Elle est forte en milieu très acide, passe par un minimum pour un pH de 4,5, puis croît avec le pH jusqu'à un palier atteint pour un pH de 10. Les solutions à titrer sont donc basifiées. En fait, la base est ajoutée au moment du lavage des filtres, car on a observé que l'extraction de l'uranine en était facilitée.

Le filtre de référence, qui est hydrophobe, est mouillé avec 2 cm$^3$ d'éthanol avant d'être immersé dans un litre d'eau distillée contenant 50 cm$^3$ d'ammoniac décinormale. Chaque membrane est lavée dans 10 cm$^3$ d'eau distillée additionnée de 0,5 cm$^3$ d'ammoniac décinormale. La solution de lavage du filtre de référence est donc diluée cent fois par rapport aux solutions de lavage des membranes, ce qui se justifie par les différences entre les quantités d'uranine recueillies.

Pour le dosage proprement dit, les solutions sont transvasées dans des cuves de mesure d'une contenance de quelques centimètres cubes. Des précautions doivent être prises pour garantir la justesse des mesures, particulièrement en ce qui concerne le titrage des solutions à faible concentration d'uranine. Les flacons d'extraction, les pipettes de transvasement et les cuves de mesure sont nettoyés au mélange sulfo-chromique et leur propreté est vérifiée avant chaque mesure au moyen d'une "mesure blanche" avec de l'eau distillée ammoniaquée.

5.2 - Fluorimètre

On utilise un photomètre équipé pour les mesures de fluorescence des liquides. On obtient une sensibilité de l'ordre de 10$^{-8}$ g/l en sélectionnant, au moyen de filtres optiques appropriés, les longueurs d'onde des radiations excitatrices et de fluorescence. La fluorescence de l'uranine est maximum pour un rayonnement excitateur d'environ 490 nm et le spectre de fluorescence
présente un maximum d'intensité vers 520 nm. La source lumineuse choisie est une lampe à décharge électrique dans le xénon. La radiation de 490 nm est séparée au moyen d'un filtre interférentiel primaire. La fluorescence des solutions est mesurée à travers un filtre secondaire séparant les radiations voisines de 520 nm. En réalité, on est conduit à augmenter l'écart des longueurs d'onde des radiations sélectionnées par les filtres primaire et secondaire, compte tenu de leur résolution, afin d'éviter un recouvrement des plages de transmission, qui se traduirait par un "bruit de fond" important.

L'appareil est étalonné avec des solutions obtenues par dilutions successives d'une solution mère à 10 grammes par litre. La courbe d'étalonnage correspondante est représentée figure 6.

6 - RESULTATS - COMPARAISON AVEC LA METHODE AU DOP MONODISPERSE

Des résultats comparés de mesure d'efficacité sur filtre plan avec la méthode à l'uranine et avec la méthode au DOP monodispersé de 0,3 μ sont donnés tableau I pour trois qualités de filtre.

Le premier filtre est constitué de fibres de cellulose et de fibres d'amiante, le deuxième filtre est en fibre de verre, le troisième est en fibre d'amiante.

Les mesures à l'uranine ont été faites dans les conditions du contrôle du filtre de référence (cf. paragraphe 4), c'est-à-dire, à la vitesse de 8 cm/s.
Comparaison des résultats obtenus par la méthode à l'uranine et par la méthode au DOP monodispersé de 0,3 μ sur des échantillons plans de papiers filtrants

<table>
<thead>
<tr>
<th>Référence du filtre</th>
<th>Efficacité Méthode à l'uranine</th>
<th>Efficacité Méthode au DOP 0,3 μ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vitesse : 8 cm/s</td>
<td>Vitesse : 5 cm/s</td>
</tr>
<tr>
<td>Schneider-Poelman rose</td>
<td>200 (99,5 %)</td>
<td>1 300 (99,92 %)</td>
</tr>
<tr>
<td>Sofiltra GLF 3</td>
<td>400 (99,75 %)</td>
<td>5 000 (99,98 %)</td>
</tr>
<tr>
<td>Schneider-Poelman amiante</td>
<td>2 000 (99,95 %)</td>
<td>100 000 (99,999 %)</td>
</tr>
</tbody>
</table>

Les résultats au DOP sont extraits d'une étude expérimentale que nous avons faite sur la comparaison des papiers américains et des papiers français, étude pour laquelle les vitesses 5 cm/s et 14 cm/s avaient été choisies.

On constate que, dans ces conditions, la méthode à l'uranine donne une valeur beaucoup plus faible que la méthode au DOP, c'est-à-dire que l'aérosol d'uranine est beaucoup plus pénétrant que l'aérosol de DOP. Il en résulte, avec la première méthode, une sensibilité plus grande pour la mesure des filtres très efficaces comme le Schneider-Poelman amiante. En effet, la valeur de 100 000, trouvée avec la deuxième méthode, correspond au maximum mesurable.

On obtient, au contraire, des résultats comparables entre les deux méthodes, pour les mesures d'efficacité d'éléments filtrants, ainsi qu'on peut le constater sur le tableau II. Les causes probables sont la présence de microfuites et l'influence de la vitesse de filtration, qui est, dans ce dernier cas, comprise entre 0,5 et 1 cm/s.

Comparaison des résultats obtenus par la méthode à l'uranine et par la méthode au DOP monodispersé de 0,3 μ sur des éléments filtrants

<table>
<thead>
<tr>
<th>Elément</th>
<th>Efficacité (vitesse : 0,5 à 1 cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>à l'uranine</td>
</tr>
<tr>
<td>Dièdre Schneider-Poelman rose</td>
<td>900 (99,89 %)</td>
</tr>
<tr>
<td>Dièdre Schneider-Poelman amiante</td>
<td>500 (99,8 %)</td>
</tr>
</tbody>
</table>
7 - OBSERVATIONS - DISCUSSION

7.1 - Extension de la méthode

La méthode a été conçue pour le contrôle des filtres à haute efficacité, dans des conditions qui correspondent à leur perméabilité maximum.

Pour détecter les fuites éventuelles, en particulier sur les installations en place dont les joints peuvent être défectueux, on prévoit un contrôle supplémentaire, avec l'aérosol liquide tel qu'il sort du pulvérisateur, c'est-à-dire, sans élimination des grosses particules et sans évaporation.

Le médium filtrant est beaucoup plus efficace vis-à-vis de cet aérosol "gross" et les fuites, dont la perméabilité varie peu avec les dimensions de l'aérosol, sont aisément décelées.

7.2 - Reproductibilité

Les résultats sont reproductibles à environ 10 % près pour les efficacités moyennes, de l'ordre de 500. Pour les haute efficacités, voisines de 2 000, la reproductibilité semble moins bonne. Le nombre de mesures est encore insuffisant pour la préciser.

Les différents facteurs susceptibles de faire varier les résultats ont été examinés. Une mesure brute montre que l'aérosol d'essai est électriquement chargé à 90 %. Après neutralisation, c'est-à-dire à l'équilibre de Boltzman, cette proportion tombe à 80 %. Bien que ces mesures brutes ne tra- duisent pas la variation du nombre moyen des charges des particules qui peut être très importante [5] [6], il semble que les résultats d'efficacité soient peu modifiés pour les filtres industriels.

L'efficacité et la rétention éventuelle des membranes de prélèvement ont été contrôlées. Pour les membranes de nylon choisies, la rétention est inférieure à 10 %, c'est-à-dire que le rendement d'extraction de l'uranium recueilli est supérieur à 90 %, mais l'efficacité est comprise entre 4 et 10 (75 et 90 %) vis-à-vis de la fraction de l'aérosol d'essai qui traverse le filtre de référence. Bien que ces valeurs soient faibles, nous choisissons actuellement ces membranes, eu égard à leurs autres qualités (faible "bruit de fond", faible rétention, caractère hydrophile).

7.3 - Limites d'emploi

La concentration la plus faible décelable au fluorimètre est voisine de $10^{-8}$ g/l. Compte tenu du "bruit de fond" des membranes, qui est du même ordre, et de la pente de la caractéristique du fluorimètre, on peut prendre comme concentration minimum mesurable, une valeur cinq fois plus grande, soit $5.10^{-8}$ g/l. Cela correspond à une masse de $5.10^{-10}$ g recueillie sur une membrane puisque le volume de la solution de lavage est de 10 cm$^3$. Avec un volume d'air prélevé de 2,5 m$^3$, soit un essai d'une heure, la concentration minimum mesurable d'aérosol correspondante en aval du filtre à contrôler est $2.10^{-10}$ g/m$^3$. Donc, pour contrôler un filtre d'efficacité 1000, la concentration d'aérosol minimum nécessaire en amont est égale à $2.10^{-7}$ g/m$^3$, soit 0,2 $\mu$g/m$^3$.

Le générateur, ayant un débit de 20 mg/h, permet d'assurer cette concentration pour un débit d'air de 100 000 m$^3$/h.

Le même générateur peut être utilisé sans dilution pour le contrôle des éléments filtrants d'un débit de 100 m$^3$/h, puisque la concentration de l'aérosol en amont du filtre ne sera que de 0,2 mg/m$^3$, valeur pour laquelle ni la coalescence de l'aérosol, ni le colmatage du filtre ne sont à craindre.

8 - CONCLUSION

La méthode décrite se caractérise par sa sensibilité qui procède d'une part, de la technique de mesure (fluorimétrie), d'autre part, des dimensions
de l'aérosol d'essai. Elle convient particulièrement au contrôle des filtres à très haute efficacité pour lesquels les autres méthodes sont à la limite de leur sensibilité. Elle permet aussi bien le contrôle des installations à grand débit (100 000 m³/h) que celui des éléments filtrants individuels, sans appareillage encombrant et sans risque de colmatage ou de coalescence.

REFERENCES


[3] British Standards Institution : Methods of test for air filters used in air-conditioning and general ventilation, BS 2831 (1957)


DISCUSSION

J. D. JOUBERT: The aerosol used appears to have been smaller than that obtained by the DOP method. This might explain the lower efficiency value. Another explanation might be found in the different physico-chemical nature of the particles.

J. PRADEL: I agree. The mean diameter is 0.1 microns, whereas that obtained by the DOP method is 0.3 microns.

D. W. BALLARD: Regarding Mr. Joubert's question, uranine aerosol challenges to HEPA filters used at Sandia Laboratory show spherical particles in the size range reported by Mr. Pradel. We shadowed the electron microscope grids and determined that the aerosols were spherical. We have also used microbiological challenges for HEPA filters, both spores and vegetative cells, in the 0.1-0.5 micron range, incubating and counting the micro-organisms to determine percentage penetration.

H. J. ETTINGER: When obtaining uranine aerosol characteristics from their electron micrographs, did the authors also attempt to estimate particle shape, to determine if the particles were spherical or flat?

J. PRADEL: Our aim was to obtain a reproducible aerosol and we did not give much attention to its shape.
TESTING HEPA FILTERS FOR USE IN A HIGH NOISE LEVEL ENVIRONMENT *

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Abstract

TESTING HEPA FILTERS FOR USE IN A HIGH NOISE LEVEL ENVIRONMENT. During the pulsed cooling phase of nuclear reactor rocket engine tests, as part of the Rover Program at Los Alamos Scientific Laboratory, the possibility of atmospheric release of radioactive particulates exists. To control this potential release, a special air cleaning system employing High Efficiency Particulate Aerosol (HEPA) filters was designed, constructed, and tested. A primary concern was the structural integrity of these filters under the intense noise levels that exist during reactor tests.

Commercially available HEPA filters were subjected to noise levels simulating the acoustic environment that exists near a reactor during testing. These acoustic exposures included both reverberant and progressive fields of varying time intervals and reached maximum sound pressure levels of 148 db. Filter efficiency tests using air-generated dioctyl phthalate (DOP) were performed before and after acoustic exposures and are reported. Details of the acoustic and DOP test methods are also discussed.

INTRODUCTION

During the pulsed cooling phase of nuclear reactor rocket engine tests, as part of the Rover Program at Los Alamos Scientific Laboratory, the possibility of a release of radioactive particulates exists. Although this does not constitute a problem of atmospheric contamination, the resultant procedures required and costs involved in decontamination of the immediate testing area could be quite extensive. It was, therefore, desirable to control this potential release with a special air cleaning system capable of removing as much of the contamination as feasible.

High Efficiency Particulate Aerosol (HEPA) filters meeting the requirements of the U.S. Atomic Energy Commission (USAEC)[1] would serve as the most simple and convenient means of obtaining the desired filtration. These filters are designed for a minimum efficiency of 99.97% when subjected to a dioctyl phthalate (DOP) monodisperse, 0.3 μm aerosol. However, prior to the incorporation of HEPA filters into the design for the air cleaning system, it was necessary to determine their structural integrity in an acoustical environment simulating that found near a Rover reactor during testing.

Calculations, based on noise levels measured during the Kiwi reactor series,[2] established sound pressure levels that could be anticipated during the testing of two future reactors. Table I indicates the predicted

* Work performed under the auspices of the US Atomic Energy Commission.'
TABLE I

PREDICTED LEVELS FOR ACOUSTIC EXPOSURES

<table>
<thead>
<tr>
<th>Octave Band (Hz)</th>
<th>Low Level</th>
<th>High Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 - 75</td>
<td>112</td>
<td>139</td>
</tr>
<tr>
<td>75 - 150</td>
<td>121</td>
<td>141</td>
</tr>
<tr>
<td>150 - 300</td>
<td>127</td>
<td>141</td>
</tr>
<tr>
<td>300 - 600</td>
<td>127</td>
<td>140</td>
</tr>
<tr>
<td>600 - 1200</td>
<td>126</td>
<td>138</td>
</tr>
<tr>
<td>1200 - 2400</td>
<td>125</td>
<td>136</td>
</tr>
<tr>
<td>2400 - 4800</td>
<td>122</td>
<td>133</td>
</tr>
<tr>
<td>4800 - 9600</td>
<td>119</td>
<td>131</td>
</tr>
<tr>
<td>Overall</td>
<td>133.5</td>
<td>148</td>
</tr>
</tbody>
</table>

levels within specific octave bands. The anticipated exposure times to these levels was 45 min for the low levels and approximately 20 min for the higher levels. Sandia Corporation, Sandia Laboratory (SCSL), Albuquerque, New Mexico, was contracted to expose selected HEPA filters to the predicted noise levels for varying time periods.

Specifications for the filters to be used in the proposed air cleaning system followed the requirements set forth in Reference 1. Briefly, these specifications required a filter medium of waterproof glass with aluminum separators, a sealant (medium to frame) of ceramic glass, and the frame or exterior of the filter constructed of 16 gauge cadmium plated steel, 24 x 24 x 11\(\frac{1}{2}\) in. Each filter had a rated capacity of 1250 cfm air flow with 1 in. water gauge or less differential pressure across the filter media.

It was decided that the integrity testing should involve, in addition to the above, HEPA filters that are commonly used in air filtration systems throughout USAEC installations. Consequently, filters from various manufacturers and of varying sizes and construction were selected to be subjected to the acoustic exposures. Table II is a list of all filters exposed.

Test procedures would involve in-place testing for filter efficiency against a polydisperse DOP aerosol prior to and after each acoustic exposure.
TABLE II
LIST AND DESCRIPTION OF HEPA FILTERS TESTED

<table>
<thead>
<tr>
<th>Filter No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2, 3</td>
<td>1000 cfm (23-7/16 x 23-7/16 x 11(\frac{1}{4}) in.) aluminum separators, 16 gauge cadmium-plated steel frame.</td>
</tr>
<tr>
<td>3, 4, 5</td>
<td>1150 cfm (24 x 24 x 11(\frac{3}{4}) in.) asbestos separators, 3/4 in. plywood frame.</td>
</tr>
<tr>
<td>6, 7</td>
<td>600 cfm (24 x 24 x 5(\frac{7}{8}) in.) aluminum separators, 3/4 in. plywood frame.</td>
</tr>
<tr>
<td>8, 9, 10</td>
<td>750 cfm (24 x 24 x 5(\frac{7}{8}) in.) asbestos separators, 3/4 in. plywood frame.</td>
</tr>
<tr>
<td>11, 12</td>
<td>500 cfm (18 x 18 x 11(\frac{1}{4}) in.) asbestos separators, 3/4 in. plywood frame.</td>
</tr>
<tr>
<td>13, 14</td>
<td>Same as above, different manufacturer.</td>
</tr>
<tr>
<td>Framework (3 filters)</td>
<td>3 ea., 1250 cfm (24 x 24 x 11(\frac{3}{4}) in.). Aluminum separators, 16 gauge cadmium-plated steel frame.</td>
</tr>
</tbody>
</table>

I. PRE-ACOUSTIC EXPOSURE

An aluminum framework capable of holding four filters was constructed to simulate the proposed framework for the Filtration for Reactor Out-Gassing (FROG) assembly (see Fig. 1). This framework also provided a means of subjecting the sealing gaskets and retention hardware to the acoustic exposures and in-place tests. It was necessary, for in-place testing, to seal one portion of the framework as only three filters meeting the specifications for the FROG assembly were received for testing. All other filters exposed would be individually suspended in the acoustic chamber.

A. In-Place Testing

Each filter, except those contained in the aluminum framework, was individually in-place tested for filtration efficiency using a polydisperse, liquid DOP aerosol. The aerosol generator used is a modification of a design by the Naval Research Laboratory.[3] When the generator is operated at 25 psi air pressure within the nozzles, the aerosol has a count median diameter of 0.8 \(\mu\)m and a geometric standard deviation of 1.6[4]

The aerosol detection equipment consists of a forward light-scattering photometer and amplifier combination.[5] Figure 2 shows the test
assembly, aerosol detection equipment, and sampling probes used for in-place testing of individual HEPA filters.

Three-hundred cubic feet per minute of air was drawn through each filter, with the DOP aerosol being introduced at the intake duct. A Stairmand disk contained in the duct ensures proper mixing of the aerosol with the airstream. An air sample is then drawn into the sensing chamber of the light-scattering photometer and relative concentrations of the aerosol upstream (A) and downstream (B) are measured. The efficiency, in percent, is indicated by \( \left( 1 - \frac{B}{A} \right) \times 100 \).

The three filters contained in the aluminum framework were in-place tested as a complete assembly, using the test methods described above. Airflow through the assembly for testing purposes was approximately 800 cfm. Figure 3 shows the test assembly with its transition plenums attached, the aerosol detection equipment, sampling probes, and blower providing airflow.

Filter number 2, Table II, indicated a filtration efficiency, prior to acoustic exposures, of 99.98%. The three-filter assembly indicated an efficiency of 99.96% and all other filters, 99.99% or greater.

After the initial in-place tests, all filters were packaged in their original shipping cartons and transported to SCSL by private carrier. It
was hoped that this means of transportation would negate the possibility of filter damage that occasionally occurs in transit.

II. ACOUSTIC EXPOSURES AND TESTS

The initial exposure procedure called for the three filters contained in the framework to be exposed to the predicted sound pressure levels in reverberant and progressive sound fields. The loose or individual filters would be subjected to both sound pressure levels but in a reverberant field only.

A. Filter Assembly (Aluminum Framework and Three HEPA Filters)

Exposure No. 1. Reverberant field. The filter assembly was suspended in the acoustic testing chamber (see Fig. 4) and the sound pressure level established at 133 db. The chamber was then equalized, as near as possible, to the low-level spectrum listed in Table I. Total exposure time to this level was approximately 45 min.

Visual inspection after exposure of the framework, filters and gaskets indicated no apparent defects. It was decided to forego efficiency tests at this time and continue to the higher sound pressure level.
Exposure No. 2. Reverberant field. Sound pressure levels were increased to approximately 148 db and the chamber equalized to approximate the high-level spectrum. These levels were maintained for approximately 20 min. Visual inspection of the filters revealed no defects in the filter media, however, a small amount of fiber glass packing at the periphery of the filter had started to become dislodged (see Fig. 5). Efficiency tests of the assembly with DOP aerosol indicated no loss in efficiency of filtration.

Exposure No. 3. The assembly was then subjected to progressive wave fields of the low-level spectrum. This level was maintained for approximately 40 min. A post-exposure visual inspection indicated no change in the filter's condition from that found after the second exposure.

Exposure No. 4. The overall SPL was established at 148 db and equalized under progressive wave conditions. This high-level spectrum was maintained for 20 min and the assembly visually inspected at the end of the exposure. It was noted that the fiber glass packing had been further dislodged. Efficiency testing conducted immediately after acoustical exposure indicated that filtering efficiency had not been impaired.
B. Individual Filters

It was decided at this time to forego the exposure of these filters to the low level spectrum and proceed directly to the high levels.

Exposure No. 1. Fourteen individual filters, as listed in Table II, were suspended in the test chamber and exposed for a period of 20 min to a reverberant field of the high-level spectrum. Visual inspection of the filters after exposure revealed that the filters closest to the sound source had more loose fiber glass packing than the others, indicating the possibility of higher noise levels at this point. By relocating the microphones in the acoustic chamber, it was determined that three of the filters had been exposed to overall sound pressure levels of 152 db.

Exposure No. 2. All filters were removed from the chamber except the three that received the highest levels on the previous exposure. These filters were subjected to a measured overall sound pressure level of 152 db for an additional 20 min.

More detailed data on the sound pressure levels, accelerometer measurements and techniques of the acoustic exposures are given in reference.\[6\]
FIG. 5. Partial dislodging of fibre glass packing.

III. POST-EXPOSURE TESTING

The three-filter assembly and all individual HEPA filters were again in-place tested as previously outlined. There was no significant loss in filtration efficiency indicated by the final tests.

IV. SUMMARY AND DISCUSSION

Three HEPA filters contained in an aluminum framework were exposed, under reverberant and progressive wave conditions, to SPL's of 133 db and 148 db. Total time of exposures was 85 and 45 min, respectively. In-place tests of the assembly, before and after exposure, indicated no loss in filtration efficiency.

Fourteen HEPA filters of various sizes and construction were subjected to an overall sound pressure level of 148 db, under reverberant conditions, for a period of 20 min. Three of these filters were then exposed for an additional 20 min to a reverberant field of 152 db.

All of these filters were individually tested for filtration efficiency against a polydisperse, liquid DOP aerosol before and after their acoustic exposure. The post-exposure tests indicated that the efficiency of the
filters was not significantly impaired by exposures to the stated SPL's for the times involved.

However, visual inspections of the filters revealed structural changes that, with subsequent exposures, could cause the filters to suffer a loss in efficiency. It was noted that the fiber glass packing material, acting as an additional sealant between the medium and frame, had become partially dislodged. This condition increased with time and, potentially, could allow an aerosol to bypass the filter medium.

It was also observed that some of the aluminum separators, in those filters constructed with steel frames, migrated away from the filter medium so as to protrude as much as 0.5 in. from the face of the filter. It is believed that additional migration, creating a lack of proper support for the filter medium, would result in eventual failure of the filter.

Based on the results of the acoustic exposures and efficiency testing, a full-scale filtration system was constructed incorporating 56 of the 24 x 24 x 11\(\frac{1}{2}\) in. filters. This system is capable of handling approximately 70,000 cfm of effluent with, as indicated by in-place DOP tests, an overall efficiency greater than 99.95%.

V. ACKNOWLEDGMENT

Special acknowledgment is given to Sandia Corporation, Sandia Laboratory, Albuquerque, New Mexico, who, on a contract basis, provided the acoustic environment in which the HEPA filters were exposed.

REFERENCES

REMOVAL OF NOBLE GASES

(Session IV, Part 2)
Chairman: P.J. LINDER
CONCENTRATION AND COLLECTION OF KRYPTON
AND XENON BY SELECTIVE ABSORPTION IN
FLUOROCARBON SOLVENTS*

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Abstract

CONCENTRATION AND COLLECTION OF KRYPTON AND XENON BY SELECTIVE ABSORPTION IN
FLUOROCARBON SOLVENTS. One of the most direct methods for removing krypton and xenon is selective
absorption of the gases from a compressed, contaminated air stream using a chilled fluorocarbon solvent, such
as refrigerant-12 (dichlorodifluoromethane). A development program is under way at the Oak Ridge Gaseous
Diffusion Plant to provide the engineering scale-up data required for design of a krypton-xenon recovery plant
using the absorption technique. The ORGDP work involves pilot-plant testing to collect performance data, as
well as conceptual design and optimization studies. The goal of this program is to provide designers of
nuclear reactors, reprocessing plants and similar installations with another tool useful in ensuring public
safety.

Workers at the Brookhaven National Laboratory discovered that krypton and xenon are markedly more
soluble in liquid refrigerant-12 than argon, oxygen and nitrogen, especially at low temperatures. Thus, the
first step in the absorption process involves contacting the contaminated air with the solvent at a low tempera­
ture and a high pressure so that most of the krypton and xenon will be dissolved in the liquid, leaving the air
stream relatively free from radioactive components. The liquid stream is then sent to one or more fractionating­
stripping units, operated at higher temperatures and lower pressures, where the absorbed krypton and xenon
 can be concentrated further and then revolatilized from the solvent for storage in cylinders or other treatment.

Construction and installation of the pilot plant required for these studies have recently been completed,
and a series of tests has been designed to encompass wide ranges of temperatures, pressures, and flows, as
well as the use of higher temperature solvents. In this paper preliminary pilot-plant results are presented
and plans for future experiments are discussed.

Radioactive isotopes of krypton and xenon are produced in significant quantities during irradiation of nuclear fuel. In the event of fuel element cladding rupture or fuel meltdown, during fuel reprocessing, and even during normal operations for certain types of nuclear reactors, these fission product gases are released to the surrounding containment. Because of this, the importance of noble gas handling is increasing substantially with the growth of nuclear power. It appears probable, in fact, that systems for processing gas streams containing these radioactive constituents will, in the future, be required to allow safe disposal of nuclear process off-gases in many instances.

Several methods for isolating krypton and xenon have been proposed in the past, and many of these have been demonstrated for specific applications. Some of the schemes which have received serious attention are

* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by
Union Carbide Corporation for the US Atomic Energy Commission.
mentioned in reviews by Browning[1] and by Keilholtz[2]. In general, it is possible to categorize basic noble gas recovery operations either as
(a) selective adsorption, using such sorbent materials as charcoal or molecular sieves; (b) cryogenic distillation, (c) preferential absorption in liquid solvents; or (d) special techniques; for example, underground disposal, retention in clathrates, or separation by selective permeation. Because krypton and xenon are essentially inert, suitable chemical means for collection are not available.

In view of revised requirements envisioned for noble gas control, the Environmental and Sanitary Engineering Branch of the U. S. Atomic Energy Commission, Division of Reactor Development and Technology, is sponsoring engineering development projects at Oak Ridge aimed at evaluating two especially promising processes for controlling krypton and xenon releases. The first technique, being investigated at the Oak Ridge National Laboratory, employs a unique silicone rubber membrane; the krypton and xenon selectively permeate this material and are concentrated after passage through cascaded membrane packages[5]. A second method, the subject of this paper, is being tested at the Oak Ridge Gaseous Diffusion Plant and is based on preferential absorption of the noble gases in a high capacity fluorocarbon solvent. In both projects, the primary emphasis is on determining scale-up data necessary to design plant systems for a variety of applications, including the treatment of (a) air within a nuclear reactor containment building in the event of an accidental fission gas release; (b) off-gases from processing plants reclaiming values from irradiated fuel; and (c) gases which blanket the cores of certain types of nuclear reactors, for example, the molten salt breeder reactor, which continuously vent fission product gases.

KRYPTON-XENON ABSORPTION PROCESSES

One of the most direct methods for stripping the noble gases, krypton and xenon, from contaminated air streams is selective absorption. The process can readily be made continuous, because the essential steps are conventional gas-liquid contacting operations. Several solvents, including carbon tetrachloride[4,5,6], kerosene-base liquids[7,8], liquid nitrogen[2], nitrous oxide[9], and dichlorodifluoromethane[10], i.e., refrigerant-12, have been proposed. A summary of solubility data points for krypton in these and other solvents considered is given in table I.

Several factors influence the selection of a process solvent. Considering solvent capacities, separation factors, and thermal and radiation stabilities, as well as overall process safety and economic features, Steinberg has suggested the preferability of absorption processes utilizing fluorocarbon solvents and has collected solubility data for refrigerant-12[9].

As shown in Fig. 1, with refrigerant-12, krypton and xenon are markedly more soluble than argon, oxygen, and nitrogen, especially at temperatures below 52°F; the separation factor between these two elements and the other gases shown increases considerably with decreasing temperature. Coupled with an essentially direct pressure dependency for the solubilities, the temperature relationships allow a considerable latitude in the choice of processing conditions to achieve a given separation. Conceptually, then, an efficient absorption process can be devised from the solubility data by specifying an absorption step at some relatively low temperature and high
### TABLE I

**SOLUBILITY OF KRYPTON IN VARIOUS LIQUIDS**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting Point °F</th>
<th>Boiling Point °F</th>
<th>Solubility Data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>32</td>
<td>212</td>
<td>86</td>
<td>0.05</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>-62.9</td>
<td>328.5</td>
<td>77.9</td>
<td>0.63</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>55.8</td>
<td>280.4</td>
<td>86</td>
<td>0.72</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>-139</td>
<td>154.4</td>
<td>77</td>
<td>1.05</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>-131.8</td>
<td>209.1</td>
<td>77.4</td>
<td>1.16</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>14.7</td>
<td>421.3</td>
<td>77</td>
<td>0.82</td>
</tr>
<tr>
<td>59.6% paraffin, 27.2% naphthene, 13.2% aromatics</td>
<td>77</td>
<td>67</td>
<td>1.50</td>
<td>[7]</td>
</tr>
<tr>
<td>80% paraffin, 20% naphthene</td>
<td>73.4</td>
<td>0.58</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>Terphenyl</td>
<td>186.8</td>
<td>784.4 (exp)</td>
<td>77</td>
<td>0.30</td>
</tr>
<tr>
<td>CCl₄</td>
<td>-9.4</td>
<td>170.2</td>
<td>77</td>
<td>ca. 1.3</td>
</tr>
<tr>
<td>N₂O</td>
<td>-131.4</td>
<td>-127.3</td>
<td>77</td>
<td>ca. 1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-112</td>
<td>8.5</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>-252.4</td>
<td>21.6</td>
<td>77</td>
<td>ca. 1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-112</td>
<td>12.6</td>
</tr>
</tbody>
</table>

*Volume of gas (corrected to 59°F and 1 atmosphere) absorbed under total system pressure of 1 atmosphere per unit volume (corrected to 59°F) of solvent.*

Pressure to maximize both total noble gas absorption and separation, followed by a stripping operation conducted at a higher temperature and lower pressure to reclaim the noble gases as a product stream. Also, in some cases, an intermediate fractionating step may be desirable to allow further concentration of the krypton and xenon in the absorbed gas prior to recovery as product.

**THE ORGDP PROGRAM**

The purpose of the ORGDP noble gas collection program is the development on an engineering scale of an absorption process for the separation and concentration of radioactive krypton and xenon from contaminated gas streams. The scope of the work includes pilot plant testing, conceptual design work, and process optimization studies. The ORGDP efforts were begun in the latter part of 1966, and progress made in each of these areas since that time has been summarized in two USAEC reports [10, 11].

**Pilot Plant Testing**

*Flow Patterns and Equipment Design.* A schematic pilot plant flow diagram is shown in Fig. 2. The feed gas is compressed to the absorber column operating pressure, passed through a desiccant for moisture removal, and then cooled to the desired column temperature. This stream is next...
FIG. 1. Relative solubilities of gases in refrigerant-12.

FIG. 2. Krypton-xenon absorption process pilot plant, schematic flow diagram.

introduced at the bottom of the packed column and is contacted with the downflowing liquid solvent stream. Gas leaving the top of the absorber, depleted in krypton and xenon, is used as a coolant for the incoming feed gas before being recycled or, perhaps, vented. Similarly, the liquid effluent from the bottom of the column, containing absorbed gas enriched
in krypton and xenon, is first heated by the inlet solvent and is then fed, after some further warming, to a higher temperature, lower pressure fractionation system consisting of a flash unit, a packed column, a reboiler, and primary and secondary condensers. Use of cold exiting process streams to chill incoming feed streams allows a considerable reduction in refrigeration requirements and, consequently, in processing costs. In the fractionator, a portion of the absorbed nitrogen and oxygen is preferentially desorbed to concentrate the noble gases contained in the liquid phase further; the resulting gas stream, containing recycle krypton and xenon, in addition to argon, oxygen, and nitrogen, is returned to the bottom of the absorber. Liquid exiting from the fractionator is routed to a stripping system, again involving a flash unit, a packed column, a reboiler, and condensers. The stripper is operated at a still lower pressure to facilitate liquid transfer and gas desorption.

Temperatures and pressures recommended for these processing steps on the basis of earlier Brookhaven National Laboratory experiments with refrigerant-12 are minus 94°F and 14 atmospheres for absorption, 32°F and 3 atmospheres for fractionation, and 10°F and 2 atmospheres for stripping. The pilot plant design, however, is flexible enough to permit processing of up to 15 standard cubic feet of gas per minute at a variety of temperature and pressure conditions, for example, in the case of the absorber column, the temperature and pressure can be varied from minus 100°F to ambient temperature and up to 40 atmospheres. In addition, solvents other than refrigerant-12 can be tested. The maximum solvent flow rate is about 2.5 gallons per minute.

It should be noted that, in terms of equipment, the pilot plant flow sheet is probably more complex than that which would be required for many plant applications. To ensure the maximum yield of information from test results, however, it was considered desirable to have an equipment configuration which would allow performance testing of several equipment items which might be utilized in a plant-scale version. Thus, the pilot plant can be operated either with the fractionator flash unit, the fractionator column, the stripper flash unit, and the stripper column in series, or with any of these units bypassed completely. It is expected that test data may well show that some of the pilot plant units are not required for specific plant designs, thereby resulting in significant flow sheet simplifications for the larger scale applications.

The sizes of the major pilot plant equipment items are listed in table II. Not summarized in this table are the two flash units, which have tangential gas inlets, liquid drains, and gas outlet pipes with mist shields, and are approximately 6 inches in diameter and 30 inches high. More complete descriptions of the pilot plant equipment, including discussions of the design approaches taken, are given in the progress reports for this project[10,11].

Current Status. The pilot plant design was completed by July, 1967, and construction and procurement of the various processing and mechanical equipment items and of the initially required instrumentation were essentially finished by the end of the year. Installation was completed during the first four months of 1968, and leak checking, shakedown operations, and preliminary testing were begun shortly thereafter. It was decided to conduct the shakedown operations using refrigerant-11 (trichloromonomfluoromethane, CC13F) instead of refrigerant-12 to check system hydraulics.

---
1 Status as of July 1, 1968.
<table>
<thead>
<tr>
<th>Packed Column Name</th>
<th>Diameter inch</th>
<th>Packing Height feet</th>
<th>Type</th>
<th>Total Surface Area sq ft</th>
<th>Total Number of Tubes</th>
<th>Average Length of Tubes feet</th>
<th>Outside Tube Diameter inch</th>
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<tr>
<td>Absorber</td>
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<td>9</td>
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<td></td>
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<tr>
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<td>4</td>
<td>6</td>
<td>7/8</td>
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<tr>
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<td>U-Tube</td>
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<td>18.3</td>
<td>1</td>
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<tr>
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<td>Shell and Tube</td>
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<td>10.8</td>
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<td>19</td>
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<td>Coil in Refrigerated Bath</td>
<td>3.8</td>
<td>1</td>
<td>23.4</td>
<td>3/4</td>
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<tr>
<td>Fractionator and Stripper Reboilers</td>
<td></td>
<td>Electric Heater</td>
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<td>-</td>
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<tr>
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<td>1</td>
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<td>Type</td>
<td>Total Surface Area sq ft</td>
<td>Total Number of Tubes</td>
<td>Average Length of Tubes feet</td>
<td>Outside Tube Diameter inch</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
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<td>------------------------</td>
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<tr>
<td>3.2</td>
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<td>6.5</td>
<td>37</td>
<td>Tube Bundle in Refrigerated Bath</td>
<td>6.5</td>
<td>37</td>
<td>3.5</td>
<td>1/4</td>
<td></td>
</tr>
</tbody>
</table>

a The columns are filled with Goodloe Packing, a wire mesh material manufactured by the Packed Column Corporation, Springfield, New Jersey.
This substitution was made because the comparatively high boiling point of refrigerant-11, 74.8°F, permitted operation without final insulation, thus facilitating equipment and piping modifications. Also, as will be noted, refrigerant-11 is, itself, being considered as a potential process solvent, so the initial testing period was extended somewhat to permit collection of preliminary performance data for this material.

Results of Shakedown Tests. A summary of preliminary data obtained during the pilot plant shakedown operations is given in Table III. Although the system probably was not operated at the optimum conditions for a refrigerant-11 based process, and even though the operations were not always smooth because of the surges, etc, normally encountered in starting up a new system, the results were, nevertheless, encouraging. The pressures and temperatures used were absorption at about 28 atmospheres and 40°F, fractionation at about 3 atmospheres and 127°F, and stripping near 1.3 atmospheres and 87°F. The solvent flow rate was approximately 1 gpm, while the gas feed rate to the absorber column ranged between 5.1 and 6.6 scfm. This choice of gas flow rates was arbitrary, and higher rates have been employed without encountering flooding difficulties.
With krypton concentrations in the absorber gaseous feed stream between 470 and 2,740 ppm, the krypton removal appeared to be satisfactorily high; in these tests, krypton removals of from 85 to 98% were indicated.

The gas product flow rate, i.e., the stripper off-gas rate, was between 0.01 and 0.06 scfm, or approximately two orders of magnitude below the absorber feed rate. The krypton concentrations in the product were between 1.2 and 7.2%, resulting in overall krypton concentration factors of from 11 to 100. Because of the high oxygen content (49 to 65%) of the product stream and its relatively low flow rate, small, inexpensive chemical traps could have been used to remove the product oxygen, thereby increasing the concentration factors by more than a factor of two.

It should be emphasized that the primary purpose of these preliminary tests was to determine system performance and indicate necessary modifications prior to initiating the formal testing program, rather than to evaluate the potential of refrigerant-11 as a process solvent. The fact that krypton concentration factors near 100 (which is also the value reported for the carbon tetrachloride process[3]), were observed in some of the tests, however, is encouraging, and indicates that further work with this solvent is warranted.

Plans for Future Tests. The first series of pilot plant tests will be conducted with refrigerant-12 as the solvent. In these tests, the effects of varying temperatures, pressures, gas and liquid flow rates, and krypton feed concentrations will be studied, and data regarding stage lengths, pressure drops, and general performance will be collected. A similar testing series, centered around a somewhat higher temperature, will then be undertaken with refrigerant-11, to permit a comparison of the two solvents. Also, it is expected that various simplified flow sheets, obtained by bypassing some of the installed equipment items, and cleaning of special gas mixtures, e.g., argon-krypton mixtures, will be examined.

Conceptual Design Studies

The purpose of the conceptual study efforts is to provide preliminary equipment configurations and cost evaluations for noble gas systems designed for various radioactive gas cleaning applications. As an example, a mobile absorption plant, for emergency use in the case of a nuclear reactor accident, was considered in detail[10] in the early part of our program. The goal of this evaluation was to establish tentatively the basic design features and hardware availability and costs for a transportable system which could be moved to a reactor site soon after an accident, installed there, and then be used to process the gas in the containment vessel, decreasing the krypton concentration by a factor of 100 in one week. Since pilot plant data were not then available, the flow sheet selected was not necessarily the optimum one but was essentially the one recommended by the Brookhaven National Laboratory, i.e., use of refrigerant-12 as the solvent with a low temperature, minus 94°F, absorption step. The total capital cost for this system, including installation of the equipment in standard van-type trailers, was estimated to be between $630,000 and $880,000, depending on the technique used to supply low temperature refrigeration.

It is planned to continue these studies at a later date to develop information for other cases, including reactor systems and fuel reprocessing plant systems. Of course, the pilot plant results and also the results of the optimization studies will be valuable aids in establishing, for each application, the operating parameters and flow sheets which result in the most reliable and most economic plant units.
Absorption process optimization studies are being made to furnish guidelines for the conceptual plant work and to assist in the pilot plant testing program. A mathematical model of the process was developed, and a computer program was then written to facilitate parametric case studies. Equipment sizing and costing routines have been incorporated into the computer code so that estimates can be made of the optimum processing conditions for a given separation job, considering equipment size and performance, refrigeration costs, etc.

Initial calculations, using estimated stage heights, will be used to direct the refrigerant-12 and refrigerant-11 testing programs toward the most promising temperature, pressure, and flow ranges. Then, once pilot plant data have been obtained and added to the computer program, it will be used for final selection of processing conditions for the conceptual plant cases.

ACKNOWLEDGEMENTS

It is a pleasure for the authors to acknowledge the assistance of several persons who are involved in this program. At the ORGDP, Dr. D. I. Dunthorn, Messrs. D. L. Burkett and G. K. Haseltine, of the Gaseous Diffusion Development Division, are assisting in the pilot plant work; Messrs. B. F. Crump, J. L. Hammontree, S. W. Fiveash, R. E. Cooper, and T. Shapiro, of the Plant Engineering Division, participated in the conceptual plant studies; and Dr. E. von Halle and Mr. S. Blumkin, of the Operations Analysis Division, are performing the optimization studies. Also, the authors wish to acknowledge Drs. W. G. Belter and C. B. Bartlett, and Messrs. W. P. Gammill and I. C. Roberts, of the Environmental and Sanitary Engineering Branch, Division of Reactor Development and Technology, U. S. Atomic Energy Commission, for their technical suggestions, project guidance, and support.

REFERENCES

DISCUSSION

R. I. NEWMAN: Have you considered other fluorocarbons which would lend themselves to lower temperature operation? I had in mind the recovery of krypton in a reprocessing plant. Here the gas will be acidic and high-pressure operation could be difficult because of corrosion. It might be desirable to trade low temperature for high pressure.

J. R. MERRIMAN: In general, we have been more interested in considering fluorocarbons which would permit higher temperature operation. This is largely due to the fact that our preliminary economic analyses have shown refrigeration costs to be the most significant expense item in a scaled-up plant. It is likely, in addition, that gases which are acidic in nature could be treated before being fed to the noble gas collection system; for example, it should be possible to eliminate nitrous oxide using a straightforward catalytic decomposition. I appreciate your comment, and we will look into this matter in more detail.

H. ISBIN: Have you considered the possibility of applying your method of isolating krypton and xenon to boiling-water reactors operating with a nominal amount of fuel failure?

J. R. MERRIMAN: As yet, we have not made plans to consider, in terms of conceptual design studies, any application other than the three outlined in the first section of the paper. Of course, we would be interested in studying application of this process to any krypton-xenon removal problem which might be of concern.
RECOVERY OF XENON AND KRYPTON IN THE TREATMENT OF GASEOUS RADIOACTIVE WASTES

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Abstract

RECOVERY OF XENON AND KRYPTON IN THE TREATMENT OF GASEOUS RADIOACTIVE WASTES. In the course of investigations into the chemical recovery of radioactive krypton and xenon the possibility of a quantitative separation of both gases using fluorine as a reacting agent was studied as a basic problem. The influence of the reactants' mole ratios and reaction temperature on the synthesis of xenon fluorides is described. The results obtained during the study of the xenon-fluorine reaction kinetics are given. During this study 1: 10 and 1: 5 mole ratios of both reactants with an absolute pressure amounting to 3.3 atm at 22°C and temperatures of 110, 120 and 130°C were employed. It was found that under these conditions krypton does not react with fluorine and does not influence the xenon-fluorine reaction rate and direction. Experiments performed to remove traces of xenon from a bulk of krypton are described.

In April 1963, less than a year after the discovery of the first noble gas compound, Pomeroy [1] pointed out the possibility of the practical application of the discovery in reactor technology. He suggested an investigation into the chemical separation of radioactive xenon, which is formed in the fission process in a reactor, and it later became apparent that it might be possible to separate both krypton and xenon chemically.

The laboratory for fluorine chemistry at the Jožef Stefan Nuclear Institute in Ljubljana began research work on noble gas chemistry soon after the xenon tetrafluoride synthesis had been published by Argonne National Laboratory [2], and published the synthesis of xenon hexafluoride independently and practically at the same time as several American laboratories [3-7]. Fluorination in static systems under pressure was used for the synthesis and during the past few years the method has been further developed and refined.

Since 1967 much of the activity in our laboratory has been devoted to the investigation of the possibility of the preparation of xenon and krypton compounds which could be used in radioactive disposal. The project described is being investigated under the auspices of the International Atomic Energy Agency in Vienna and includes the following topics: (1) Fluorination of xenon and krypton under various conditions (2) Investigation of possible quantitative separation of xenon from krypton (3) Synthesis of stable krypton compounds, and (4) Study of the physical and chemical properties of the compounds obtained.

To try and solve some of these problems we decided (1) to investigate the influence of pressure, mole ratio and temperature on the xenon-fluorine reactions, (2) to determine the reaction conditions where xenon reacts with fluorine while krypton does not, and (3) to purify krypton from traces of xenon.
The xenon fluoride synthesis was carried out in vessels like that shown in Fig. 1. The reactor is equipped with a pressure transmitter for continuous pressure measurements. In our first experiments the pressure was measured as a function of temperature for a gaseous mixture of xenon and fluorine at different pressures and mole ratios. In a typical experiment a xenon-fluorine mixture of known mole ratio was compressed in the reaction vessel up to a certain pressure. The reactor was then heated at a rate of 2.5 degC per minute and the pressure was measured continuously. A typical graph is shown in Fig. 2. It was found that the xenon-fluorine reaction proceeds at a detectable rate at 140°C regardless of the pressure and mole ratio used in the experiment.

Contrary to the published data, the formation of xenon di-, tetra- and hexafluoride [8] was found to depend only on the temperature and not on the mole ratios of the reactants. This is clear from Fig. 3.

Three identical pressure vessels were filled with a fluorine-xenon mixture in a mole ratio 10:1 up to 33 atm abs measured at 22°C. All three vessels were heated at 120°C until the pressure was constant and then cooled down to 22°C before the pressure was measured again, neglecting vapour pressures of xenon fluorides at this temperature which amounted to a few mm Hg. Two vessels were heated further up to 150°C, while the contents of the third one were analysed. As soon as the pressure in the two vessels was constant, they were cooled down to 22°C, and the pressure measured. Again, the contents of one vessel were analysed while the remaining one was heated up to 200°C. The procedure was repeated also with this vessel. The results of this experiment are given in Table I.
The reaction rates were estimated from the time dependence of pressure at constant temperature. Fluorine-xenon mixtures with mole ratios of 10:1 and 5:1, the absolute pressure amounting to 33 atm and temperatures of 110, 120 and 130°C, were employed during this study. From the diagrams shown in Figs 4 and 5 the reaction rate for the xenon-fluorine reaction was calculated in the second part of the curve to be of first order with respect to xenon, while the activation energy was estimated to be 24 kcal/mole.

The influence of krypton on the xenon-fluorine reaction was also investigated. 3.5 atmospheres of krypton were added to a mixture of fluorine and xenon with a mole ratio of 10:1, the total pressure amounting to 36.5 atm at 22°C. The reaction vessel containing this mixture was heated
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure at 22°C (atm)</th>
<th>Pressure drop (atm)</th>
<th>Product composition</th>
<th>Fluorine content (%)</th>
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<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Calculated(^a)</td>
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<tr>
<td>120</td>
<td>33.0</td>
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<tr>
<td>200</td>
<td>33.0</td>
<td>20.9</td>
<td>12.1</td>
<td>XeF(_{6.05})</td>
</tr>
</tbody>
</table>

\(^a\) On the basis of the pressure drop.
FIG. 4. The reaction curve for xenon difluoride formation at 5:1 molar ratio.

\[ \text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2 \]

\( F_2 \text{ Xe} = 10 \text{ atm} \)

\( \rho^{298K} = 33 \text{ atm cm} \)

\( T = 120^\circ \text{C} \)

FIG. 5. The reaction curve for xenon difluoride formation at 10:1 molar ratio.
simultaneously with another identical reaction vessel containing xenon and fluorine only. From the graph shown in Fig 6 it is evident that krypton does not interfere with the formation of xenon fluorides.

According to Weinstock [9], during the formation of lower xenon fluorides small fractions of xenon can remain unreacted. Attempts were made by this laboratory to remove traces of xenon from krypton. Several preliminary experiments were run using a tracer method to follow the removal of xenon from the mixture of xenon, krypton and fluorine. 8 ml of activated xenon were added to 600 ml of krypton-fluorine mixture at normal conditions with a mole ratio of 1:2 at room temperature and atmospheric pressure. The mixture was subjected to a high-frequency, high-voltage electrical discharge at -80°C in a glass reactor. The krypton difluoride formed is probably consumed by fluorination of xenon, forming higher xenon fluorides. Using this method, it is possible to purify krypton containing 4% xenon within 24 hours to 99.998% krypton.

So far we have found out that it is possible to bind xenon by direct fluorination, whereas krypton remains unreacted. This reaction yields xenon difluoride at lower temperatures (around 120°C). The reaction rate for such a reaction was determined to be of first order in regard to xenon. The xenon-fluorine reaction can be directed into the formation of xenon di-, tetra- or hexafluoride merely by variation in temperature. We could prepare as much as 50 g xenon fluorides in one batch or, in other words, bind approximately 5 litres of xenon at normal temperature and pressure. Using a high-frequency, high-voltage spark discharge on a gaseous mixture of krypton, xenon and fluorine, we were able to remove traces of xenon from krypton. The method proposed could be applied for the removal of radioactive xenon from krypton, and for the preparation of solid compounds which are more easily stored than the radioactive gases. After decay to non-radioactive xenon-131, the xenon fluoride, which is now
XeF_x can be used as a fluorinating agent. Before this work can be properly evaluated, it is necessary to design and test remote-controlled equipment which can be used on radioactive xenon straight from a reactor.

The work would be also of much greater value if some effort could be devoted to the preparation of stable krypton compounds.

ACKNOWLEDGEMENTS

I would like to mention the names of co-workers who took part in this investigation: A. Šmalc, B. Žemva, A. Zemljič, B. Sedej, B. Frlec and J. Kristan of the Jožef Stefan Nuclear Institute, Ljubljana, A. N. Mosevič of the University of Leningrad and J. H. Holloway of the University of Aberdeen.

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REFERENCES

SEPARATION OF RADIOACTIVE XENON AND KRYPTON FROM OTHER GASES BY USE OF PERMSELECTIVE MEMBRANES*

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OAK RIDGE, TENN., UNITED STATES OF AMERICA

Abstract

SEPARATION OF RADIOACTIVE XENON AND KRYPTON FROM OTHER GASES BY USE OF PERMSELECTIVE MEMBRANES. A process is being developed for separating radioactive xenon and krypton from other inert gases or from air by use of a dimethyl silicone rubber membrane. This separation is based on the solubilities of the gases in, and their rates of transport through, the membrane. Applications include the removal of the noble gases from: (1) the air within a reactor containment building, e.g. after an accidental release of fission products; (2) the off-gas from a processing plant for spent reactor fuels, and (3) the gas that blankets nuclear reactors, especially those which continuously vent volatile fission products, such as the molten salt or the sodium-cooled breeder reactors.

The transport of a gas through a permselective membrane is measured in terms of a permeability factor, which is defined as the product of the thickness of the membrane and the flow rate of gas through the membrane per unit area of membrane and per unit differential partial pressure of the gas across the membrane. The relative values of these factors for xenon, krypton, oxygen and nitrogen through dimethyl silicone rubber are 203, 98, 60 and 28, respectively. The factors were about one-half these values when the membrane was mounted between two Dacron mats for physical support.

In our experiments the permeability factors decreased, but the stage separation factors, the ratio of the concentrations of the gases in the product and reject streams, increased, as the pressure across the membrane increased or as the temperature decreased. The stage separation factor was also larger with countercurrent than with cocurrent flow of the gases through the membrane unit. Attempts to correlate experimental with computed separation factors have been partially successful. Efforts are under way to improve the membrane and to design a compact, reliable multimembrane stage unit. Preliminary calculations of the cost of removing and concentrating the noble gases by a cascade of permselective membrane units indicate that this method is economically competitive with other proposed processes.

1. INTRODUCTION

A process is being developed for removing xenon and krypton from other gases by use of a permselective membrane composed of thin sheets of methylphenyl silicone rubber. This separation is based on the difference in the solubility of the gases in, and their different rates of transport through, the membrane. Applications for the process include the removal of noble gas fission products from: (1) the air within a reactor containment building, for instance, after an accidental release of fission products; (2) the off-gas from a plant for processing spent reactor fuels; and (3) the gas that blankets nuclear reactors, especially the reactors, such as the molten salt and the sodium-cooled breeder reactors, which continuously vent volatile fission products.

The removal of noble gases from air has been studied extensively in USAEC-sponsored research. The most frequently used method involves adsorption of the noble gases

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* Research sponsored by the US Atomic Energy Commission under contract with the Union Carbide Corporation.
** Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn.
on charcoal either at ambient or low temperature [1, 2]. Except for the permselective membrane process and the Freon extraction process currently being considered by J. R. Merriman [3], all the separation processes require either low temperatures (less than -70°C) or facilities that occupy large volumes [4] or require locally available favorable geological formations [5]. Processes that occupy a small volume and that may be conducted at ambient temperature may have advantages in cost, reliability, and transportability.

The different rates of permeation of gases through polymers have been recognized for more than a hundred years [6]. However, commercial separations have become practical only recently, that is, after the development of very thin sheets of synthetic polymers that are highly permeable but free of holes [7]. Although any membrane may be used for separating gases, silicone rubber has a much higher permeability than any other material that has been tested [8].

The process described in this paper is being developed jointly by personnel from the Oak Ridge National Laboratory, the Oak Ridge Gaseous Diffusion Plant, and the General Electric Research and Development Center at Schenectady, New York. This report includes the results of laboratory experiments and engineering design calculations based on these results. Future work includes effects on the membrane of irradiation and contaminants such as water, iodine, and particulates; design and testing of engineering components; and operation of a pilot plant unit. The laboratory development, engineering design, and component testing are being done at Oak Ridge. The membrane development is conducted at Schenectady. The personnel at the Oak Ridge Gaseous Diffusion Plant have assisted with data calculations, especially in determining cost values for a membrane cascade. Students from the School of Chemical Engineering Practice, Massachusetts Institute of Technology, under the direction of S. M. Fleming and H. D. Cochran, Jr., made valuable contributions to the program. R. C. Lovelace, R. H. Shigley, C. L. Roggenkamp, and T. E. Harmon conducted many of the experiments.

2. EQUIPMENT AND PROCEDURE

The membrane used in this study was prepared by the General Electric Company and has the following composition:

100 parts (by weight) methylphenyl polymer containing 5.3 mole % \(^1\) phenyl groups and 0.1% vinyl groups (specific gravity = 0.98)

44 parts (by weight) fumed silica

Volume fraction of filler (calculated) = 0.164

It was partially cured with 0.5% bis-2,4-dichlorobenzoyl peroxide; then it was heated at 150°C for 1 hr in an oven. This silicone rubber was prepared, free of holes, in sheets about \(4.6 \times 10^{-3}\) cm thick, and was bonded between two sheets of 0.01-cm-thick Dacron mat for support.

The test unit contained a sheet of this material, about 30 by 60 cm, held between two stainless steel plates to withstand 150 lb/in\(^2\) operating pressure. The membrane unit was separated from the stainless steel plates by plastic screens that also acted as gas turbulence promoters. (For a description of an optimized membrane unit, see Sect. 5.)

\(^1\) Calculated as percentage of total substituent groups on silica.
FIG. 1. Laboratory equipment for determining the permeabilities and separation factors of gases by using a permselective membrane.
Equipment to regulate the pressure and the flow of gases, to determine and record the radioactivity of the gas streams, and to recycle the used gas to the feed vessel is shown in Fig. 1.

The gases were oxygen, nitrogen, or argon, either pure or mixed with less than 0.5 vol.% krypton or xenon containing $^{85}\text{Kr}$ or $^{133}\text{Xe}$, respectively, as a radioactive tracer.

3. DIFFUSION THEORY

The transport of a gas through a membrane requires the following steps: (1) contact of the gas with the surface of the membrane, (2) dissolution of the gas in the membrane, (3) diffusion of the gas through the membrane, and (4) evaporation of the gas from the low-pressure surface of the membrane. This process is quite different from the transport of gases through a porous membrane (Fig. 2). With porous membranes, the separation of gases is proportional to the ratio of the square roots of their molecular weights. With a permselective membrane, the separation is proportional to the ratio of the products of the solubilities in, and the diffusivities through, the membrane.

The properties of most gases in polymers have been found to obey Henry's Law of solubility:

$$S = K \ p$$

and Fick's Law for diffusion [9]:

$$N_i = -AD_i \frac{dC_i}{dt}$$

where

- $S$ = solubility,
- $K$ = solubility constant,
- $p$ = partial pressure,
- $N_i$ = flow rate of the gas $i$ through the membrane,
- $A$ = membrane area,
- $D_i$ = diffusivity of the gas in the rubber,
- $C_i$ = concentration of the gas in the membrane,
- $t$ = distance into the membrane.

If we assume that $D$ and $K$ are not functions of the thickness of the membrane, substituting and solving the differential equation yields:

$$N_i = \frac{AK_iD_i\Delta p_i}{t}$$
FIG. 2. Diagram explaining differences in the actions of gases flowing through (a) a porous and (b) a permselective membrane.

where

$$\Delta p = \text{difference in the partial pressures of component } i \text{ on the two sides of the membrane},$$

$$t = \text{thickness of the membrane}.$$  

We can define the permeability $$P_i$$ as

$$P_i = K_i D_i$$

then by substituting this equation into the preceding one and rearranging, we obtain:

$$P_i = \frac{N_i \cdot t}{A \Delta p_i}$$

The units used in our study are:

$$N = \text{ml (STP) per sec},$$

$$t = \text{cm},$$

$$A = \text{cm}^2,$$

$$\Delta p = \text{cmHg}.$$  

For convenience we have multiplied the permeability by $$10^9$$ in this paper. The permeation of gases through this type of membrane has been shown to be related to the critical temperatures of the gases [10].
Our test equipment is arranged as follows:

![Diagram of test equipment](image)

We have defined "percent cut" or "cut" as the flow rate of the extract multiplied by 100, divided by the flow rate of the feed. In our experiments we used dilute mixtures (less than 0.5%) of xenon or krypton containing tracer quantities of 133 Xe or 85 Kr, respectively. We assumed that there was no concentration gradient perpendicular in the "x" direction to the membrane since this distance is about 3 mm and since the system contains a turbulence promoter. Because of the different rates of transport of gases through the membrane at any practical operating condition, a concentration gradient will exist along the membrane in the "y" direction. We have assumed that the change in composition is linear and have, therefore, used the average of the concentrations of the feed and the raffinate as the concentration on the high-pressure side of the membrane and the concentration of the exiting extract as the concentration on the low-pressure side. Experiments at various cuts gave a series of permeabilities which when extrapolated to zero cut (no concentration gradient in y direction) is defined as a "true permeability."

The stage separation factor for a two-gas mixture is defined as:

$$\alpha = \frac{E_1}{E_2} = \frac{E_1}{E_2}$$

where

- $E_1$ = mole fraction of noble gas in the extract,
- $E_2$ = mole fraction of carrier gas in the extract,
- $R_1$ = mole fraction of noble gas in the raffinate,
- $R_2$ = mole fraction of carrier gas in the raffinate.

In our system the mole fraction of the carrier gas was more than 0.99 in both the extract and the raffinate ($E_2$ and $R_2$); therefore, the stage separation factor of the noble gas was approximately equal to the ratio of the concentrations of noble gas in the extract gas to its concentration in the raffinate gas. The stage separation factor at zero cut and zero back pressure $\alpha_0$ may also be shown to be:

$$\alpha_0 = \frac{p_1}{p_2}$$

Our system operates with atmospheric pressure on the low-pressure side. The effect of this back pressure on separation factor has been shown by Blumkin [11] to be:

$$\alpha^* = \frac{\alpha_0}{1 + R(\alpha_0 - 1)}$$
where $R$ is the ratio of the low pressure to the high pressure and $\alpha^*$ is the separation factor at zero cut.

The mathematical relationship between cut and the permeability or the separation factor could not be integrated analytically but the solution was approximated numerically by use of a computer [11].

4. LABORATORY EXPERIMENTAL DATA

The laboratory program has included the measurement of the permeability and the separation factors for xenon, krypton, oxygen, and nitrogen over the range of operating conditions. Preliminary evaluations have indicated that a process plant would be operated at ambient temperature, and at a pressure of about 150 lb/in$^2$ on the high-pressure side and at atmospheric pressure on the low-pressure side of the membrane. Calculations indicate that about one-third of the gas should flow through the membrane at each stage of the cascade for most efficient operation.

The original measurements for silicone rubber membrane were made by Robb at the General Electric Company [12]. He found that this membrane, when unbonded to a support mat, gave permeabilities of 28, 60, 98, and 203 for pure nitrogen, oxygen, krypton, and xenon, respectively. The permeabilities determined at both General Electric Company and Oak Ridge National Laboratory by using membrane that was bonded on each side to Dacron mats were approximately one-half these values and decreased slightly with increasing pressure (see data for argon, nitrogen, and oxygen in Fig. 3). This decrease in permeability has been shown to be due to the compression of the support material, which, in effect, increases the back pressure on the membrane. Most of this effect has been eliminated by improving the support material (see Sect. 5).

The permeability for components of a gas mixture, as measured in our system, varied with the pressure drop, percentage of the gas passing through the membrane (cut), composition of the gas mixture, and temperature. Because of the large volume of gas that
would have been required, the permeabilities of krypton and xenon could not be measured in our existing equipment by using the pure gases. Hence, the permeabilities of krypton and xenon were obtained by extrapolating a plot of permeability versus cut for dilute mixture of the noble gas in a carrier gas to zero cut. When dilute mixtures of each of these noble gases in oxygen or nitrogen were tested, no measurable effect of the dilute gas on the permeability of the carrier gas was noted — as can be seen by comparing the permeability of pure oxygen and nitrogen in Fig. 3 with the permeability of these gases mixed with less than 0.5% xenon in Fig. 4. However, the type of carrier gas had a large effect on the permeability of the xenon (Fig. 4). Figure 5 shows the effect of cut on the permeabilities of a mixture of krypton and nitrogen. As expected, there was no effect of cut on the permeability of the nitrogen. The permeability of the krypton decreased sharply with cut and the permeability of the krypton was obtained by extrapolation to zero cut. The decrease in permeability of the dilute gas varied with cut and with type of carrier gas. As can be seen from the data for mixtures of xenon in nitrogen, helium, or oxygen at 50% cut (Fig. 6), the permeability of the xenon was directly proportional to the permeability of the carrier gas.

In the temperature range -20°C to 80°C, the plot of log permeability vs 1/°K gave a linear relationship [10, 13, 14]. (A plot of the data over the temperature range 20 to 80°C is given in Fig. 7.) These data were obtained with small membrane samples where the membrane thickness was known only to about ±20%. Hence, the absolute permeability values will differ from other permeability data by this amount. However, a single membrane sample was used for testing each gas and thus the effect of temperature is precise.

FIG. 4. Effect of the carrier gas on the permeability of xenon in a mixture containing less than 0.5% xenon in nitrogen or oxygen.
FIG. 5. Permeabilities of krypton and nitrogen as functions of cut and pressure drop across the membrane.

FIG. 6. Effect of the permeability of the carrier gas on the permeability of xenon in mixtures containing less than 0.5% xenon in nitrogen, oxygen, or helium.
FIG. 7. Effect of temperature on the permeabilities of krypton, oxygen, air, and nitrogen.

An important parameter in cascade calculations is the stage separation factor $\alpha$, which varies with both the pressure drop and the cut. We have shown that the separation factor at zero cut, $\alpha^*$, increases with increasing pressure drop (Fig. 8); this agrees with theoretical considerations. The $\alpha^*$, obtained by extrapolating the stage separation factor to zero cut, can be fitted to the following equation which has been proposed by S. Blumkin (see Sect. 3):

$$\alpha^* = \frac{\alpha}{1 + R(\alpha - 1)}$$

As the flow of gas through the membrane increases, $\alpha$ increases. It was shown that $\alpha$ increases with both cut and pressure drop, becoming greater than $\alpha_0$ (the permeability of krypton divided by the permeability of nitrogen or oxygen) at 100 lb/in$^2$ pressure difference and a cut greater than about 10%. Using either cocurrent or countercurrent flow made no measurable difference in the permeability or separation factor of any system tested. Efficient separation of noble gases from air or argon is, therefore, practical under the proposed operating conditions of 150 lb/in$^2$ pressure drop and 30% cut.

5. DEVELOPMENT OF IMPROVED MEMBRANE

The General Electric Company Research and Development Center developed the membrane package used in this program under a subcontract from the USAEC. As discussed previously, the permeability of the membrane package (i.e., membrane that is
supported between two sheets of Dacron mat) was about half of that of unbonded mem­brane. Investigations by H. P. Briggs at General Electric have shown that about 40% of this loss in permeability may be recovered by bonding the membrane to a properly selected mat on only the low-pressure side and by proper selection of support and turbu­lence promoting screens.

Briggs and his co-workers tested numerous backing materials and supporting screens in order to select a combination of materials that would give the lowest flow resistance in the directions normal and parallel to the membrane. The tests consisted in measuring the permeation of oxygen under pressure drops ranging from 15 to 150 lb/in$^2$ for each support combination. Using similar membrane samples, some backing materials exhibited low permeation rates, while other samples of the same material, but having different thicknesses and weights, exhibited higher permeation rates. Also, some of the samples were found to have a satisfactory porosity normal to their surfaces under low pressure but were relatively nonporous (i.e., showed a decrease in the permeation rate) as the pressure drop across the membrane increased to 150 lb/in$^2$.

In many of the tests the membrane showed evidence of being depressed, or deformed, by the openings in the supporting screen. The permeabilities obtained by using these supporting materials were generally lower than those obtained with the other materials, and they decreased as the pressure increased. The deformation of the support mat into the openings in the screen would reduce the cross-sectional volume of the screen that is available for gas flow; it would also create many points of high stress. Therefore, the fibers of the support mat must have sufficient strength to span the openings in the screen, as well as exhibit high resistance to compression. However, the fibers must not puncture the membrane.

The most favorable permeability data were obtained with a mat, 0.018 cm thick and weighing 30 g/m$^2$, that was composed of polyester fibers and a polyvinyl binder. The

![Figure 8](image-url)
FIG. 9. Schematic diagram for removing xenon and krypton from the argon cover gas of a 1000 MW(e), sodium-cooled fast reactor.
oxygen permeability factor for this material was 56.5, as compared with 60 for an un­
bonded membrane. No decrease in permeability occurred with pressure drops up to 150
lb/in\(^2\) across the membrane.

Briggs and his co-workers conducted a similar study to choose the best screen sup­
port. They investigated screens made of polyester nonfilament or stainless steel wire
having various diameters and sizes of mesh openings. They found that two screens on the
low-pressure side of the membrane provided the most satisfactory arrangement. A poly­
ester screen (0.028-cm threads, 60 threads per centimeter, 0.081-cm mesh opening, 55%
open area) was positioned adjacent to the support mat, and a stainless steel screen
(0.019-cm wire, 61 wires per centimeter, 0.087-cm mesh opening, 67.2% open area) was
placed behind the plastic screen. These two screens have similar fiber spacing, but the
stainless steel wire is smaller than the plastic filament, thereby resulting in a larger
open area. The stainless steel screen could not be used immediately adjacent to the mat
because it contained sharp wire points that would puncture the membrane. Also, it had
a tendency to buckle under high stress conditions to form sharp ridges, which would also
puncture the membrane.

A polyester nonfilament screen (0.114-cm threads, 44.5 threads per centimeter,
0.114-cm mesh opening, 58% open area) was included on the high-pressure side of the
membrane to induce turbulent flow. The large, smooth fibers of this screen exhibited a
negligible tendency to puncture the unprotected rubber membrane.

6. DESIGN OF ENGINEERING-SCALE MEMBRANE UNIT

A 10-yd\(^2\) multimembrane single-stage unit containing 45 sheets of 1- by 2-ft mem­
brane is being developed by the General Electric Company for evaluation by the Oak
Ridge National Laboratory. A 6- by 6-in unit that has satisfactory operating character­
istics has been fabricated. It contains a membrane surface equivalent to about 500 ft\(^2\)
per cubic foot of active volume (membrane, spacers, intermembrane space, etc., but not
end plates). Design calculations given in this report are based on the assumption that
the full-size engineering membrane packages will have the same operating character­
istics as the present existing single membrane units used in our laboratory studies; the
membrane package volume was assumed to be 500 ft\(^2\) of membrane per cubic foot. The
membrane price used in the design calculations was $10 per square yard of membrane
surface installed in a membrane package; this price is based upon General Electric
Company's projected cost of producing this membrane in commercial quantities. This
cost is much lower than that for experimental membrane units presently being made.

7. APPLICATION OF GAS SEPARATION PROCEDURES TO THE NUCLEAR INDUSTRY

Costs have been estimated for permselective membrane plants to remove xenon and
krypton from the cover gas that blankets nuclear reactors, or from a reactor containment
building following an accidental release of fission products. For example, the size and
cost of a plant (Fig. 9) for removing and concentrating the noble gases from the argon
cover gas from a sodium-cooled 1000-MW(e) fast breeder reactor (designed by Babcock
and Wilcox Co.) with vented fuel elements was evaluated [15]. This plant would con­
tinuously process a small stream (0.01 to 10 standard ft\(^3\)/min) of the cover gas, decon­
taminating it sufficiently to allow greater than 90% of the gas to be recycled to the
reactor cover gas or discharged to the atmosphere. The concentrated gas from the top
of the cascade would be compressed to 2200 lb/in\(^2\) and stored in conventional gas cylinders. The equilibrium activity of the cover gas is a function of the processing rate; data are given in Table I for gas feed rates of 0.01, 1.0, and 10 standard ft\(^3\)/min. The activity in the gas would increase from \(5.5 \times 10^6\) to \(3.1 \times 10^7\) curies in the 25,000-ft\(^3\) gas space as the processing rate decreases from 10 to 0.01 standard ft\(^3\)/min. Xenon-133 would account for 80 to 95% of the total activity.

The data in Table II show the performance, size, and cost of cascades for three modes of operation at a gas feed rate of 10 standard ft\(^3\)/min. The first, second, and third columns of the table give the results for recycling 90, 99, and 99.8%, respectively, of the feed. In each case, the activity of the recycle gas is reduced to slightly less than 5000 \(\mu\)Ci/sec, a value that is acceptable for either recycle or discharge to the atmosphere.

It is interesting to note that the concentrated product may be stored in a very small volume. The number of conventional gas cylinders required per week are 50, 5, and 1, respectively, for the three cases calculated. The gas from one week's operation would produce about \(3.2 \times 10^6\) W of heat.

The costs of the three plants do not vary widely. A plant for concentrating the original volume of gas by a factor of 10 would cost $289,000 versus $366,000 for concentration by a factor of 500.

Similarly, the application of a membrane system to remove the noble gases from a reactor containment vessel following a reactor accident was evaluated. In order to compare various processes for removing radioactive materials from a containment shell following a nuclear accident, it was necessary to choose a standard accident [16]. We selected a maximum credible loss-of-coolant accident involving an advanced water-cooled reactor with the following characteristics (based on the letter from J. A. Lieberman, "Request for Review by Water Reactor Safety Program Office of Proposals on Filter Tests and Noble Gas Removal"):

<table>
<thead>
<tr>
<th>Power, MW</th>
<th>3200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>1000</td>
</tr>
<tr>
<td>Flux, n cm(^{-2}) sec(^{-1})</td>
<td>(3 \times 10^3)</td>
</tr>
<tr>
<td>Fuel loading</td>
<td></td>
</tr>
<tr>
<td>Tonnes of uranium</td>
<td>100</td>
</tr>
<tr>
<td>Grams of uranium</td>
<td>(10^8)</td>
</tr>
<tr>
<td>Fuel enrichment</td>
<td>2.3</td>
</tr>
<tr>
<td>235(^U), % moles</td>
<td>(10^4)</td>
</tr>
<tr>
<td>atoms</td>
<td>(6 \times 10^{27})</td>
</tr>
<tr>
<td>Containment shell volume, ft(^3)</td>
<td>(3 \times 10^6)</td>
</tr>
<tr>
<td>Time to accident (at end of fuel life)</td>
<td></td>
</tr>
<tr>
<td>Days</td>
<td>625</td>
</tr>
<tr>
<td>Seconds</td>
<td>(5.4 \times 10^7)</td>
</tr>
<tr>
<td>Fuel irradiation, MWd/tonne</td>
<td>20,000</td>
</tr>
</tbody>
</table>
Under these conditions, the concentrations of krypton and xenon in the containment shell would be about 100 and 660 ppm, respectively; and, since most of the xenon and krypton would be nonradioactive, these concentrations would not decrease appreciably with time. After a period of 1 d, the activity of the xenon would be about 150 times that of the krypton, and the total activity in the containment shell would be more than $2 \times 10^8$ Ci (3.5 x $10^5$ W). However, because of the relatively short half-life of the xenon (the longest half-life, 5 d, is that of $^{133}$Xe) and the long half-life of much of the krypton (10–$^\gamma Kr$), the total activity would decrease rapidly until, after about 45 d, the krypton would become the limiting radioactive isotope. The activity level (due to krypton) would then remain at about $10^6$ Ci for several years.

It was assumed that the noble gases in the containment shell will be removed by three mechanisms simultaneously: radioactive decay, discharge to the atmosphere at $10^4$ Ci per day, and a noble gas-air separation facility. The following equation was developed by E. D. Arnold and J. N. Lyness, of ORNL, to determine the amount of xenon remaining in the containment shell after various periods of time:

$$X(t) = X_0 e^{-\alpha t} \left(1 - \mu \int_0^t \frac{dT}{X_0 e^{-\alpha T} + Y_0 e^{-\beta T}}\right), \quad 0 \leq t \leq \gamma$$

where

- $X(t)$ = activity of xenon at time, $t$, after processing starts,
- $X_0$ = activity of xenon when processing starts,
- $Y_0$ = activity of krypton when processing starts,
- $\alpha$ = xenon decay constant plus the process removal constant for xenon,
- $\beta$ = krypton decay constant plus the process removal constant for krypton,
- $\mu$ = rate at which gases are vented to the atmosphere,
- $\gamma$ = maximum value of $t$.

A similar equation may be used for krypton. Since neither of these equations can be integrated analytically, solutions were obtained with a code, RARGAS, that is programmed for the CDC-1604 computer. The application of this mathematical evaluation to the removal of krypton and xenon from a reactor containment shell by recycling the gas through a permeable membrane unit showed that the remaining activity was always limited by the krypton removal. Based on noble-gas removal conditions for a preliminary process design, calculations show that the time required to decrease the activity in the containment shell to $10^6$ Ci would increase from 7 d at a processing rate of 1382 ft$^3$/min to 26 d at a rate of 276 ft$^3$/min.

The system for removing noble gases in 7 d of operation has been described by Blumkin [17]. This process would require 31,300 yd$^2$ of membrane in 17 stages, and the

\[2\] The process removal constant is the reciprocal of the time required for the volume of gas in the containment shell to go through the membrane plant.
Table I. Calculated Concentration of Noble Gases Above the Sodium Coolant at a 1000 MW(e) Reactor Designed by the Babcock and Wilcox Company

Blanket Gas Volume = 25,000 ft$^3$

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>10 Ci</th>
<th>Atom/ft$^3$</th>
<th>1.0 Ci</th>
<th>Atom/ft$^3$</th>
<th>0.01 Ci</th>
<th>Atom/ft$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{83m}$Kr</td>
<td>9,800</td>
<td>0.140135 x 10$^{15}$</td>
<td>10,600</td>
<td>0.151575 x 10$^{15}$</td>
<td>10,700</td>
<td>0.153005 x 10$^{15}$</td>
</tr>
<tr>
<td>$^{85m}$Kr</td>
<td>39,800</td>
<td>0.134638 x 10$^{16}$</td>
<td>46,500</td>
<td>0.157303 x 10$^{16}$</td>
<td>47,300</td>
<td>0.16009 x 10$^{16}$</td>
</tr>
<tr>
<td>$^{85}$Kr</td>
<td>43</td>
<td>0.311655 x 10$^{17}$</td>
<td>418</td>
<td>0.302958 x 10$^{18}$</td>
<td>4,310</td>
<td>0.312380 x 10$^{19}$</td>
</tr>
<tr>
<td>$^{87}$Kr</td>
<td>70,000</td>
<td>0.681579 x 10$^{15}$</td>
<td>73,600</td>
<td>0.716632 x 10$^{15}$</td>
<td>74,000</td>
<td>0.720526 x 10$^{15}$</td>
</tr>
<tr>
<td>$^{88}$Kr</td>
<td>108,000</td>
<td>0.232494 x 10$^{16}$</td>
<td>119,000</td>
<td>0.256174 x 10$^{16}$</td>
<td>121,000</td>
<td>0.260480 x 10$^{16}$</td>
</tr>
<tr>
<td>$^{89}$Kr</td>
<td>9,660</td>
<td>0.396253 x 10$^{13}$</td>
<td>9,680</td>
<td>0.397073 x 10$^{13}$</td>
<td>9,680</td>
<td>0.397073 x 10$^{13}$</td>
</tr>
<tr>
<td>$^{131}$Xe</td>
<td>16,300</td>
<td>0.360976 x 10$^{17}$</td>
<td>97,500</td>
<td>0.215921 x 10$^{18}$</td>
<td>216,000</td>
<td>0.478348 x 10$^{18}$</td>
</tr>
<tr>
<td>$^{133}$Xe</td>
<td>89,400</td>
<td>0.379552 x 10$^{17}$</td>
<td>245,000</td>
<td>0.104016 x 10$^{18}$</td>
<td>302,000</td>
<td>0.128216 x 10$^{18}$</td>
</tr>
<tr>
<td>$^{133}$Xe</td>
<td>4,470,000</td>
<td>0.434665 x 10$^{19}$</td>
<td>18,800,000</td>
<td>0.182812 x 10$^{20}$</td>
<td>29,000,000</td>
<td>0.281997 x 10$^{20}$</td>
</tr>
<tr>
<td>$^{135}$Xe</td>
<td>62,200</td>
<td>0.127519 x 10$^{15}$</td>
<td>66,800</td>
<td>0.136950 x 10$^{15}$</td>
<td>66,900</td>
<td>0.137155 x 10$^{15}$</td>
</tr>
<tr>
<td>$^{135}$Xe</td>
<td>356,000</td>
<td>0.251855 x 10$^{17}$</td>
<td>479,000</td>
<td>0.338872 x 10$^{17}$</td>
<td>498,000</td>
<td>0.352314 x 10$^{17}$</td>
</tr>
<tr>
<td>$^{137}$Xe</td>
<td>33,900</td>
<td>0.182444 x 10$^{14}$</td>
<td>34,000</td>
<td>0.182982 x 10$^{14}$</td>
<td>34,000</td>
<td>0.182982 x 10$^{14}$</td>
</tr>
<tr>
<td>$^{138}$Xe</td>
<td>258,000</td>
<td>0.562025 x 10$^{15}$</td>
<td>261,000</td>
<td>0.568560 x 10$^{15}$</td>
<td>261,000</td>
<td>0.568560 x 10$^{15}$</td>
</tr>
<tr>
<td>$^{41}$Ar</td>
<td>2,200</td>
<td>0.309506 x 10$^{14}$</td>
<td>2,200</td>
<td>0.309506 x 10$^{14}$</td>
<td>2,200</td>
<td>0.309506 x 10$^{14}$</td>
</tr>
</tbody>
</table>

Total Ci

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>10 Ci</th>
<th>Atom/ft$^3$</th>
<th>1.0 Ci</th>
<th>Atom/ft$^3$</th>
<th>0.01 Ci</th>
<th>Atom/ft$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>237,303</td>
<td>259,798</td>
<td>266,990</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>5,258,800</td>
<td>19,983,300</td>
<td>30,377,900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5,523,103</td>
<td>20,243,098</td>
<td>30,644,890</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II. Performance and Cost of Several Cascades of Permselective Membranes for Separating Krypton and Xenon from Cover Gas of a Sodium-Cooled, 1000 MW(e) Reactor

Gas feed rate to cascade = 10 standard ft³/min

<table>
<thead>
<tr>
<th>Product Gas Rate (standard ft³/min)</th>
<th>1</th>
<th>0.1</th>
<th>0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cascade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number enriching stages</td>
<td>9</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Number stripping stages</td>
<td>19</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>Membrane area, yd²</td>
<td>4630</td>
<td>5020</td>
<td>5140</td>
</tr>
<tr>
<td>Cascade volume, ft³</td>
<td>~9</td>
<td>~10</td>
<td>~11</td>
</tr>
<tr>
<td>Power requirement, kW</td>
<td>126</td>
<td>136</td>
<td>140</td>
</tr>
<tr>
<td>Largest compressor, horsepower</td>
<td>9.2</td>
<td>7.9</td>
<td>7.7</td>
</tr>
<tr>
<td>High-pressure side of membrane, lb/in²</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Low-pressure side of membrane, lb/in²</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Feed Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr concentration, at.%</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Xe concentration, at.%</td>
<td>0.136</td>
<td>0.136</td>
<td>0.136</td>
</tr>
<tr>
<td>Kr activity, Ci/ft³</td>
<td>24.4</td>
<td>24.4</td>
<td>24.4</td>
</tr>
<tr>
<td>Xe activity, Ci/ft³</td>
<td>542.6</td>
<td>542.6</td>
<td>542.6</td>
</tr>
<tr>
<td>Recycle (or Vented) Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr concentration, at.%</td>
<td>0.47 x 10⁻⁵</td>
<td>0.49 x 10⁻⁵</td>
<td>0.46 x 10⁻⁵</td>
</tr>
<tr>
<td>Xe concentration, at.%</td>
<td>0.53 x 10⁻⁹</td>
<td>0.51 x 10⁻¹⁰</td>
<td>0.25 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Kr + Xe activity, Ci/ft³</td>
<td>0.029</td>
<td>0.030</td>
<td>0.028</td>
</tr>
<tr>
<td>Kr + Xe activity, μCi/sec</td>
<td>4350</td>
<td>4950</td>
<td>4657</td>
</tr>
<tr>
<td>Product Gas (to be stored)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kr concentration, at.%</td>
<td>0.04</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td>Xe concentration, at.%</td>
<td>1.4</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>Ar concentration, at.%</td>
<td>98.6</td>
<td>85.0</td>
<td>30</td>
</tr>
<tr>
<td>Kr activity, Ci/ft³</td>
<td>244</td>
<td>2440</td>
<td>12,200</td>
</tr>
<tr>
<td>Xe activity, Ci/ft³</td>
<td>5426</td>
<td>54,260</td>
<td>271,300</td>
</tr>
<tr>
<td>Concentration factor, product/feed</td>
<td>10</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>Number storage cylinders per week</td>
<td>50</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Installed cost, dollars</td>
<td>289,000</td>
<td>342,000</td>
<td>366,000</td>
</tr>
</tbody>
</table>

°Standard N₂ cylinders at a pressure of 2200 lb/in².
estimated capital cost is about $1,100,000. Later considerations have indicated that there would be little incentive for removing the noble gases from the reactor building so rapidly. A smaller plant that would remove the noble gases within 26 days, for instance, would have to be only one-fifth as large as the plant just discussed.

We have not yet accumulated sufficient data concerning the volume and composition of the off-gas from a reactor fuel processing plant to permit a membrane plant to be designed for this application.

In all of these systems we have assumed that iodine, particulates, excess water, and heat have been removed from the gas stream before the gas is fed to the membrane plant. (However, the permselective membranes are known to be highly efficient for removing particles and iodine.) In future studies, we will determine how these materials would affect the life of the plant.

8 CONCLUSIONS

We are investigating a process that uses a cascade of permselective membrane units for separating noble gases from other gases. Silicone rubber membranes with permeabilities for nitrogen of about 0.27 ft$^3$ per hour through 1 ft$^2$ of membrane that is about 2 mils thick at 150 lb/in$^2$ of pressure difference have been made. A stage separation factor of krypton from nitrogen of at least four was measured in laboratory experiments. Methods of mounting 2-mil-thick membrane that will allow it to withstand an operating pressure of 150 lb/in$^2$ without breaking have been developed; the decrease in permeability due to mounting is less than 20%.

Preliminary design calculations indicate that the cost of a plant to remove krypton and xenon from the argon blanket of a 1000-MW(e) reactor would be about $300,000. The cost of a plant to remove the noble gases from a reactor containment building following a nuclear accident may be about the same when removal times are realistic, i.e., approximately 30 days versus the previously postulated 7 days.

A 10-ya$^2$ engineering test unit is being developed, but no tests have been made. Current plans are to obtain engineering data on this unit and to determine membrane life expectancies and chemical and irradiation effects with small units.

REFERENCES


DISCUSSION

W. SCHIKARSKI: Have you made a comparison of your separation plant costs and those of a steel-shell double containment with low leakage, which probably could also solve the noble-gas problem?
R. H. RAINEY: We made no cost comparisons with other systems, but have merely attempted to evaluate the cost of our own system. Moreover, a steel-shell containment system is not a satisfactory solution for the disposal of $^{85}$Kr. This long-lived fission product has to be removed from the reactor building before inspection and recovery of the reactor can take place.
SPECIAL PROBLEMS RELATED TO HEAT AND MOISTURE

(Session V, Part 1)
Chairman: K. LEE
THE EFFECTS OF MOISTURE ON THE CHARACTER AND FILTRATION OF UO₂-STAINLESS STEEL AEROSOLS*

R.J. DAVIS, J. TRUITT, J.S. GILL AND W.D. YUILLE
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN., UNITED STATES OF AMERICA

Abstract

THE EFFECTS OF MOISTURE ON THE CHARACTER AND FILTRATION OF UO₂-STAINLESS STEEL AEROSOLS. Our program has the general purpose of understanding and ameliorating the hazards associated with aerosols which might result from a serious accident in the operation of a water-cooled, nuclear reactor. The filtration studies are for the purpose of demonstrating efficiencies of filtration of practical aerosol materials with commercially available absolute fibrous filters as a function of several practical parameters. The experiment is run as follows; the aerosol is generated by recirculating air over an electric arc in which the consumed electrode is an irradiated stainless steel tube with a cylindrical UO₂ insert. The aerosol is then recirculated through filter packs which contain three filters in series. The method has been shown to be reproducible to one part in $10^{-4}$.

Efficiencies have been measured for several commercial media as a function of velocity with dry and humid aerosol. Efficiencies are decreased above velocities of 7.5 ft/min. Non-waterproofed papers filter humid aerosol less efficiently than dry aerosol. The efficiency of waterproofed papers is also decreased by the humidity of the aerosol, particularly at high velocities and for particular media. A deleterious effect on filtration efficiency results when the media are stored for extended periods in a damp atmosphere. The filter penetrations were increased by as much as a factor of 20 as a result of storage in 100% humidity for six weeks. It was suggested, and theoretically justified, that this effect results from condensation of water between tiny fibers and the subsequent clumping of fibers due to the force of surface tension.

An exploratory study of the reaction between moisture and stainless steel-UO₂ aerosol particles generated in an electric spark has been performed using electron microscopy. Moisture affects the shape of the agglomerates. In dry air the agglomerates are chains of primary particles, in moist air the agglomerates are clumps. A calculation of the rate of removal of particles from a containment by the two phenomena: thermophoresis and diffusiophoresis is presented. Under conditions of interest the time for removal of half the particles by these mechanisms was estimated to be $10^2$-$10^5$ seconds.

Experiments were done to demonstrate that spark generated UO₂-stainless steel particles grow substantially in condensing steam due to condensation of water and that the rate of settling is thereby enhanced. In the experiment, aerosol was mixed with steam and the mixture led into the bottom of an air-cooled condensor. Control experiments were run without steam. The number concentration, the mass concentration and the particle size distribution of the effluent aerosol were measured. The results show that the mass and number concentrations of the effluent aerosol are substantially reduced and the relative number of the larger particles is substantially increased by condensing steam. Theoretical extrapolation of the data to estimate the enhancement by condensing steam of the rate of settling of particles in a containment vessel was made.

INTRODUCTION

If the coolant system of a large, water-cooled, nuclear, power reactor develops a hole; an abundance of steam will come out into the containment. The steam might be followed by a smoke of fuel and cladding material. Additional steam might issue as a result of emergency core cooling. In the extreme accident, therefore, the radioactive smoke and the containment filter would be expected to suffer the effects of high humidity and condensing steam.

* Research sponsored by the US Atomic Energy Commission under contract with the Union Carbide Corporation.
There are two objectives of our efforts which relate to the effects of humidity. One is to provide the data to show how well or how poorly available filter media function with practical aerosols at high humidities and temperatures. The second is to assemble quantitative descriptions of the important phenomena into formulations with which to calculate the rates of disappearance of aerosol particles from a containment.

**EFFECT OF HUMIDITY ON FILTRATION**

Measurements of filtration efficiencies of a selection of commercially available filter media to both wet and dry stainless steel-UO$_2$ aerosol have been made. The aerosol was generated in an electric arc in which the consumed electrode was an irradiated stainless steel tube with a cylindrical UO$_2$ insert. Figure 1 is a schematic diagram of the system. The procedure was to recirculate air past the arc through the 100-liter tank for 1-2 min, to valve off the arc loop and recirculate aerosol for about 15 min through two parallel filter assemblies, each of which contained three 1-1/4" discs of filter media in series, to replace the filter assemblies with a new set of filter discs and to recirculate aerosol for about 30 min through the fresh filters. In this way two determinations in duplicate of the efficiency of the filter media for a particular set of conditions was made. Dry aerosol (< 5% relative humidity) was obtained by flushing the system prior to use with dry air. Wet aerosol (~ 100% relative humidity) was obtained by maintaining water in the bottom of the tank. The filter efficiencies were taken to be the ratio of radioactivity on the first filter disc to the total activity on all three filter discs and the assembly parts between the filter discs.

The procedure has been demonstrated to be reproducible to one part in $10^4$, i.e., filter efficiencies in the range 99.97% can be measured to ± 0.01. This reproducibility is shown by data in Table I.

Data are shown in Fig. 2 and Fig. 3 as plots of percent penetration (100 minus percent efficiency) vs velocity. The dry aerosol (Fig. 2) at a velocity of 5 ft/min was filtered with approximately the nominal 99.97% efficiency (penetration 0.03%) by the waterproofed media. A small increase (a factor of 1.5 to 3) in penetration resulted from increasing the velocity. The non-waterproofed media were more readily penetrated than (about three times as much as) the waterproofed media.
Table I. Reproducibility of Filtration Efficiency Values
(Flanders 700 paper with dry aerosol at 5 ft/min)

<table>
<thead>
<tr>
<th>Efficiency (%)</th>
<th>Penetration (%)</th>
<th>Deviation from Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.990</td>
<td>0.010</td>
<td>-0.023</td>
</tr>
<tr>
<td>99.987</td>
<td>0.013</td>
<td>-0.020</td>
</tr>
<tr>
<td>99.983</td>
<td>0.017</td>
<td>-0.016</td>
</tr>
<tr>
<td>99.974</td>
<td>0.026</td>
<td>-0.007</td>
</tr>
<tr>
<td>99.974</td>
<td>0.026</td>
<td>-0.007</td>
</tr>
<tr>
<td>99.971</td>
<td>0.029</td>
<td>-0.004</td>
</tr>
<tr>
<td>99.968</td>
<td>0.032</td>
<td>-0.001</td>
</tr>
<tr>
<td>99.966</td>
<td>0.034</td>
<td>+0.001</td>
</tr>
<tr>
<td>99.965</td>
<td>0.035</td>
<td>+0.002</td>
</tr>
<tr>
<td>99.963</td>
<td>0.037</td>
<td>+0.004</td>
</tr>
<tr>
<td>99.960</td>
<td>0.040</td>
<td>+0.007</td>
</tr>
<tr>
<td>99.958</td>
<td>0.042</td>
<td>+0.009</td>
</tr>
<tr>
<td>99.954</td>
<td>0.046</td>
<td>+0.013</td>
</tr>
<tr>
<td>99.950</td>
<td>0.050</td>
<td>+0.017</td>
</tr>
<tr>
<td>99.948</td>
<td>0.052</td>
<td>+0.019</td>
</tr>
<tr>
<td>99.680*</td>
<td>0.320*</td>
<td>*</td>
</tr>
</tbody>
</table>

Average

99.97 ± 0.01

Range

+ 0.02

*Discarded

Three things seem to characterize the penetration by wet aerosol (as shown in Fig. 3). One is that the non-waterproofed media are less efficient, i.e., the penetration is about twice that for dry. The second point is that the increase in penetration with velocity (especially at 10 ft/min) is generally greater for wet aerosol. The highest penetration value (observed at 10 ft/min) was about 30 times the nominal 0.03%. The third point is that two of the waterproofed media tested were more affected by moisture than the others; in fact, the others did not show any significant increase in penetration at velocities 7.5 ft/min and lower.
FIG. 2. Filter efficiencies - dry stainless steel-UO₂ aerosol at 25°C.

FIG. 3. Filter efficiencies - wet stainless steel-UO₂ aerosol at 25°C.
Table II. Effect of Moisture on Filter

<table>
<thead>
<tr>
<th>Type of Filter</th>
<th>Penetration (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flanders 600</td>
<td>MSA Ultrahepa</td>
<td>Flanders 600</td>
</tr>
<tr>
<td>Stored in 100% relative humidity at room temperature 12-13 days</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Stored in 100% relative humidity at room temperature 43-45 days</td>
<td>0.57</td>
<td>0.35</td>
<td>0.67</td>
</tr>
<tr>
<td>Stored in 100% relative humidity at 80°C 24-48 hours</td>
<td>0.21</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>One drop of water put on filter disc</td>
<td>0.63</td>
<td>1.07</td>
<td>2.02</td>
</tr>
</tbody>
</table>

The effect of storing the filter media for long periods in high humidity prior to use is shown in Table II. In these tests, samples of filter media were stored in a closed container over water for the times and temperatures indicated. In one case (samples of non-waterproofed Flanders 600 media) were treated with one drop of water on each 1-1/4" disc just prior to use. The test aerosol was wet (100% relative humidity) stainless steel-UO2 aerosol at room temperature and the velocity was 5 ft/min.

The data in Table II show that storage in a damp atmosphere can significantly increase the penetration of filter media. The results were not very reproducible; the penetrations were 10-70 fold higher than the nominal 0.03%. 

The primary value of the above filtration efficiencies will be to indicate directly the effects of humidity and other parameters studied. It may, however, be valuable to relate the observations to filtration theory. Such an effort might suggest ways to improve the filter or ways to use the filter.

To relate the above effects on filter efficiencies to theory it is necessary to measure fiber diameter distribution in the media tested and particle size distribution. The fiber diameter distributions were measured both by optical and electron microscopy. (This work was done by T. E. Willmarth, Analytical Chemistry Division, ORNL.) The samples for optical microscopy were prepared by dispersing some of the filter media in water by use of an ultrasonic generator. Drops of the suspension were put on glass slides; the slides viewed with an optical microscope and the number of fibers as a function of diameter were observed. The data are shown in Fig. 4. The data show a predominance of fibers of about 2 micron diameter. In the second examination samples of the filter media were mounted in butyl-methyl methacrylate and sections of the mount, including fibers in cross section, were cut with an ultra microtome and viewed under an electron microscope. Again fiber count vs fiber diameter were made and the results are recorded in Fig. 5. These data show a second predominant fiber diameter of about 0.15 micron.

![Graph](image)

**FIG. 4.** Fibre diameter distribution obtained by optical microscopy.

The particle size distribution of fresh, dry, arc-generated stainless steel oxide aerosol was measured [1]. The measurement was made with a battery of instruments which give the number of particles in each of several particle size ranges: a GE condensation nuclei counter, a Whitby aerosol...
Analyzer and a Royco optical counter. No effort has been made yet to interpret the response of the instruments to the non-spherical agglomerates; the results shown in Fig. 6 were calculated from the particle sizes indicated directly by the instruments. The normalized weight-size frequency distribution was calculated from the number of particles, \( \Delta n_i \), in each particle size range, \( \Delta D_{p1} \) in which the average size was \( D_{p1} \), as follows:

\[
\text{Normalized wt.-size freq. distribution} = \frac{(\Delta n_i / \Delta D_{p1})^3}{\sum_{i=1}^{n} (\Delta n_i / \Delta D_{p1})^3} \quad (1)
\]

![Graph showing fibre diameter distribution obtained by electron microscopy.](image)

**FIG. 5.** Fibre diameter distribution obtained by electron microscopy.

![Graph showing normalized weight-size frequency distribution.](image)

**FIG. 6.** The distribution of the weight of disperse phase for an agglomerated stainless steel aerosol.
FIG. 7. Dry arc-generated stainless steel-UO₂ aerosol.

The area under the curve of this function vs particle size, between two values of particle size, is the fraction of the total weight or volume of particle phase which is in that particle size range. The size distribution in Fig. 6 is in good agreement with the "self-preserving" size distribution[2];

\[
\frac{dn}{dD_p} = K D_p^{-1.5} \tag{2}
\]

in the range \( D_p = 0.15 \) microns to \( D_p = 1.5 \) microns.
Particle shapes have been observed via electron microscopy of samples prepared with a thermal precipitator. The dry aerosol particles are chain agglomerates (as shown in Fig. 7) whereas the wet particles are clumps (as in Fig. 8).

The above data on fiber diameters and particle sizes have been used along with filtration theory [3,4] to see if the observed effects of aerosol velocity and of humidity on filtration efficiency are reasonable.
There are two predominant fiber sizes in the filter media tested: 2 microns and 0.15 microns. For the purpose of calculation it was assumed that typical filter media are made up of 95% (by weight) of 2 micron fibers and 5% of 0.15 micron fibers. Other assumed parameters were: temperature, 25°C; fiber density, $2.4 \text{g/cm}^3$; mat density, $0.0084 \text{g/cm}^2$; aerosol velocity, 5 ft/min; and particle density, $1 \text{g/cm}^3$. The filtration efficiency as a function of particle size was calculated for a mat ($0.008 \text{g/cm}^2$) of 2 micron fibers ($\varepsilon_1$ in Fig. 9) and for a mat ($0.0004 \text{g/cm}^2$) of 0.15 micron fibers ($\varepsilon_2$ in Fig. 9). It was presumed that these two sets of fibers act independently; that the 2 micron fibers collect a fraction $\varepsilon_1$ and pass a fraction $(1 - \varepsilon_1)$ and that the 0.15 micron fibers collect a fraction $\varepsilon_2$ of that which passes the 2 micron fibers, i.e., $\varepsilon_2(1 - \varepsilon_1)$. Hence the total filter efficiency, $\varepsilon_{\text{tot}}$, is:

$$\varepsilon_{\text{tot}} = \varepsilon_1 + \varepsilon_2(1 - \varepsilon_1)$$  (3)

Filtration theory [3] involves the summing up of three mechanisms which are active in filtration: diffusion (which is particularly efficient for very small particles), interception and inertial impaction (which are more efficient for larger particles). Intermediate-sized particles are not filtered very efficiently by any mechanism, hence there is a minimum in the efficiency-particle size curve shown in Fig. 9.

The first notable point from Fig. 9 (or the 5 ft/min curve in Fig. 10) is that the calculated filter efficiencies are too low compared to the nominal value of 99.97%; for instance, a 0.3 micron particle (which is the size of the standard test aerosol of dioctyl phthalate) is commonly filtered by absolute media with 99.97% efficiency but the calculated value is only 99.6%. This discrepancy is accepted as due to inexactness of filter theory as applied here and subsequently in this paper the theory is only used to indicate relative effects. The second point from Fig. 9 is that the small fibers are largely responsible for the work of filtration (i.e., $\varepsilon_2 > > \varepsilon_1$).
A set of similar calculations (to that shown in Fig. 9) was done to demonstrate the effect of aerosol velocity on filter efficiency. These are shown in Fig. 10. Higher velocity decreases efficiency of filtration (of smaller particles) by diffusion and increases the efficiency of filtration (of larger particles) by interception and impaction. The results on Fig. 10 show that the decrease in that part of the filtration efficiency contributed by the diffusion mechanism is the more significant under conditions of interest. It is apparent from Fig. 10 that a change of velocity from 5 ft/min to 10 ft/min of an aerosol with particles mostly in the range 0.1 to 0.4 microns (as in the case of interest) would approximately double the fraction of material which penetrates the filter. Indeed this was about what was observed with dry aerosol (Fig. 2). It is suggested, therefore (but not proven), that the observed effect of velocity for dry aerosol (as shown in Fig. 2) is simply a result of mechanical effects accounted for in filtration theory. The effect of velocity with wet aerosol (Fig. 3) was greater (a factor of 6-10 increase in penetration from 3 ft/min to 10 ft/min) and probably results in part from other effects.

It was postulated that a likely effect of humidity on the filter media was for water to condense as a film on the tiny (0.15 micron diameter) fibers and for surface tension to pull fibers together into bundles. This idea is pictured in Fig. 11. The bundles would function as single fibers of larger diameters. An idea of the magnitude of the effect of bundling of fibers on the filter efficiency is illustrated in Fig. 12, which shows the calculated filter efficiency (vs particle size) of the typical filter mat with 95% (by weight) 2 micron fibers, 5% 0.15 micron fibers, compared to the calculated filter efficiency of the same mat if all the 0.15 micron fibers had become bundles with diameters of 0.3 microns. It is shown that indeed this could be a very large effect; large enough to account for the effects of moisture observed. It is suggested (but again not proven) that bundling of fibers is the cause of the decrease in filter efficiency which results from storing the media in a high relative humidity for a long time (as shown by the data in Table II). Bundling of fibers may also be partly responsible for the increased penetration of particles in humid aerosol (Fig. 3) over that observed with dry aerosol (Fig. 2).
Another likely effect of humidity on filtration is a result of the clumping of particles in humid aerosol (as shown in Fig. 8 and as compared to dry aerosol in Fig. 7). Clumping will (presumably) decrease the effective diameter of the larger agglomerates; which will tend to put more of the particles in the size range which is not filtered efficiently (i.e., the minimum in the curves in Fig. 9). We are not able at present to quantitatively estimate the magnitude of this effect on filtration efficiency.

**FIG. 11. Effect of moisture.**

**FIG. 12. Effect on filtration efficiency of doubling diameter of small fibres by condensing moisture.**

In summary, filtration efficiencies were decreased by effects of moisture. One effect is on the filter media; this was demonstrated by the decrease in filter efficiency (for a wet aerosol) which resulted from storing the media for a long time in a damp atmosphere prior to use. It was suggested that bundling (or drawing together) of small fibers by the force of surface tension of touching, wet fibers was the cause. There is probably also a deleterious effect on filtration efficiency resulting from the effect of moisture on the particles. The particles clump in high humidity, which makes the effective size (of the larger agglomerates) smaller and closer to the particle size of minimum filtration efficiency.

**EFFECT OF HUMIDITY ON REMOVAL OF PARTICLES BY NATURAL EFFECTS IN A CONTAINMENT**

In the following, two questions are (partially) answered: how effective are thermophoresis and diffusiophoresis in removing particles from a containment atmosphere? How important is particle growth in high humidity (and the resultant enhanced settling rates) in removing particles?
Diffusiophoresis is the sweeping action which tends to carry particles toward a surface onto which condensation is occurring. Thermophoresis is the sweeping action of a thermal gradient; particles are swept toward the lower temperature.

If a water-cooled reactor loses its coolant and blows, like a great mechanical Moby Dick, then there will be steam in abundance. More steam may be generated by emergency cooling. All this steam will presumably condense within the containment; either onto spray drops or onto cool surfaces. Diffusiophoresis and thermophoresis are phenomena which will use the enormous power of decay heat to sweep particles from the containment atmosphere.

Diffusiophoresis and thermophoresis in steam-air systems is described by P. Goldsmith and F. G. May [5]. They briefly discuss the theory and present the results of a few very elegant experiments. They demonstrated very satisfactory agreement between theory and observation for diffusiophoresis and thermophoresis of particles generated from a hot nichrome wire.

The following development is largely from Goldsmith and May. The velocity of a particle due to diffusiophoresis in a flux of water vapor is:

\[ v_D = - \frac{257 \, dC}{dr} \]  

(4)

where \( v_D \) has units of cm/sec and the concentration gradient of water molecules, \( dC/dr \), has units of \((g/cm^3)/cm\). If the condensation is occurring onto spray drops, then the rate of growth of the drops is also related to the water molecule concentration gradient; hence:

\[ \frac{dm}{dt} = - 4\pi r^2 \frac{dC}{dr} \]  

(5)

where \( D \) is the diffusion coefficient for water in air and \( dm/dt \) has units of g/sec. It follows that

\[ v_D = \frac{257}{4\pi r^2 D} \frac{dm}{dt} \]  

(6)

The number of particles deposited on \( S \) drops (of containment spray) in time \( t \) is:

\[ \int_0^t \int_S v_D n \, 4\pi r^2 \, dt \]

where \( n \) is the concentration of particles \((no./cm^3)\). This number of particles is equal to the loss of particles from the containment atmosphere:

\[ - v \int_0^n \frac{dn}{n_o} \]

where \( V \) is the containment volume. Hence:

\[ \int_0^n \frac{dn}{n_o} = - \frac{257}{DV} \int_0^n \frac{dm}{dt} \, dt \]  

(7)

but \( S \) (the total number of drops) times \( m \) (the mass of water condensed on each drop) is simply the total mass of water condensed; let's call it \( W \).

\[ \log \frac{n}{n_o} = - \frac{257W}{2.303DV} = - \frac{257}{2.303(0.288)} \frac{W}{V} = - 387 \frac{W}{V} \]  

(8)
The mass of water condensed can be related to the heat removed from the core by evaporation:

$$w = \frac{H_L}{\Delta H} = \frac{H_L}{2.26 \times 10^3}$$  \hspace{1cm} (9)

where $H_L$ is the heat (in watt-sec) used to evaporate water and $\Delta H$ is the latent heat of evaporation (in watt-sec/g). Hence:

$$\log \frac{n}{n_0} = -0.170 \frac{H_L}{V}$$  \hspace{1cm} (10)

An analogous development for thermophoresis follows. Again from Goldsmith [5], the velocity of a particle in a temperature gradient is about:

$$V_T = -\frac{0.0660}{T} \frac{dT}{dr}$$  \hspace{1cm} (11)

The temperature gradient is also related to heat transfer by conduction (to a cold drop of surface area $4\pi r^2$)

$$\frac{dq}{dt} = K \frac{4\pi r^2}{dr} \frac{dT}{dr}$$  \hspace{1cm} (12)

where $K$ is the thermal conductivity (about $2.8 \times 10^{-4}$ watt sec/cm sec°C). Hence:

$$V_T = -\frac{0.0660}{T} \frac{dq}{dt}$$  \hspace{1cm} (13)

The number of particles deposited from $n$ particles/cm$^3$ onto $S$ drops in time $t$ is

$$\int_{0}^{t} SV_T n(4\pi r^2) dt$$

This is equal to the number of particles lost from the container,

$$-V \int_{0}^{n} dn.$$  \hspace{1cm} Hence:

$$n_o = -\frac{0.0660}{K V} \int_{0}^{t} \frac{dq}{dt} dt$$  \hspace{1cm} (14)

The integral $\int_{0}^{t} \frac{dq}{dt} dt$ is simply the total heat transferred to the drops via conduction which we will call $H_c$. Hence:

$$\log \frac{n}{n_0} = -\frac{0.0660}{2.303(373)(2.8 \times 10^{-4})} \frac{H_c}{V} = -0.324 \frac{H_c}{V}$$  \hspace{1cm} (15)

The sum of the two effects will result in

$$\log \frac{n}{n_0} = -0.170 \frac{H_L}{V} - 0.324 \frac{H_c}{V}$$  \hspace{1cm} (16)

where $H_L$ and $H_c$ are, respectively, the amounts of heat transferred to drops by condensation of water and by conduction. One could, in principle, determine
the fraction of heat transferred by each mechanism but it hardly seems worthwhile. It seems more appropriate to observe that the two heat transfer mechanisms (in the steam-air system) are similarly efficient; i.e., the constants in the above equations are only a factor of two different. Since condensation surely transfers most of the heat and since condensation is the least efficient in removing particles (and therefore to ignore thermophoresis is conservative) one can in fact ignore thermophoresis and

$$\log n/n_0 = -0.170 \frac{H_{\text{total}}}{V}$$  \hspace{1cm} (17)$$

The calculation has been done for two cases. One case is for the assumption that all the decay heat (of a 100 metric ton, 3200 Mw core which has operated 625 days) goes to form steam which later condenses on drops. The values for decay heat vs time for this case came from E. D. Arnold [6]. The second case was for the assumption that a 1 megawatt heater was used to generate steam which later condensed on drops. A containment volume of $10^{11}$ cm$^3$ was taken for both cases. The results are given in Fig. 13. Good mixing is implicitly assumed.

The conclusion is that indeed diffusiophoresis (and thermophoresis) are important mechanisms of particle removal from a containment vessel.

If the particles are soluble in water or contain soluble components (like CrO$_3$ in stainless steel oxide) then the particle may be expected to absorb considerable water. Such particles continue to be hygroscopic even after they dissolve; the drops of concentrated solution are hygroscopic. In other words, soluble nuclei can quickly become drops of water which are much larger and will settle faster than the original particles.

We have done an experiment to show that stainless steel oxide particles do grow, and to show approximately how much they grow. In the experiment aerosol was generated in an electric spark in which the consumed electrode was stainless steel. This aerosol, at a flow rate of 2 liter/min was mixed with 6 liter/min of clean air to which could be added (3 g/min of) steam. This mixture was brought into the bottom of an air-cooled condenser (a 4-inch diameter, 4 ft long glass tube). The effluent from the top of the condenser was analyzed for the case in which steam was added and for the case in which steam was not added.
The efficiency of particle removal by the condenser (i.e., the particle throughput without steam minus the throughput with steam; the difference divided by the throughput without steam) was 60–80% both in terms of particle number (as measured by a GE condensation nuclei counter) and in terms of weight of (dried) disperse phase (as measured by weighing dried samples on filters). The particle size distribution was estimated by analysis of the wet and dry effluent aerosols with an optical (Royco Model 220) particle counter (which covers the particle size range 0.3 microns and larger). A portion (600 ml/min) of the effluent aerosol was mixed with 14 l/min of clean air and 3 l/min of the mixture was fed into the optical counter. The particle count from the condensation nuclei counter (which counts particles > 0.01 micron) was used as an indication of number concentration of particles 0.01 to 0.3 microns. The results are shown in Fig. 14 as a plot of \( \frac{dn}{dD_p} \), the change in concentration per unit of particle diameter, as a function of particle diameter. (The values of \( \frac{dn}{dD_p} \) were calculated from the number of particles \( \Delta n_i \) in the size range \( \Delta D_p \), in which the average value of particle diameter is \( D_{p_i} \); as follows):

\[
\frac{dn}{dD_p} \sim \frac{\Delta n_i}{\Delta D_{p_i}}
\]

(18)

There are two points of importance in Fig. 14. The wet aerosol includes particles to 10 microns; there were no particles greater than 3 microns in the dry aerosol. The second point is that the distribution is flatter in the wet aerosol, i.e., there are more 1 micron particles in proportion to the number of 0.01 micron particles. Another way to make this point is as follows: if the particle size distribution takes the form:

\[
\frac{dn}{dr} = K r^{-x}
\]

then \(x\) is a smaller number for the wet aerosol than for the dry.

In the following paragraphs a simple reiterative, computer calculation is described which has the purpose of estimating the rate of removal of particles from a containment vessel as a result of coagulation and settling. This calculation is then applied to the above results to show the approximate effect of particle growth on removal rates by settling and coagulation.

The calculation of the rates of disappearance of airborne sodium aerosol as a result of agglomeration and settling (in a stirred tank) has been made in detail from first principles [7]. That calculation is, however, rather complicated and consumes much computer time. The following model is much simpler and may be found to be useful (for dilute aerosol). The calculation and its physical basis are outlined:

1. Establish a value of the initial volume fraction of the disperse phase, \(\phi_0\).

2. Assume that agglomeration and other natural processes give the self-preserving size distribution, that is:

\[
\frac{dn}{dr} = 0.05 \phi_0 r^{-4}
\]

where \(n\) is the concentration of particles of radius \(r\). (Other size distribution functions could be used here if desired). By integration of Eq. (20) one obtains:

\[
n_{ij} = 0.0167 \phi_{j-1} (r_{i+1}^3 - r_{i}^3)
\]

where \(n_{ij}\) is the number of particles of size between \(r_i\) and \(r_{i+1}\) during the \(j\)th time increment. Values of the maximum and minimum radius values have to be stated. (In the second time interval the corresponding formula is:

\[
n_i(j + 1) = 0.0167 \phi_j (r_{i+1}^3 - r_{i}^3)
\]

where the \(i\) subscripts refer to size fraction and the \(j\) subscript refers to the time increment.)

---

1 A part of this effect is probably only apparent and due to an increase in light-scattering power of the particle surfaces on wetting. This was pointed out by R. E. Kratel (DELBAG-Luft-filter GmbH, Berlin-West, Halensee, Germany) as a personal communication and by D. Lundgren and D. Cooper, "Effect of Humidity on Light-Scattering Methods of Measuring Particle Concentration," 61st Annual Meeting, Air Pollution Control Assoc., St. Paul, Minn., June 1968.
3. Calculate the number of particles that settle from each size range, \( \Delta r_i \), during the first time increment, \( \Delta t_1 \); according to Stokes Law for stirred settling [8]:

\[
\Delta n_{i1} = \frac{2r_i^3 \rho g C}{9 \mu} \frac{1}{h} \frac{dn}{dr_i} \Delta r_i \Delta t_1
\]  

(23)

where

- \( \rho \) = particle density,
- \( g \) = acceleration due to gravity,
- \( C \) = Cunningham slip coefficient,
- \( \mu \) = viscosity of air,
- \( h \) = height of the tank,

or, substituting the self-preserving function for \( (dn/dr)_i \),

\[
\Delta n_{i1} = \frac{0.011 \rho g C}{\mu r_i^2} \phi_0 \Delta r_i \Delta t_1
\]  

(24)

4. Calculate the new volume fraction of disperse phase, that is:

\[
\phi_1 = \sum_i \frac{1}{3} \frac{\pi r_i^3}{\pi/r_i} (n_{i1} - \Delta n_{i1})
\]  

(25)

where \( \phi_1 \) is the volume fraction of material still suspended at the end of the time increment \( \Delta t_1 \).

5. Repeat step 2 (i.e., presume that agglomeration will have proceeded in order to reestablish the self-preserving distribution) and also steps 3 and 4. In this way the value of \( \phi_2 \) (volume fraction after \( \Delta t_1 + \Delta t_2 \)) is calculated. Values of \( \phi_3, \phi_4, \ldots \), are also calculated in the same manner.

The effect of particle growth, in steam, in the context of the above calculation, is: (1) to increase the maximum particle radius and (2) to change the particle size distribution function from

\[
\frac{dn}{dr} = 0.05 \phi r^{-4}
\]  

(20)

(the self-preserving function which has been observed for fresh, dry aerosol) to

\[
\frac{dn}{dr} = Kr^{-x}
\]  

(19)

where \( x \) is less than 4.

Calculations were done to show the effect of increased maximum particle size. The results are shown in Fig. 15. The particle density is uncertain, so two values, 1 and 10 g/cm\(^3\), were used. The effect of increased maximum particle size (from 3 micron diameter to 10 micron diameter) was to decrease the time for half of the particles to settle by nearly a factor of ten; an important effect to be sure.
In brief summary, the natural effects of humidity and condensing steam to remove particles from a containment vessel are important. Diffusiophoresis (and thermophoresis) may remove half the particles in 10^3-10^5 sec; the rate can be related to the quantity of steam which condenses (if good mixing can be assumed). Particle growth by pickup of water and the resultant enhanced settling also promised to be important. A systematic survey is needed of particle size distributions under the variety of conditions and residence times for particle growth by pickup of water. This is required to confidently predict enhanced settling.

![Graph](https://example.com/graph.png)

**FIG. 15.** Calculated effect of steam on removal rate.

**REFERENCES**


DISCUSSION

G. BURLEY: To what extent are the aerosol characteristics affected by surface characteristics, e.g. hydrophobic or hydrophilic?

R.J. DAVIS: I'm afraid I cannot answer that. Most of the substances we were using were hydrophilic, if not hydroscopic.

V. PRODI: In answer to Mr. Burley's question, I think that we must distinguish between the effect of diffusiophoresis and the effects of nucleation and vapour condensation on the particles. While condensation is typically and strongly dependent on contact angle, i.e. on surface characteristics, diffusiophoresis is a hydrodynamic effect of drag, and therefore not dependent on particle nature and size, except for some second-order effects.

W. SCHIKARSKI: According to your theory and in the light of your experimental experience, what elementary process has most effect on the decontamination of the containment atmosphere? Is it thermophoresis or diffusiophoresis?

R.J. DAVIS: It is more likely to be diffusiophoresis. Given reasonable conditions, the two processes are of roughly equal efficiency.
EFFICACITE DES PIEGES A CHARBON IMPREGNE VIS-A-VIS DES PRODUITS DE FISSION DEGAGES LORS D'UN ACCIDENT DE PILE PISCINE

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Abstract — Résumé

EFFICIENCY OF IMPREGNATED CHARCOAL TRAPS FOR FISSION PRODUCTS RELEASED IN A SWIMMING-POOL REACTOR ACCIDENT. It is now a well-known fact that any significant increase of humidity in a reactor containment may considerably reduce the efficiency of iodine filters. In view of the interesting laboratory work carried out in the last few years, particularly on different techniques of charcoal impregnation, we decided to induce the melt-down of a fuel element in a swimming-pool reactor — by means of a power transient — in order to study the behaviour of the iodine released above the water in filters containing impregnated charcoal of different types. The fraction of iodine not retained in the reactor pool (representing about 1/20 000 of all the iodine released by the fuel) is in three forms. Relative humidity reached 100% in the containment, and in these conditions the decontamination factor of a 5-cm carbon layer varied between $2 \times 10^4$ and $7 \times 10^6$, depending on impregnation, for the iodine form most easily trapped, while remaining consistently below 5 for the most penetrating form.

1. INTRODUCTION

La mise en évidence, il y a quelques années, de formes organiques d'iode parmi les produits radioactifs échappés des circuits primaires des réacteurs [1-9] remettait en cause l'efficacité des pièges à charbons, leurs performances vis-à-vis de ces composés s'étant avérées très insuffisantes, particulièrement en présence de forte humidité [10-14].

Bien que les informations que l'on possédait sur les quantités de ces composés pénétrants par rapport à l'iode total ne fussent pas très concordantes [4, 13, 15-17], des études furent aussitôt entreprises, notamment en Grande-Bretagne et aux États-Unis. Elles aboutirent à la mise au point de techniques d'imprégnation des charbons qui redonnaient à ceux-ci une efficacité acceptable vis-à-vis de l'iodyde de méthyle qui est considéré comme le composé le plus pénétrant.
Les charbons imprégnés furent essayés en laboratoire et les résultats très encourageants furent, pour la plupart, exposés lors de l'«Air Cleaning Conference» à Boston en septembre 1966 [18-23]. Au cours de cette conférence, nous avons acquis, quant à nous, la certitude que ces essais, pour intéressants qu'ils fussent, devaient être complétés par des expériences dans lesquelles on disposerait de contamination réelle relâchée dans des conditions d'accident réelles ou aussi voisines que possible de la réalité [24]. Dans le domaine de la filtration, c'est donc vers cet objectif que nous avons orienté nos études des deux dernières années.

L'expérimentation la plus significative a été menée dans le réacteur CABRI, au Centre d'études nucleaires de Cadarache, nous compléterons les résultats que nous y avons obtenus par quelques informations recueillies sur un dispositif hors pile, PIREE.

2. DESCRIPTION DES DISPOSITIFS EXPERIMENTAUX

2.1. Réacteur CABRI

Les trois premières expériences ont été faites sur un premier cœur qui permettait de faire des excursions de puissance de plusieurs centaines de mégawatts et de faire des paliers de 10 MW environ. La quatrième expérience a été faite sur un second cœur, CABRI-Puissance, qui a été implanté dans une autre cuve placée dans le même bâtiment. Ses performances sont notablement plus élevées puisqu'il est maintenant possible de maintenir une puissance de 100 MW pendant 10 minutes.

Destiné également aux études de sûreté des réacteurs, CABRI-Puissance est, comme le premier réacteur, du type piscine et recevra prochainement une boucle à sodium [25] qui permettra d'étudier le comportement d'éléments combustibles de réacteurs à neutrons rapides dans certaines conditions critiques et d'y mener, pour ce qui nous concerne, des recherches en matière de sûreté radiologique.

Le cœur est composé de 350 plaques du type MTR (alliages contenant en poids 20% d'uranium et 60% d'aluminium) qui représentent 4 kg d'uranium enrichi à 93% en uranium-235. Il est immergé dans une cuve à section rectangulaire. Pendant la durée des expériences, l'eau de refroidissement du cœur est prise dans une cuve cylindrique de 6 m de diamètre et 10 m de hauteur, située à l'extérieur du bâtiment. Après son passage à travers le cœur, l'eau est renvoyée directement au sommet de cette cuve par une tuyauterie de 60 cm de diamètre et environ 30 m de long et un diffuseur limitant les échanges entre eau froide et eau chaude (fig. 1).

2.2. Dispositif PIREE

Il est essentiellement constitué par une cuve en acier inoxydable de 3 m de diamètre et de 6 m de hauteur que l'on peut remplir d'eau déminéralisée pour simuler une piscine de réacteur.

A la base de la cuve, un dispositif d'injection permet de libérer dans l'eau un gaz chaud et sous pression, contaminé par des produits de fission ou toute autre forme de contamination (fig. 2). L'analyse des dispositifs d'épuration placés dans le volume libre de la cuve, au-dessus du niveau
FIG. 1. CABRI-Puissance – Schéma du circuit de refroidissement.

FIG. 2. PREE – Schéma du dispositif expérimental.
d'eau, permet, non seulement de déterminer la fraction de contamination qui s'échappe de l'eau, mais également de connaître son comportement dans les charbons.

Ajoutons que cette expérimentation était destinée à étudier les conséquences radiologiques de la rupture dans l'eau d'une boucle à gaz du réacteur PEGASE ou du circuit de refroidissement d'une pile du type EL4 refroidie au gaz et modérée à l'eau lourde.

3. CONDITIONS EXPERIMENTALES

3.1. Expériences CABRI

Nous ne décrirons ici que les conditions expérimentales relatives à l'expérience spécifiquement destinée à l'étude du comportement de la contamination dans les charbons. En effet, trois autres expériences d'un type analogue ont été faites sur le premier cœur de CABRI mais elles étaient surtout destinées à déterminer le taux d'émission des produits de fission à partir de combustible fondu ainsi que leur coefficient de transmission à travers l'eau. Dans ces expériences, les filtres ne servaient que pour la détermination de la fraction de contamination s'échappant de l'eau. Toutefois, des dispositifs du type «Maypack» furent utilisés pour la troisième expérience mais nous ne disposions pas encore de charbons imprégnés. Nous nous contenterons d'indiquer plus loin les points les plus importants concernant la pénétration de l'iode dans le charbon non imprégné.

FIG. 3. CABRI, expérience n°4 - Photographie de l'élément fondu.
En ce qui concerne l'expérience réalisée spécialement pour l'étude des performances des charbons imprégnés, le niveau de l'eau dans la cuve extérieure était de 8 m, ménageant un volume d'air de 40 m$^3$.

La circulation de l'eau à travers le cœur se faisait pendant l'expérience dans le sens descendant avec un débit de 1100 m$^3$/h, puis l'eau était rejetée au sommet de la cuve par un tuyau de 60 cm de diamètre terminé par un diffuseur de forme conique.

Dix-huit plaques ont fondu au cours de cette expérience, soit 5% du cœur (fig. 3), elles appartaient à un élément neuf qui avait été irradié seulement au cours des trois excursions de puissance qui avaient précédé la fusion (fig. 4). Dans ces conditions, leur taux d'irradiation était d'environ 100 MWj/t.

Le volume libre de la cuve extérieure dans laquelle ont été faits les prélèvements d'air s'est trouvé saturé d'humidité après la fusion, l'indication de l'hygromètre ayant toujours avoisiné 100% pendant la durée des prélèvements, une condensation s'est produite à l'intérieur des dispositifs de filtration. Avant l'expérience, le degré hygrométrique était de 78%.

Dans ce même volume, la température est passée de 21°C avant l'expérience à 50°C après la fusion, cependant que la température de l'eau rejetée en haut de la cuve atteignait 51°C alors qu'elle était de 26°C avant son passage à travers le cœur.

3.2. Expériences PIREE

Etant donné que l'objectif principal de ces expériences n'était pas, comme nous l'avons dit, l'étude spécifique du comportement de la contamination dans les filtres, nous nous bornerons à préciser les conditions expérimentales indispensables à la bonne compréhension des résultats partiels qui vont suivre. De la même façon, pour les raisons qui ont été indiquées au début de ce mémoire, nous ne parlerons pas de la première partie de l'expérimentation [26] ni de la troisième, la première partie ayant consisté à injecter dans l'eau de l'iode provenant du laboratoire.
de radioéléments tandis que la troisième partie consistait à injecter dans l'eau de l'iode de méthyle. Nous nous limiterons à la seconde partie au cours de laquelle ont été utilisés des produits de fission provenant de la fusion d'un échantillon d'uranium irradié.

Au début de chaque expérience, l'échantillon d'uranium placé dans un four à résistance était porté à la température de fusion, que l'on maintenait pendant plusieurs minutes avant d'injecter les produits de fission dans l'eau par l'intermédiaire d'un courant de gaz carbonique chaud (400°C) et sous pression (20 kg/cm²). Le débit de gaz entraîneur était de 20 g/s (fig.5) et la durée de l'injection de 1 minute environ.
Les prélèvements atmosphériques étaient effectués dans le volume libre de la cuve, ménagé au-dessus du niveau d'eau. Dans ce volume, le degré hygrométrique a varié entre 85 et 95% au cours des prélèvements.

La durée du fonctionnement des dispositifs d'épuration a varié entre 3 heures et 6 heures.

4. DISPOSITIFS DE PRELEVEMENTS ATMOSPHERIQUES

Nous avons utilisé au cours de nos expériences des ensembles composites voisins des dispositifs britanniques «Maypack» formés d'éléments filtrants de diverses natures (fig. 6) que nous précisons ci-après en adoptant le sens entrée-sortie du filtre.
4.1. Expérience CABRI n°3

(Nous rappelons que les résultats des trois premières expériences ne concernent pas directement les problèmes de filtres mais que la troisième expérience a toutefois permis de recueillir quelques informations que nous indiquerons rapidement plus loin.)

Suivant le cas:
1 ou 2 papiers d'amiante
1 ou plusieurs papiers-charbon
1 ou plusieurs tampons de laine de cuivre activé à l'argent de 1 cm d'épaisseur («Knitmesh» type 9030-U, surface spécifique: 1200 m²/m³, volume libre: 93%)
3 à 6 couches de 1 cm d'épaisseur de charbon de noix de coco non imprégné (type NC-SA-1184).

4.2. Expérience CABRI n°4

2 papiers d'amiante ,
12 couches de charbon imprégné de 1 cm d'épaisseur
1 papier d'amiante

Les types de charbon utilisés étaient, suivant le cas:

NC-SA-1184 (charbon de noix de coco non imprégné)
207 B imprégné avec 5% de triéthylènediamine (207B-5% TEDA)
TS imprégné avec 5% de triéthylènediamine (TS-5% TEDA)
207 B imprégné avec 0,5% d'iodure de potassium (207B-0,5% KI)
TS imprégné avec 0,5% d'iodure de potassium (TS-0,5% KI)

4.3. Expériences PIRSEE

2 papiers d'amiante
6 ou 12 couches de 1 cm d'épaisseur de charbon TS imprégné avec 5% de triéthylènediamine (TS-5% TEDA)
1 papier d'amiante.

Dans ces diverses expériences, nous nous sommes efforcés de maintenir une vitesse frontale de l'air de 30 cm/s à l'entrée des dispositifs de filtration. Les variations accidentelles seront indiquées avec les résultats de l'expérience CABRI n°4 au cours de laquelle certaines d'entre elles furent assez importantes.

5. RESULTATS

Les mesures d'activité des différents éléments filtrants ont été faites par spectrométrie γ, la précision étant généralement comprise entre 15 et 30%; elles sont toutes ramenées à la date de l'expérience.
5.1. Expérience CABRI

Avant de concentrer notre attention sur les dispositifs de filtration, nous indiquerons à toutes fins utiles que l'ensemble de ces expériences a montré que le taux d'émission de l'iode à partir du combustible fondu se situait entre 1% et 3% et le facteur de transmission à travers l'eau était très voisin de $5 \cdot 10^{-5}$ [27].

FIG. 7. CABRI, expérience n°3 - Répartition de l'iode dans le charbon NC-SA 1184 non imprégné.

Expérience n°3

Les premières informations concernant la filtration des iodes furent recueillies, comme nous l'avons dit, au cours de l'expérience CABRI n°3, elles n'étaient pas suffisamment complètes pour que nous nous attardions sur les résultats détaillés, elles représentèrent essentiellement pour nous une confirmation recueillie in situ. En effet, les courbes de la figure 7 achevèrent de nous convaincre que, en cas d'accident mettant en cause des humidités importantes (95% dans cette expérience) et particulièrement en cas d'accident de réacteurs refroidis à l'eau, l'efficacité des charbons non imprégnés était très faible vis-à-vis de l'ensemble des formes d'iode qui risquent d'être relâchées dans l'atmosphère. Nous
avions alors évalué très grossièrement le rendement de filtration à 10% environ pour 5 cm de charbon, on verra que l'ordre de grandeur de cette valeur a été confirmé dans l'expérience n°4 où nous avons trouvé un rendement de filtration de 35%.

A noter que les papiers d'amiant, les papiers-charbon ainsi que les éléments en laine de cuivre activé à l'argent n'ont arrêté que des quantités d'iode négligeables devant les activités retenues par les couches de charbon.

**Expérience n°4**

L'ensemble des conditions d'utilisation des dispositifs de filtration ainsi que les résultats détaillés sont portés dans les tableaux I à V et sur les figures 8 à 11.

La quantité d'iode relâchée dans le volume libre a été de 0, 5 mCi, ce qui représente une concentration d'1 environ 10^{-2} mCi/m³.

**TABLEAU I. CABRI – EXPERIENCE N° 4 CONDITIONS EXPERIMENTALES**

<table>
<thead>
<tr>
<th>Filtre</th>
<th>V</th>
<th>P</th>
<th>t₁</th>
<th>t₂</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>N°1</td>
<td>36</td>
<td>15,5</td>
<td>0</td>
<td>7 h</td>
<td>7 h</td>
</tr>
<tr>
<td>NC-SA-1184 non imprégné</td>
<td>10</td>
<td>18,9</td>
<td>0</td>
<td>7 h</td>
<td>7 h</td>
</tr>
<tr>
<td>N°2</td>
<td>31</td>
<td>16,2</td>
<td>0</td>
<td>7 h</td>
<td>7 h</td>
</tr>
<tr>
<td>TS - 0,5% KI</td>
<td>31</td>
<td>16,9</td>
<td>0</td>
<td>3 h 43</td>
<td>3 h 43</td>
</tr>
<tr>
<td>N°4</td>
<td>32</td>
<td>16,9</td>
<td>3 h 53</td>
<td>6 h 58</td>
<td>3 h 05</td>
</tr>
<tr>
<td>TS - 5% TEDA</td>
<td>51</td>
<td>14,2</td>
<td>0</td>
<td>3 h 43</td>
<td>3 h 43</td>
</tr>
<tr>
<td>N°5</td>
<td>59</td>
<td>14,2</td>
<td>3 h 53</td>
<td>6 h 58</td>
<td>3 h 05</td>
</tr>
</tbody>
</table>

V Vitesse (cm/s) de l'air sur la face d'entrée des filtres
P Poids (g) de charbon sec dans chaque élément de filtre (diamètre 6 cm hauteur 1 cm).
\( t_1 \) Heure de mise en service des filtres (les temps de fonctionnement sont comptés à partir du temps 0 de la fusion, en réalité, les premiers filtres ont été mis en service 10 min avant celle-ci).
\( t_2 \) Heure d'arrêt.
T Durée de fonctionnement.
TABLEAU II. CABRI - EXPERIENCE № 4
CONDITIONS EXPERIMENTALES

<table>
<thead>
<tr>
<th>Type de charbon</th>
<th>Filtre</th>
<th>Q</th>
<th>A</th>
<th>P</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>131</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td>NC-SA-1184</td>
<td>n° 1</td>
<td>3.6</td>
<td>3</td>
<td>14.7</td>
<td>5.43</td>
</tr>
<tr>
<td>TS 5% TEDA</td>
<td>n° 2</td>
<td>1</td>
<td>5.3</td>
<td>16.4</td>
<td>5.33</td>
</tr>
<tr>
<td>TS 0.5% KI</td>
<td>n° 3</td>
<td>3.1</td>
<td>15.9</td>
<td>61.7</td>
<td>11.12</td>
</tr>
<tr>
<td>207 B</td>
<td>n° 4</td>
<td>3.1</td>
<td>11</td>
<td>28.5</td>
<td>8.29</td>
</tr>
<tr>
<td>5% TEDA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>207 B</td>
<td>n° 5</td>
<td>3.2</td>
<td>4.7</td>
<td>29.7</td>
<td>7.39</td>
</tr>
<tr>
<td>0.5% KI</td>
<td>n° 6</td>
<td>5.1</td>
<td>14.3</td>
<td>42.4</td>
<td>9.84</td>
</tr>
<tr>
<td>207 B</td>
<td>n° 7</td>
<td>5.9</td>
<td>4.8</td>
<td>28.4</td>
<td>8.95</td>
</tr>
</tbody>
</table>

Q - Débit (m³/h) de l'air à travers les filtres.
A - Activité (μCi) de l'iode adsorbée dans la première couche de charbon (épaisseur 1 cm).
P - Poids (g) d'eau mesuré après expérience dans la première couche de charbon.
R - Rapport (%) du poids d'eau au poids de charbon sec.

TABLEAU III. CABRI - EXPERIENCE № 4
CONSTANTES D'ADSORPTION DES FORMES D'IODE
DANS LES CHARBONS

<table>
<thead>
<tr>
<th>Type de charbon</th>
<th>Filtre</th>
<th>k₁</th>
<th>k₂</th>
<th>k₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS 5% TEDA</td>
<td>n° 2</td>
<td>2.7 - 2.8</td>
<td>0.05 - 0.3</td>
<td></td>
</tr>
<tr>
<td>TS 5% KI</td>
<td>n° 3</td>
<td>3 - 3.2</td>
<td>1 - 1.1</td>
<td>0.18 - 0.38</td>
</tr>
<tr>
<td>207 B</td>
<td>n° 4</td>
<td>2 - 1.4</td>
<td>1.1 - 1.1</td>
<td>0.15 - 0.06</td>
</tr>
<tr>
<td>5% TEDA</td>
<td>n° 5</td>
<td>2.5 - 2.6</td>
<td>1 - 1</td>
<td>0.08 - 0.08</td>
</tr>
<tr>
<td>207 B</td>
<td>n° 6</td>
<td>3.9 - 3.3</td>
<td>1.1 - 0.8</td>
<td>0.24 - 0.17</td>
</tr>
<tr>
<td>0.5% KI</td>
<td>n° 7</td>
<td>1.5 - 1.8</td>
<td>0.9 - 0.9</td>
<td>0.12 - 0.2</td>
</tr>
</tbody>
</table>

a Les deux valeurs indiquées dans chaque case ont été déterminées à partir des courbes d'adsorption des formes d'iode-131 et 133 respectivement (voir chapitre 6, Discussion).
### TABLEAU IV. CABRI - EXPERIENCE N° 4  
FRACTION DE LA FORME LA PLUS PENETRANTE

<table>
<thead>
<tr>
<th>Type de charbon</th>
<th>Filtre</th>
<th>F1</th>
<th>F2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS 5% TEDA</td>
<td>n° 2</td>
<td>0,7</td>
<td>2,5</td>
</tr>
<tr>
<td>TS 0,5% KI</td>
<td>n° 3</td>
<td>1,4</td>
<td>3,5</td>
</tr>
<tr>
<td>207 B 5% TEDA</td>
<td>n° 4</td>
<td>0,9</td>
<td>2,4</td>
</tr>
<tr>
<td></td>
<td>n° 5</td>
<td>1,3</td>
<td>6,6</td>
</tr>
<tr>
<td>207 B 0,5% KI</td>
<td>n° 6</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>n° 7</td>
<td>Détermination imprécise</td>
<td></td>
</tr>
</tbody>
</table>

F1, F2: Valeurs (%) calculées à partir des courbes d'adsorption des formes d'iode-131 et 133.

Les valeurs élevées sont probablement dues à une migration importante de l'iode dans le charbon en raison de la vitesse frontale accidentellement élevée du gaz vecteur.

### TABLEAU V. CABRI - EXPERIENCE N° 4  
EFFICACITE DES CHARBONS (Epaisseur 5 cm)

<table>
<thead>
<tr>
<th>Type de charbon</th>
<th>Filtre</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-SA-1184</td>
<td>n° 1</td>
<td>7 · 10⁴ - 10²</td>
<td>1,3 - 4,8</td>
<td>185 - 135</td>
<td></td>
</tr>
<tr>
<td>TS 5% TEDA</td>
<td>n° 2</td>
<td>4 · 10⁶ - 7 · 10⁴</td>
<td>145 - 165</td>
<td>2,4 - 2,7</td>
<td>94 - 38</td>
</tr>
<tr>
<td>TS 0,5% KI</td>
<td>n° 3</td>
<td>2 · 10⁴</td>
<td>240 - 205</td>
<td>2,2 - 1,5</td>
<td>225 - 30</td>
</tr>
<tr>
<td>207 B 5% TEDA</td>
<td>n° 4</td>
<td>4,5 · 10⁵ - 4 · 10⁴</td>
<td>135 - 125</td>
<td>1,5 - 1,5</td>
<td>58 - 20</td>
</tr>
<tr>
<td></td>
<td>n° 5</td>
<td>Détermination imprécise</td>
<td>190 - 55</td>
<td>3,3 - 2,3</td>
<td>13 - 6</td>
</tr>
<tr>
<td>207 B 0,5% KI</td>
<td>n° 6</td>
<td>Détermination imprécise</td>
<td>Détermination imprécise</td>
<td>1,8 - 2,5</td>
<td>42 - 18</td>
</tr>
</tbody>
</table>

E1, E2, E3: Efficacités de 5 cm de charbon pour les formes I, II, III.
E: Efficacité de 5 cm de charbon pour l'ensemble des formes en présence.
E5 cm = (Ap+As)/As. Ap: Activité piégée par 5 cm de charbon.
As: Activité non piégée par le charbon.

Les deux valeurs indiquées dans chaque case ont été déterminées à partir des courbes d'adsorption des formes d'iode-131 et 133 respectivement (voir chapitre 6, Discussion).

Etant donné la répartition de l'iode dans ce charbon (fig.8 et 9), ces efficacités ont été déterminées approximativement par comparaison de l'activité totale arrêtée par ce charbon et des activités des autres charbons.
Filtres papier

La fraction de l'activité arrêtée sur les deux papiers d'amiant placés en tête de chaque filtre a varié entre $10^{-3}$ et $2 \cdot 10^{-3}$ suivant le dispositif, ce qui prouve que, dans ces conditions, une très faible partie de l'iode se trouvait associée à des aérosols. A noter cependant que l'air entrant dans la cuve provenait de l'enceinte du réacteur équipée de pré-filtres.

Aucune activité n'a été décelée sur le filtre papier placé en sortie de chaque dispositif.

Pièges charbon

Formes d'iode

La distribution de l'iode dans les charbons (fig. 8 et 9) fait penser à l'existence de plusieurs formes, cette hypothèse dans laquelle nous allons nous placer provisoirement pouvant d'ailleurs être discutée (voir chapitre 6).
Etant donné les conditions expérimentales, il n'a pas été possible d'analyser les différentes formes d'iode en présence, par effusion ou chromatographie. D'autre part, aucune activité n'a pu être détectée sur les tubes à diffusion qui étaient associés aux dispositifs de filtration.

L'adsorption d'une forme d'iode dans une couche de charbon est caractérisée par une loi de la forme $e^{-kx}$ où $k$ représente la constante d'adsorption de la forme considérée et $x$ l'épaisseur de la couche de charbon. Il est évident que le coefficient $k$ varie avec la forme d'iode et le type de charbon, mais il dépend également de plusieurs autres paramètres parmi lesquels la nature, la température et l'humidité du charbon.

Lorsque plusieurs formes sont en présence, on a affaire à une loi plus complexe de la forme:

$$y = e^{-k_1x} + e^{-k_2x} + e^{-k_3x} + \ldots + e^{-k_nx}$$

Cependant, il est généralement possible de déterminer graphiquement en coordonnées semi-logarithmiques l'équation caractéristique de l'adsorption de la forme la plus pénétrante puis, par soustractions successives, d'isoler les différentes formes, et ceci d'autant plus aisément que les écarts entre les constantes d'adsorption sont plus grands.

L'application de cette méthode a permis de mettre en évidence trois formes d'iode, sauf dans un seul cas. Dans le tableau III sont indiquées pour chaque forme les constantes d'adsorption, qui varient suivant le type de charbon et les conditions expérimentales de 1,4 à 3,9 pour la première
forme, de 0,8 à 1,1 pour la seconde et de 0,05 à 0,38 pour la forme la plus pénétrante.

D'autre part, la fraction de la forme la plus pénétrante ne dépasse pas quelques pour cent (tableau IV).

Efficacités

Le coefficient d'épuration ou de déséchantillonnage d'un élément filtrant (dans le texte nous emploierons parfois le mot «efficacité») s'exprime de la façon suivante :

\[ E = \frac{A_e}{A_s} \]

A_e : Activité pénétrant dans l'élément
A_s : Activité non retenue par l'élément.

On peut également définir le rendement de filtration

\[ R = \left( 1 - \frac{1}{E} \right) \cdot 100 \]

\[ = \frac{A_r}{A_c} \cdot 100 \text{ (exprimée en pour cent)} \]

A_r : Activité retenue par l'élément.

La valeur de A_s (\( A_s = A_c - A_r \)) sera dans la suite déterminée par extrapolation, jusqu'à l'infini, de la courbe d'adsorption de l'iode dans les éléments.

La distribution de l'iode dans les charbons est indiquée sur les figures 8 et 9, l'efficacité globale des charbons en fonction de l'épaisseur de couche pour l'ensemble des formes d'iode étant portée sur les figures 10 et 11. Nous avons dû faire la distinction entre iode-131 et iode-133 car leur comportement apparent dans les charbons n'est pas le même, ce qui n'a pas manqué de nous surprendre, nous reviendrons sur ce point dans la discussion.

A nouveau on remarquera (tableau V) que l'efficacité du charbon non imprégné est très faible puisqu'elle est voisine de 1,6, c'est-à-dire 35%, pour une épaisseur de 5 cm.

Par contre, on s'aperçoit que les charbons imprégnés sont beaucoup plus efficaces puisque leur rendement de filtration varie entre 85% et 99,5% pour 5 cm suivant le type de charbon et suivant les conditions de fonctionnement des filtres.

Nous avons également déterminé pour chaque type de charbon le coefficient d'épuration d'une couche de 5 cm vis-à-vis des trois formes mises en évidence (tableau V).

Atteignant des valeurs dépassant 10^6 pour la première forme, l'efficacité décroît jusqu'à environ 10^2, c'est-à-dire 99%, pour la seconde et n'est plus que de quelques dizaines de pour cent pour la forme la plus pénétrante.
5.2. Expériences PIREF

Quatre expériences ont été faites dans les conditions indiquées précédemment. Nous ajouterons que la concentration moyenne de l'iode dans le gaz carbonique au niveau du point d'injection a varié suivant l'expérience de 6 \cdot 10^{-7} \mu g/g CO₂ à 1,5 \cdot 10^{-5} \mu g/g CO₂. Pour l'iode envoyé dans la cuve, le coefficient d'épuration par l'eau est passé de 2 \cdot 10^2 pour une couche d'eau de 1,5 m à 2 \cdot 10^4 pour une couche de 6,5 m. La concentration moyenne dans le volume libre de l'iode relâché par l'eau a varié de 3 \cdot 10^{-8} \mu g/m³ à 4 \cdot 10^{-5} \mu g/m³.

Filtres papier

La fraction d'iode arrêtée par les deux filtres papier placés en tête de chaque dispositif d'épuration a été très faible comme dans les expériences CABRI: elle s'est située entre 5 \cdot 10^{-3} et 10^{-2}. A noter que, dans ces expériences, l'air entrant dans le volume libre de la cuve était également filtré.
Pièges charbon

Ici encore la distribution de l'iode dans les charbons n'est pas exponentielle (fig. 12) et il est permis de penser que l'on se trouve en présence de plusieurs formes dont il est difficile dans le cas présent d'isoler les valeurs des constantes d'adsorption. Mais, comme dans le cas de CABRI, cette hypothèse peut être mise en doute et sera discutée dans le paragraphe suivant.

![Graphique de CABRI, expérience n°4 - Efficacité des charbons (iode-133).](image)

Le facteur de décontamination du charbon TS imprégné avec 5% de TEDA a varié suivant l'expérience de $10^2$ à $10^3$ pour une couche de 5 cm (fig. 13), le temps d'aspiration à travers les dispositifs de filtration ayant varié entre 3 heures et 8 heures.
6. DISCUSSION

Nous avons souligné dans le paragraphe précédent que la distribution de l'iode dans les charbons imprégnés permettait de supposer l'existence de plusieurs formes distinctes, mais que cette hypothèse pouvait être dis-
cutée. En effet, les valeurs des constantes d'adsorption pour les formes les plus pénétrantes ne correspondent pas du tout aux résultats obtenus en laboratoire. Par contre, la constante d'adsorption caractérisant la forme la mieux arrêtée s'approche bien davantage des valeurs obtenues en laboratoire pour l'iodyde du méthyle [18, 22]. Il est alors permis d'avancer deux autres hypothèses qui supposent initialement que la totalité des formes d'iode les moins pénétrantes reste confinée dans l'eau et que seule l'iodyde de méthyle est relâché:

a) Étant donné les conditions d'humidité rencontrées dans ces expériences, il est possible que nous ayons assisté à un phénomène de percolation de l'eau contaminée à travers le charbon, ce qui aurait eu pour effet d'entraîner vers les dernières couches de charbon une partie de l'activité qui, en l'absence d'eau liquide, se serait adsorbée dans le charbon suivant une loi unique correspondant à la première partie de la courbe.

b) En considérant toujours que la première partie des courbes de distribution de l'iode dans les charbons correspond à l'iodyde de méthyle, la dernière partie de ces courbes peut être due à une légère élution à l'intérieur du charbon ou à la dissolution progressive d'une partie de l'imprégnant modifiant, après un certain temps de fonctionnement, les caractéristiques d'adsorption des charbons.

Dans tout ce qui précède, nous avons supposé que l'iodyde de méthyle était la forme d'iode la plus pénétrante, ce qui est généralement admis par les spécialistes.

Enfin, il faut signaler que, dans toutes ces expériences, il n'était évidemment pas possible de pré-conditionner les charbons, ce qui a pu modifier sensiblement les résultats par rapport à ceux qui sont obtenus en laboratoire dans des conditions analogues. Mais ce mode d'utilisation est plus conforme aux conditions d'emploi en cas d'accident.

L'examen des courbes des figures 8 et 9 fait apparaître une différence notable entre la distribution de l'iode-131 et de l'iode-133 dans les charbons. Nous n'avons pas trouvé d'explication qui nous satisfasse et nous nous contenterons d'indiquer l'essentiel de nos hypothèses. Nous pensons qu'il pourrait s'agir d'une différence dans les proportions des formes des deux isotopes, la diffusion de ces formes dans l'eau n'étant pas la même. Cette différence pourrait être due aux conditions de formation des iodes-131 et 133. En effet, le rendement propre de l'iode-133 étant beaucoup plus élevé que celui de l'iode-131 et les périodes de ses parents beaucoup plus courtes, il a été plus rapidement formé et, par conséquent, plus longtemps soumis à l'action du rayonnement et de la température, ces conditions pouvant influer sur les réactions à l'intérieur du combustible. On pourrait aussi penser que ces mêmes réactions varient suivant que l'on a affaire à de l'iode formé directement par fission à partir de l'uranium ou de l'iode formé par filiation, mais cette dernière hypothèse nous paraît très audacieuse.

Nous ajouterons qu'aucun tellure, précurseur de l'iode, n'a été détecté dans les charbons ni sur les papiers et n'a donc pu influer par sa décroissance sur le comportement apparent des deux isotopes de l'iode.

Notons enfin qu'il a été vérifié que ces différences ne pouvaient provenir d'erreurs de comptage dues, par exemple, aux variations de l'autocapération dans les charbons et leurs supports, de l'énergie des rayonnements respectifs de l'iode-131 et de l'iode-133.
Quoi qu'il en soit, ce qui vient d'être dit tendrait à prouver que, dans l'air, on n'a pas affaire à une seule forme d'iode, car on n'aurait alors aucune raison, nous semble-t-il, de distinguer $^{131}\text{I}\text{CH}_3$ de $^{133}\text{I}\text{CH}_3$, si l'on admet évidemment que cette forme unique est de l'iodeure de méthyle, mais, de toute façon, ce raisonnement serait valable pour toute autre forme.

L'examen des courbes d'efficacité du charbon en fonction de l'épaisseur (figures 9 et 10) laisse apparaître:
- d'une part, une différence significative, quoique peu importante, entre les charbons imprégnés à la triéthylénédiamine et ceux imprégnés à l'iodeure de potassium,
- d'autre part, une légère différence entre le charbon français TS et le charbon anglais 207 B, mais, si l'on tient compte des variations accidentelles de la vitesse frontale de l'air, cette différence n'est pas significative.

7. CONCLUSION

Si l'on admet que, lors d'une excursion critique dans un réacteur piscine, ou à la suite d'une réduction de débit d'eau dans les éléments, seuls quelques pour cent du cœur peuvent fondre, et surtout si l'on admet que le dénoyage du cœur est impossible, ces expériences montrent qu'une faible fraction de l'iode, probablement de l'ordre de $10^{-6}$ de la quantité totale contenue dans la partie endommagée, risque d'être relâchée dans l'enceinte.

Ces résultats d'ensemble s'ajoutant à d'autres expériences dans des réacteurs piscines, notamment sur les réacteurs SPERT et SNAPTRAN [28, 29], et à certaines expériences hors pile [26, 30-32] tendent à réduire l'importance relative du rôle des filtres à iode dans des telles installations. Cependant, le problème garde toute son acuité dans le cas des réacteurs à eau pressurisée ou à eau bouillante.

De toute manière, quel que soit le type de réacteur, il nous paraît indispensable de ne point dissocier le problème des filtres à iode dans de telles installations. Cependant, le problème garde toute son acuité dans le cas des réacteurs à eau pressurisée ou à eau bouillante.

C'est cette vue d'ensemble qui seule permettra d'être efficace en faisant porter l'effort en priorité sur tel ou tel point dont l'importance relative apparaîtra évidente. C'est pourquoi nous estimons indispensable que se développent des échanges soutenus entre les chercheurs, même si les études qu'ils ont entreprises ne leur paraissent pas avoir abouti à des résultats définitifs dans le ou les domaines spécifiques qui les intéressent.

Nous espérons que cet exposé aura contribué à mettre en lumière l'intérêt de telles expériences qui présentent à notre sens trois avantages essentiels:
- Obtenir in situ des informations globales concernant la sûreté radio-logique, étant bien admis qu'en cas d'accident plusieurs paramètres interviennent simultanément et que leurs influences respectives sont souvent difficiles à bien connaître et nécessitent des études analytiques longues et approfondies,
- Susciter des études complémentaires en laboratoire destinées à éclaircir certains problèmes particuliers et à déterminer l'influence réelle des paramètres qui semblent gouverner les phénomènes,
- Replacer dans le contexte général et vérifier dans des conditions voisines de la réalité les résultats déjà obtenus en laboratoire.

REMERCIEMENTS

L'auteur remercie l'ensemble des équipes responsables de l'exploitation et de l'expérimentation à CABRI et, en particulier, MM. Ailloud et Millot ainsi que les agents locaux du Service de protection contre les radiations, qui ont facilité au maximum la tâche des expérimentateurs.

Que soient également remerciés tous ceux qui ont collaboré à ces expérimentations et, en particulier, MM. Beraha, Geisse, Minguella et Wilzer.

REFERENCES

DISCUSSION

N.R. HORTON: Is the figure of 10% for the release of iodine from a melted fuel element correct?

J. DADILLON Yes. During the various experiments in the CABRI reactor, the rate of release of radioactive iodides from the damaged fuel did not exceed 10%, in fact, the highest value was about 6%.

N.R. HORTON: I have three further questions. What was the depth of water over the fuel element? Into what volume of water was the iodine released? And what was the iodine concentration in the water?

J. DADILLON: The water depth varied from 2.5 to 3.5 m according to the experiment. I should point out that the water was circulating from top to bottom through the fuel elements and was discharged at about core level. This may have facilitated trapping of the fission products by the water.

The volume of water was 150 m$^3$

The radioiodine concentration was roughly 300 mCi/m$^3$. The level of fuel element irradiation was 1%.

M.I. GOLDMAN: What was the pH of the pool water which produced the $10^{-5}$ penetration of $^{131}$I?

J. DADILLON: The water was demineralized and had a pH of about 6.

J.G. WILHELM: How long was the fuel kept in the molten state?

J. DADILLON: This varied according to the experiment, but the duration was always of the order of a few tens of seconds.
APPLICATION OF IMPREGNATED CHARCOALS FOR REMOVING RADIOIODINE FROM FLOWING AIR AT HIGH RELATIVE HUMIDITY*

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Abstract

APPLICATION OF IMPREGNATED CHARCOALS FOR REMOVING RADIOIODINE FROM FLOWING AIR AT HIGH RELATIVE HUMIDITY. In addition to elemental iodine (I₂), methyl iodide (CH₃I) constitutes a recognized species of airborne radioiodine. Certain commercial iodized charcoals have been noted to have the capability of extracting via isotopic exchange the ¹³¹I of CH₃¹³¹I transported in air and steam-air streams, even at rather high relative humidities. This work has been extended to include a greater variety of charcoals and to determine the effects of both normal and abnormal operating conditions. Several types of iodized charcoal have exhibited CH₃¹³¹I (actually, ¹³¹I of CH₃I) removal efficiencies of > 97% for a 2-inch depth at room temperature and 65% relative humidity (R. H.); the analogous efficiencies at 90% R. H. ranged from 16 to 99%. In steam-air tests, the five types of iodized charcoal tested yielded CH₃¹³¹I removal efficiencies of ≈ 90% for a 2-inch depth provided the relative humidity did not greatly exceed 90%. The question as to whether the iodizing process reduces the capacity for fission-product I₂ to an unacceptable level was found not to represent a problem at room temperature and at 98% R. H.; however, the condition of 100% R. H., together with extensive flooding of the charcoal, resulted in appreciable lowering of the I₂ removal efficiency. An apparent lowering in efficiency was also observed when the I₂ inlet concentration was decreased below 10⁻² mg/m³.

The effect of weathering on impregnated charcoals is being investigated. Results obtained indicate a small rate of decrease in CH₃¹³¹I removal efficiency for iodized charcoal exposed to flowing purified and humidified air and a somewhat greater rate of decrease for charcoal subjected to humidified air containing traces of organic impurities. The stability of iodized charcoals to elevated temperatures was investigated by labelling their impregnant(s) with *¹³¹I and then measuring any losses of *¹³¹I during successive heating periods at progressively higher temperatures. Five types of iodized charcoal were observed stable at 150°C, while three were still reasonably stable at 200°C. At 250°C all exhibited sizable *¹³¹I losses.

A program for measuring charcoal ignition temperatures under both laboratory and reactor conditions is in progress. In laboratory tests, ignition temperatures for iodized charcoals of 385°C and higher have been observed, depending on the charcoal type. In related work, in-pile, the ignition temperature of iodized charcoal was noted to decrease, presumably a result of radiation effects.

INTRODUCTION

In addition to elemental iodine (I₂), methyl iodide (CH₃I) constitutes a recognized species of airborne radioiodine. The usual types of activated charcoal, while effective for trapping I₂ even at very high relative humidities are not effective for trapping CH₃I except at lower relative humidities. This difficulty, which arises when radioactive methyl iodide is to be trapped under humid conditions, was alleviated a few years ago by the discovery that a type of commercial iodized charcoal was effective for decontaminating air streams transporting CH₃¹³¹I even though the prevailing relative humidities were fairly high [1, 2]. The predominant mechanism of trapping involves isotopic exchange:

\[ \text{CH}_3^{131}\text{I} + ^{127}\text{I} \text{(on charcoal)} \rightarrow \text{CH}_3^{127}\text{I} + ^{131}\text{I} \text{(on charcoal)} \]

* Research sponsored by the US Atomic Energy Commission under contract with the Union Carbide Corporation.
This act of decontamination is referred to, somewhat inaccurately, as $^{131}\text{I}$ removal or trapping; strictly speaking, however, the process involves the removal of the $^{131}\text{I}$ atom from the radioactive molecule, $\text{CH}_3^{131}\text{I}$. Virtually all of the resulting nonradioactive $\text{CH}_3^{127}\text{I}$ molecules are eluted from the charcoal mass.

This paper is concerned with the trapping of radioiodine occurring as $I_2$ and $\text{CH}_3\text{I}$ from air and steam-air streams at high relative humidity by impregnated (iodized) charcoals and with the effects of both normal and abnormal operating conditions on the behavior of these charcoals. Experimental procedures will not be covered herein; however, information on this is to be found in a number of the reports cited.

**IDENTIFICATION OF IMPREGNATED CHARCOALS STUDIED**

The types of impregnated charcoal for which data are to be presented are listed in Table I. Impregnation procedures are not discussed because of proprietary considerations. The types MSA 55851 and BC-727 are thought to contain about 5 wt % of iodine and/or iodine compound(s) and BC-272, about 2 wt %. The amount and nature of the impregnants for the charcoals developed in England [3] is indicated in the table. Beyond this, not much can be said, and no particular effort has been made to deduce impregnated charcoal compositions since it is the resultant behavior that is important rather than being able to manufacture similar trapping agents. However, laboratory-impregnations using $I_2$ and/or KI have yielded products which possessed good $\text{CH}_3^{131}\text{I}$ trapping capability.

**REMOVAL OF RADIOACTIVE METHYL IODIDE BY IMPREGNATED CHARCOALS**

Studies at Room Temperature and High Humidity

A selection of the test results that have been obtained with regard to the $\text{CH}_3^{131}\text{I}$ trapping capabilities of impregnated (iodized) charcoals at room temperature is presented in Table II. Included are a number of data reported previously [4, 5], and, in many cases, the lot numbers given are ORNL-assigned. As may be noted, the principal variables are charcoal type and relative humidity. For the most part, the information and data given are self-explanatory, but a few comments will be made.

Inspection of the results reveals the strong influence of relative humidity (R.H.). Charcoal type BC-117 is not very effective at 90% R.H.; however, it is intended for use in high temperature steam atmospheres, so that the 90% R.H. data for BC-117 in Table II may not be a good measure of its true worth. In the selection of a type of impregnated charcoal for a given application, other behavioral characteristics than that inferred from the data in Table II should be considered; information on some of these characteristics is given in subsequent sections of this paper.

The types OF-31 and OF-42, especially the latter, are observed highly promising according to the data in Table II. These preparations represent rather new developments in this area of investigation and, therefore, they have not been subjected to as extensive testing as that given or being given most of the other types of interest.

The effect of extremely high R.H., at room temperature, on $\text{CH}_3^{131}\text{I}$ removal capability is illustrated in Fig. 1 for MSA 55851 charcoal (lot No. 23). These data indicate that useful removal efficiencies are attainable so long as R.H. < 100%, but that if 100% R.H. truly pertains, a very severe loss in $\text{CH}_3^{131}\text{I}$ trapping efficiency may occur.
Table I. Information on Impregnated Charcoals Studied

<table>
<thead>
<tr>
<th>Type of Impregnated Charcoal</th>
<th>Base Charcoal Used in the Impregnation</th>
<th>Mesh Size</th>
<th>Manufacturer or Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA 85851</td>
<td>MSA 25725</td>
<td>8-14 Tyler</td>
<td>Mine Safety Appliances</td>
</tr>
<tr>
<td>MSA 24207</td>
<td>a</td>
<td>8-14 Tyler</td>
<td>Mine Safety Appliances</td>
</tr>
<tr>
<td>BC-727</td>
<td>BC-513</td>
<td>8-14 Tyler</td>
<td>Barnebey-Cheney</td>
</tr>
<tr>
<td>BC-272</td>
<td>BC-513</td>
<td>8-14 Tyler</td>
<td>Barnebey-Cheney</td>
</tr>
<tr>
<td>BC-239</td>
<td>a</td>
<td>10-14 Tyler</td>
<td>Barnebey-Cheney</td>
</tr>
<tr>
<td>BC-117</td>
<td>BC-513b</td>
<td>10-14 Tyler</td>
<td>Barnebey-Cheney</td>
</tr>
<tr>
<td>G601</td>
<td>a</td>
<td>12 x 16 U.S.</td>
<td>North American Carbon</td>
</tr>
<tr>
<td>OF-31</td>
<td>a</td>
<td>12 x 20 U.S.</td>
<td>Witco Chemical</td>
</tr>
<tr>
<td>OF-42</td>
<td>a</td>
<td>12 x 20 U.S.</td>
<td>Witco Chemical</td>
</tr>
<tr>
<td>0.5% KI (UK)c</td>
<td>207B</td>
<td>8-12 BSS</td>
<td>Sutcliffe, Speakman</td>
</tr>
<tr>
<td>5% TEDA (UK)d</td>
<td>207B</td>
<td>8-12 BSS</td>
<td>Sutcliffe, Speakman</td>
</tr>
</tbody>
</table>

a. Information on this point is not at hand.
b. Modified to increase the ignition temperature.
c. The symbol (UK) indicates that these charcoals were developed in England.
d. Triethylenediamine-impregnated charcoal.

Studies Under Steam-Air Conditions

If a water-cooled reactor experiences a loss-of-coolant accident, the need for trapping CH$_4^{131}$I from flowing steam-air at elevated temperatures and pressures may thereby arise. The applicability of a number of iodized charcoals for doing this has been investigated and reported [6, 7]. The essentials of the results are given in Fig. 2 where removal efficiency for a 2-in. depth of charcoal is plotted versus relative humidity and the other pertinent experimental conditions are indicated.

While identification of each data point as to charcoal type is not provided in the figure (that information can be found in tables in the detailed reports), the differences between charcoal types tended to be obscured, particularly in the very high relative humidity region, by minor operational fluctuations and by small temperature gradients in the charcoal beds. That is, in operation of a dynamic system under conditions approaching saturation, a very slight change in one variable such as pressure or
Table II. Efficiency of Impregnated Charcoals for Removing Radioactive Methyl Iodide from Flowing Humid Air at 25°C

Charcoal beds: two 1-in. depths in series, 1 in. diam.
Air velocity (superficial): 40 or 50 fpm (mostly at 40 fpm)
Pressure of air flowing through charcoal: 1 atm
Time allowed for preequilibration to relative humidity of test: > 16 hr
Duration of CH₃I injection: 2 hr
Duration of additional air flow: 4 hr
Inlet CH₃I concentration: generally around 17 mg/m³
Amount of CH₃I injected per cm³ of charcoal: 0.5 mg (or, alternately, around 1 mg CH₃I per g of charcoal)

<table>
<thead>
<tr>
<th>Charcoal Type, Lot Number</th>
<th>Relative Humidity (%)</th>
<th>CH₁³I Removal Efficiency for 1-in. Depth (%)</th>
<th>CH₁³I Removal Efficiency for 2-in. Depth (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA 85851, 93066</td>
<td>65</td>
<td>90.4</td>
<td>99.0</td>
</tr>
<tr>
<td>MSA 85851, 93066</td>
<td>90</td>
<td>64.3</td>
<td>67.0</td>
</tr>
<tr>
<td>MSA 24607, 7766</td>
<td>72</td>
<td>81.2</td>
<td>97.5</td>
</tr>
<tr>
<td>BC-727, 01345</td>
<td>65</td>
<td>95.3</td>
<td>99.7</td>
</tr>
<tr>
<td>BC-727, 01345</td>
<td>90</td>
<td>74.1</td>
<td>93.1</td>
</tr>
<tr>
<td>BC-272, 4767</td>
<td>65</td>
<td>95.3</td>
<td>99.8</td>
</tr>
<tr>
<td>BC-272, 10967B</td>
<td>90</td>
<td>52.6</td>
<td>76.4</td>
</tr>
<tr>
<td>BC-239, 22867</td>
<td>65</td>
<td>92.6</td>
<td>99.5</td>
</tr>
<tr>
<td>BC-117, 53167</td>
<td>65</td>
<td>90.4</td>
<td>99.1</td>
</tr>
<tr>
<td>BC-117, 10967A</td>
<td>90</td>
<td>8.5</td>
<td>16.3</td>
</tr>
<tr>
<td>G601, 11766</td>
<td>76</td>
<td>88.4</td>
<td>98.9</td>
</tr>
<tr>
<td>G601, 11766</td>
<td>90</td>
<td>70.3</td>
<td>90.3</td>
</tr>
<tr>
<td>OF-31, 42668A</td>
<td>65</td>
<td>97.0</td>
<td>99.92</td>
</tr>
<tr>
<td>OF-31, 42668A</td>
<td>90</td>
<td>87.2</td>
<td>98.0</td>
</tr>
<tr>
<td>OF-42, 42668B</td>
<td>65</td>
<td>99.0</td>
<td>99.99</td>
</tr>
<tr>
<td>OF-42, 42668B</td>
<td>90</td>
<td>90.5</td>
<td>99.3</td>
</tr>
<tr>
<td>0.5 KI(UK), W/310A</td>
<td>65</td>
<td>82.5</td>
<td>97.2</td>
</tr>
<tr>
<td>0.5 KI(UK), W/310A</td>
<td>90</td>
<td>61.8</td>
<td>90.8</td>
</tr>
<tr>
<td>5% TEDA(UK), W/310B</td>
<td>65</td>
<td>99.2</td>
<td>&gt; 99.99</td>
</tr>
<tr>
<td>5% TEDA(UK), W/310B</td>
<td>90</td>
<td>95.1</td>
<td>99.7</td>
</tr>
<tr>
<td>BC-513 (unimpregnated)</td>
<td>70</td>
<td>4.8</td>
<td>15.8</td>
</tr>
</tbody>
</table>
The results for CH$_3$\textsuperscript{131}I removal in steam-air systems by the five types of commercial iodized charcoal may be generalized as follows: CH$_3$\textsuperscript{131}I removal efficiencies of 90% or higher were obtained with 2-inch depths of charcoal provided the prevailing relative humidity in the charcoal did not exceed 90% by too wide a margin. For the relative humidity region of 60 to 85%, 2-inch removal efficiency values of 98% or higher were typical. Useful CH$_3$\textsuperscript{131}I trapping capability is attainable with the iodized charcoals at relative humidities higher than 90%, possibly even at relative humidities approaching 100%. However, at 100% relative humidity, circumstances may be such that bulk-phase water is associated with the charcoal, and, when this occurs, a serious loss in CH$_3$\textsuperscript{131}I removal efficiency is usually observed. These results were obtained in a single-pass type of system, and in a recirculatory system appreciably higher total removal efficiencies would very likely be achieved. In extending these results to actual applications, cognizance should be given to such factors as those resulting from weathering and poisoning of the charcoal in operating off-gas systems.

**FIG. 1.** Effect of relative humidity (R.H.) on the removal of radioactive methyl iodide from flowing air at 25°C by MSA 85851 impregnated charcoal.
As already indicated, certain types of commercial iodized charcoal have been observed to be effective for trapping radioactive methyl iodide. Because iodized charcoal itself is impregnated, during manufacture, with one or more iodine-containing substances, the question has been raised as to whether or not the capacity of such charcoal for elemental radiiodine has been reduced to a low and thereby unacceptable level. Accordingly, this question has been investigated at room temperature for four varieties of iodized charcoal under conditions of high and/or very high loading of I$_2$ and of high relative humidity. This work has already been reported separately in some detail [8]; therefore, only the essentials will be given here.

![Effect of relative humidity on the removal of radioactive methyl iodide from flowing steam-air by iodized charcoals at temperatures and pressures around 270°F and 60 lb/in$^2$ abs.](image)
In one group of experiments, all at very high I\textsubscript{2} loadings, charcoal types MSA 85551 (93066), BC-727 (0134-5), and BC-272 (V 767) were tested simultaneously in each of the four experiments performed. In the experiment involving the highest loading employed, which corresponded to around 60 mg I\textsubscript{2}/g of charcoal if based on a 2-in. depth or twice that if based on a 1-in. depth, some of the other conditions plus some procedural detail follows: 25°C; air at 40 fpm, 1 atm, and 98% R.H. during preequilibration, injection of I\textsubscript{2} for 10 hr at a concentration of around 190 mg/m\textsuperscript{3}, and an additional air sweep for 15 hr. For each of the three charcoal types so tested, the resulting I\textsubscript{2} removal efficiency for a 1-in. depth was > 99.90% and, for a 2-in. depth was > 99.92%. The other three experiments were similar in nature and gave generally similar results, with the 1-in. efficiencies obtained having ranged from 99.86 to 99.985% and the 2-in. efficiencies, from 99.89 to 99.997%. Since the loadings corresponding to the above I\textsubscript{2} removal results were all in excess of any proposed for a full-scale charcoal adsorber system, the conclusion was drawn that the three charcoals all have adequate residual I\textsubscript{2} capacity at 25°C.

In another group of experiments in which the above three charcoals plus BC-117 (53167) were included, I\textsubscript{2} removal at 100% R.H. was investigated, i.e., the charcoal beds were flooded with water during I\textsubscript{2} injection and during the first few hours of the following air sweep. The I\textsubscript{2} loadings were not as high for these tests, being of the order of 10 mg/g (based on a 2-in. depth). Removal results for 98% R.H. were obtained in conjunction with those for 100% R.H. for purposes of comparison. At 98% R.H., moderately enhanced I\textsubscript{2} removal efficiency on average relative to the very high loading results was noted, presumably a consequence of the lower I\textsubscript{2} loading. Results for BC-117 at 98% R.H. indicated that its residual I\textsubscript{2} capacity was adequate at 25°C. Now considering the results for 100% R.H. or for water-logged charcoal, the variation in performance imposed by this condition appeared to obscure small variations due to other factors as was illustrated most dramatically by the 1-in. removal efficiencies. Twelve such data points were obtained altogether and they ranged from 95.55 to 99.73% with six points having been below 99%. The analogous 2-in. efficiencies ranged from 99.49 to 99.993%. In interpreting the data, it was concluded that the erratic I\textsubscript{2} trapping performance was not associated with charcoal type or with the moderate variation in I\textsubscript{2} loading which prevailed. The more likely explanation is that the degree of sweep gas channeling was higher in the tests producing the lower efficiencies. Provided this explanation is correct, good I\textsubscript{2} removal efficiency can be obtained with a 1-in. depth of iodized charcoal even when water-logged and excellent removal efficiency for I\textsubscript{2} can be obtained with a 2-inch depth if sweep gas channeling can be limited. Of course, control of channeling would be almost impossible to achieve and it would be preferable to avoid altogether having the iodized charcoal in a water-logged condition, not only from the standpoint of trapping elemental radiiodine, but also with regard to the trapping of radioactive methyl iodide, as has already been discussed.

Studies at Room Temperature and Low Iodine Loadings

It has been observed in various I\textsubscript{2} trapping studies that the apparent I\textsubscript{2} removal efficiency of noniodized charcoal tends to decrease as the inlet I\textsubscript{2} concentration decreases. This behavior is presumably due to the presence of one or more iodine species which penetrate charcoal more readily than I\textsubscript{2} and whose proportion of the total airborne iodine increases as the I\textsubscript{2} concentration decreases. Investigation of this phenomenon as it applies to iodized charcoal has been initiated and a variety of data have been collected, but the study is as yet incomplete.
The trend the data are exhibiting is illustrated in Fig. 3 by the results for one of the iodized charcoal types under investigation. Figure 3 also includes results from the very high I₂ loading tests referred to earlier. At the higher inlet concentrations, which caused the I₂ loadings on the charcoal to be commensurately high, there is a suggestion that the capacity of the charcoal for I₂ is on the verge of being exceeded. At the lower inlet concentrations a decrease in removal efficiency is observed, as has been the case with unimpregnated charcoals. In the experiments corresponding to these results, evidence was obtained which indicated that particulates were not significantly involved. At first it did not seem too likely that the penetrating form was methyl iodide, since according to simple isotopic-exchange theory the MSA 85851 charcoal should have trapped the ¹³¹I of CH₃¹³¹I more effectively than was observed because only very small quantities of the penetrating forms were present. However, some preliminary data from other experiments on commercial iodized charcoals have revealed that at high relative humidity the CH₃¹³¹I removal efficiency increases only moderately when the amount of CH₃I injected is rather drastically decreased. This observation is contrary to the theory of isotopic-exchange trapping and suggests that under conditions of high relative humidity the rate determining step may be solution of CH₃I in the water adsorbed by the charcoal, and, since this step may involve a Henry's law type of behavior, the CH₃¹³¹I removal efficiency for a test bed of iodized charcoal may be, within limits, relatively insensitive to the amount of CH₃I injected.

Studies Under Steam-Air Conditions

This subject has been investigated only very sparsely. Two tests similar to those corresponding to Fig. 2 but with I₂ rather than CH₃I have been performed, each with MSA 85851 charcoal. At 95% R.H., the I₂ removal efficiency for a 2-in. depth was 99.95% and at 100% R.H., it was 97.8%, these results thereby being in accord with those at room temperature. Obviously, however, more data are needed before conclusions on this aspect of radioiodine trapping can be drawn with confidence.
EFFECT OF WEATHERING ON THE PERFORMANCE OF IMPREGNATED CHARCOAL

Weathering (or exposure to continued air flow), poisoning, and aging are processes which might be expected to deleteriously affect the CH$_3$I$^{131}$ removal capability of iodized charcoal, and a limited investigational effort has been and is being applied in this connection.

In an experimental study which was on MSA 85851 (93066) impregnated charcoal, one group of test beds was exposed to flowing purified, filtered, and humidified plant air in the laboratory, while another group was exposed to flowing air taken directly from the Oak Ridge Research Reactor (ORR) building. Each test bed consisted of two 1-in. depths of charcoal, in series, 1 in. in diameter. Periodically, test beds were withdrawn from the two weathering facilities employed and subjected to a CH$_3$I$^{131}$ removal test (as of Table II for the 65% R.H. condition). Results corresponding to the total depth of 2 in. are given in Fig. 4. As may be noted, the face velocity of the air was higher by a factor of two in the case of the lab-exposed test beds, i.e., in one sense the intensity of exposure was greater for the more ideal type of exposure. When compared on a cumulative flow basis, the ORR building-exposed charcoal exhibits a much larger effect due to weathering than does the lab-exposed charcoal. This is, of course, in accord with expectation, since the ORR building air would not usually be as free of impurities as would the additionally-treated plant air used in the lab-exposure. In this connection, CH$_3$I$^{131}$ removal tests made on unexposed MSA 85851 (93066) over the maximum time period involved here have not revealed a significant effect due to aging alone. The apparent recovery of removal capability exhibited in Fig. 4, for charcoal in the ORR during the period just prior to a total of 15 months, is of minor extent and significance and may be explained by assuming that the net effect of adsorption and desorption during this period was such as to cause an increase in removal efficiency.

Since different types of impregnated charcoal will probably react differently to weathering, this work is being extended to include other types of current interest, with the mode of experimentation being modified so as to encompass within a reasonable period of time a relatively large variety of charcoal types.

![Fig. 4. Effect of weathering on CH$_3$I$^{131}$ removal capability of MSA 85851 iodized charcoal (2-in. depth).](image-url)
At least until more information and experience pertaining to weathering, etc., is available, it would appear desirable, wherever possible, to avoid subjecting the charcoal to air flow except when the actual need to trap molecular radiiodine arises; in those cases where continued air flow is required, an additional upstream charcoal bed to bear the brunt of poisoning due to impurities would be helpful; and, in the majority of applications, particularly if continued flow pertains, fairly frequent and appropriately designed in-place tests would appear to be required.

**LOSS OF IMPREGNANT AT ELEVATED TEMPERATURES**

Observations made at ORNL and elsewhere have showed that iodized charcoals emit impregnant as I₂ on heating to temperatures still well below their ignition temperatures. This may be disadvantageous because of a possible loss in trapping efficiency and/or evolution of radioactivity if the charcoal has previously been used to trap radioactive I₂ or CH₃I.

To evaluate this problem and to determine the relative stabilities of impregnated charcoals, a series of laboratory tests was conducted. In these tests, each iodized charcoal sample was used to exchange-trap CH₃I and thus label the impregnant with ¹³¹I. A sample of triethylene diamine-impregnated charcoal was also similarly exposed to CH₃I and included in the study. Then the charcoals were heated at progressively higher temperatures in the presence of flowing air, and the ¹³¹I losses at the different temperatures were measured. After the CH₃I exposure and after each heating period, the charcoal in each sample was mixed to distribute the radioactivity uniformly. Therefore, the consequent ¹³¹I losses were most likely greater than would occur in an actual situation under otherwise comparable conditions.

The results obtained are summarized in Table III. All these charcoals are observed to be virtually stable at 150°C; but at 200°C and higher and as measured by radioactivity losses, small to relatively large amounts of impregnant or trapped ¹³¹I in the case of 5% TEDA (UK) are evolved and swept out of the charcoal beds. The magnitudes of these losses are a function of charcoal type and, of course, a function of temperature. As may be seen, type BC-117 is one of the more stable and, possibly, the most stable among those tested. On the other hand, this charcoal has been observed to be less effective for trapping radioactive methyl iodide than some of the other commercial iodized charcoals. Thus, selection of the most appropriate charcoal type for a specific application will need to be made on the basis of the operational conditions expected to be encountered in that application.

**STUDIES OF CHARCOAL IGNITION**

Charcoal adsorbers for radiiodine constitute an important part of the safety systems for the removal of accident-released fission products from the containment volume either during recirculation of the atmosphere or as it is being exhausted from the containment shell. During application, the charcoal adsorbers would be subject to loading with large quantities of fission products and, consequently, would be heated by decay of the trapped fission products. Situations can be postulated in which the temperature of the charcoal mass exceeds the ignition temperature and uncontrolled combustion takes place with an attendant release of the previously trapped radiiodine (or other fission products). The probability of this occurring varies from zero upward depending upon the assumed magnitude of various parameters in the accident situation. There exists a need for experimental information to aid
in the assessment of this situation and this program at ORNL is being conducted to provide some of the information to help meet this need [9].

Laboratory Studies

Laboratory experiments are being conducted (1) to develop information relative to design of the in-pile experiments and (2) to acquire the experience necessary to interpret the results of the in-pile experiments. Experiments relative to the in-pile program are usually conducted in an ignition tube identical to that used in the in-pile system. Other laboratory studies are conducted in a separate ignition facility.

In order to reduce the variations and inconsistencies of ignition temperatures measured on the same charcoal at various laboratories, a group of experimenters in this field (at ORNL, Savannah River Lab, and Barnebey-Cheney) have agreed on using a standard charcoal ignition apparatus.

Two of these standard devices, of all-quartz construction, have been placed in use at ORNL. The two devices differ only in the type of thermocouple used. Both devices have been used with various charcoals and good reproducibility of ignition temperature has been obtained at air velocities up to 70 fpm; in general, ignition temperatures are reproduced within ± 5°C.

The measured ignition temperature of charcoal will vary depending upon the operating conditions of the test. As the velocity of the air sweep is increased there is an accompanying increase in the ignition temperature.

Table III. Retention of Radioactivity by CH\textsubscript{2}\textsuperscript{131}I-Treated Impregnated Charcoals After Successive Heating Periods at Progressively Higher Temperatures

<table>
<thead>
<tr>
<th>Charcoal</th>
<th>Lot No.</th>
<th>Percentage of Initial Radioactivity\textsuperscript{a} Retained After Heating Period at Temperature Indicated\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>150°C</td>
</tr>
<tr>
<td>MSA 85851</td>
<td>93066</td>
<td>99.7</td>
</tr>
<tr>
<td>BC-727</td>
<td>01345</td>
<td>99.5</td>
</tr>
<tr>
<td>BC-272</td>
<td>4767</td>
<td>99.7</td>
</tr>
<tr>
<td>BC-117</td>
<td>53167</td>
<td>99.7</td>
</tr>
<tr>
<td>0.5% KI (UK)</td>
<td>W/310A</td>
<td>99.9</td>
</tr>
<tr>
<td>5% TEDA (UK)</td>
<td>W/310B</td>
<td>99.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Appropriate allowance has been made for radioactive decay.

\textsuperscript{b} Temperature is that of center of charcoal bed (1 in. in diameter and 2 in. deep).
Table IV contains the measured ignition temperature of several charcoals as a function of air velocity. Up to about 20 fpm there seems to be little dependence upon air velocity; above 20 fpm the effect is more pronounced. The effect of heating rate on the measured ignition temperature is similar to that of gas velocity. In the range 8°/min to 19°/min the measured ignition temperature of BC-513 charcoal changes from 323 to 340°C, and that of MSA 85851 charcoal changes from 357 to 380°C.

During the ignition tests some of the iodized charcoals were observed to be releasing iodine vapor. In some cases the iodine vapors could be detected visually when the temperature was 150 to 200°C. In a laboratory test in which a sample of MSA 85851 was held in the temperature range of 275-300°C (with air flowing through it) about 23% of the iodine was swept out in 1 hr and 39% in 3 hrs.

Laboratory ignition tests were attempted on 207B 5% TEDA charcoal, an English charcoal impregnated with triethylenediamine. In tests, at an air flow of 20 fpm and at a heating rate of 10°C/min, the TEDA volatilized around 190°C and, in some cases ignited, causing the charcoal to ignite.

In-Pile Experiments

The primary reason for conducting charcoal ignition experiments in an in-pile facility is to study, in the most realistic manner possible, the significance of the postulated "hot spot" effect and the effect of fission products on ignition temperature. It has been suggested that local variations in charcoal characteristics within an adsorber unit might result in small areas of high concentration of adsorbed iodine. The decay heat of iodine in these areas would cause hot spots in which temperature would be greater than the bulk temperature of the charcoal. Thus the temperature at which the

Table IV. Ignition Temperature of Various Charcoals Measured in the Laboratory

<table>
<thead>
<tr>
<th>Charcoal</th>
<th>Ignition Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air Velocity (fpm) at Heating Rate of 10°C (min)</td>
</tr>
<tr>
<td>BC-513</td>
<td>315 318 320 325 328 *</td>
</tr>
<tr>
<td>MSA-85851</td>
<td>365 358 361 370 * 373</td>
</tr>
<tr>
<td>BC-592</td>
<td>448a 455 * 463a 478a</td>
</tr>
<tr>
<td>BC-272</td>
<td>290 * * 290 * 307</td>
</tr>
<tr>
<td>BC-117</td>
<td>450 * * 448 * 456</td>
</tr>
</tbody>
</table>

BC-513, noniodized coconut; MSA-85851, iodized coconut; BC-592, noniodized, high ignition coconut; BC-272, iodized, coconut; BC-117, impregnated coconut.

* Not measured.

a. Average value.
charcoal mass would ignite might depend on the magnitude of the "hot spot" effect.

The most realistic experiment would be to load a charcoal adsorber with sufficient quantities of radioiodine to actually raise the temperature of the charcoal mass to the ignition point. However, the quantity of radioiodine necessary to accomplish this feat would make this an exceedingly difficult and expensive experiment. In the in-pile experiments an ignition event is simulated by introducing large quantities of fission products into a small charcoal adsorber while increasing the bulk temperature (by external heating) of the charcoal until ignition occurs.

Three in-pile experiments have been conducted in the Oak Ridge Research Reactor. The first two experiments (IGR-1 and IGR-2) utilized Barnebey-Cheney type KE charcoal (unimpregnated, coconut) were operated in the prescribed manner, and the test charcoal adsorber was ignited many times in the presence of adsorbed radioiodine, and other fission products, at decay heating densities ranging up to 4 or 5 watts per square inch of adsorber face area. A detailed account of IGR-2 has been published [10]. The principal conclusions from the first two experiments are: (1) that the presence of fission products caused the ignition temperature of KE charcoal to increase, and (2) that no evidence of "hot-spot" formation was observed.

The third in-pile experiment (IGR-3) tested the effect of fission gases on the ignition temperature of Mine Safety Appliances, Type 85851 charcoal (an iodized charcoal). A schematic of the in-pile apparatus is given in Fig. 5. In describing the results of this experiment, it is interesting to compare them with results obtained with experiment IGR-2 which tested BC-KE non-iodized coconut charcoal.

The iodized charcoal, MSA 85851, ignited, in-pile, for the first time at 327°C, which is 35°C lower than the value measured for identical charcoal in the same ignition apparatus in the laboratory. The non-iodized charcoal in IGR-2 ignited for the first time, either in-pile or in the laboratory, at essentially the same temperature. This difference in behavior can be explained by postulating that the exposure of the iodized charcoal to volatile fission products (with their high radiation field and consequent production of ozone and oxides of nitrogen) caused some, or all, of the iodine impregnant to be removed from the front of the charcoal bed. It is a recognized fact that the iodine impregnation process increases the ignition point of charcoal; it may be assumed that loss of this impregnant could re-establish the original ignition temperature.

The succeeding ignitions of the iodized charcoal, in-pile, were at temperatures not significantly different from the corresponding ignitions measured in the laboratory. In IGR-2 the non-iodized charcoal ignited at slightly increasing temperatures as the experiment progressed, to a temperature of ~ 40°C higher than the initial ignition temperature; this behavior was not observed in the laboratory with this charcoal. It is suggested that this difference in behavior between the two types of charcoal can be explained by assuming that the presence of iodine fission products was, in effect, iodizing the KE charcoal and slowly raising the ignition temperature. The MSA 85851 charcoal has ~ 5% by weight, impregnation initially so that the mass of fission product iodine was insignificant in this case.

Experiment IGR-3 also contained a small charcoal adsorber in parallel with the charcoal ignition tube; the objective was to obtain information on the distribution of fresh fission products adsorbed in the presence of a radiation field. Knowledge of this distribution will aid in fixing the
location of the heat source when considering the influence of decay heating on the temperature rise of full-scale charcoal adsorbers.

Iodine ($^{131}$I) was distributed throughout the 2 inches of charcoal in the small adsorber with the largest part (73%) in the first half-inch, 13% of the iodine was found in the next 0.8 inch, and 4% in the final 0.7 inch. About 10% of the iodine reaching the charcoal adsorber, penetrated it and was found in the backup charcoal adsorber. Analysis of the charcoal showed that uranium was present, in trace quantities, throughout the adsorber; some of the $^{131}$I may have been carried through the adsorber with solid aerosols of uranium oxide. However, the distributions of these two materials do not correspond closely so it is improbable that large quantities of $^{131}$I penetrated in this manner.

Analysis of the charcoal, both from the charcoal adsorber and the backup charcoal trap, for impregnant iodine produced information that better explains the iodine penetration. There is evidence to suggest (the data are not sufficiently precise to provide a definitive statement) that some of
the iodine impregnant moved from the charcoal adsorber into the backup charcoal trap. Values for mass of iodine impregnant on samples from the charcoal adsorber appeared lower than normal, while samples of charcoal from the backup trap gave values somewhat higher than normal. These data suggest that iodine impregnant (carrying $^{131}$I) moved from the charcoal adsorber into the charcoal backup trap.

REFERENCES


P.J. LINDER. What was the water content of the charcoal when no bulk phase condensation was observed and when bulk phase condensation was observed?

R.E. ADAMS The water content of the charcoal was equivalent to about 50% by weight when no water condensation was observed, and about 100% when condensation was observed.

L.F. FRANZEN. Figure 4 of your paper gives data on the effect of weathering the charcoal. The units used are percent efficiency versus integrated air flow per test bed (ft³). Can you express the dependence by air changes, just to facilitate easy comparison with the results of Collins at Windscale, UK?

R.E. ADAMS For the charcoal test beds used, a volume of 10,000 ft³ of air would produce approximately 1.1 × 10⁷ air changes.
TESTING IODINE FILTERS FOR NUCLEAR INSTALLATIONS

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Abstract

TESTING IODINE FILTERS FOR NUCLEAR INSTALLATIONS. The removal efficiency of iodine filters for nuclear installations has been tested. The test method in use includes laboratory tests of the adsorber material (under MCA conditions for temperature, relative humidity, pressure, loading, stay time and bed depth) and in-place tests at the site of the installation. For removal of methyl iodide under high relative humidity KI-impregnated charcoal is widely used. Most of the data for charcoal removal efficiency available today result from experiments with tracer amounts of CH$_3$H$_2$I mixed with CH$_3$I. Considering MCA conditions, the validity of those data should be confirmed for specific activities on charcoal 10$^3$ - 10$^6$ times higher. Experimental data are given for realistic loadings with CH$_3$I up to 10 Ci/g charcoal under 100% relative humidity.

For standard laboratory adsorber tests a method is discussed for humidification and control of gas streams up to 100% relative humidity at elevated temperatures. The apparatus used is described. Experimental data are given for the removal efficiency and the adsorption of water in charcoal samples from long-time tests under 100% relative humidity. The overall test period was up to 98 h, simulating the phase of elevated pressure and, therefore, high iodine release from the reactor containment. The reproducibility of long-time tests under extremely high relative humidity is shown and discussed. A description of the hardware for in-place tests is included and results are given.

INTRODUCTION

Reactor stations in Germany with its high population density are in need of reactor safeguards to protect the population from accidental fission-product release. Therefore, most reactor off-gas systems are equipped with iodine filters. The removal efficiency of these filters has to be tested and it has to be shown that the performance under simulated MCA conditions will meet the values established in the hazards reports of the individual installations. The adsorber material of the iodine filter is tested in the laboratory under standard conditions and simulated MCA conditions. Additional in-place tests are carried out on the reactor site. These tests are generally produced under normal operating conditions and no effort is made to get high humidities or elevated temperatures.

LABORATORY TESTS

Test apparatus

We have developed an apparatus for testing adsorber material. Tests can be performed in the temperature range from 10 to 80°C with relative humidities of the sweep gas between 5 and 100%. The depth of the test
FIG. 1a. Laboratory apparatus for the determination of charcoal removal efficiency.

1 particle filter
2, 15, 20 flow meters
3 evaporator
4 heater
5 cooler for dew point setting
6, 14 condensate
7 double-walled tube
8 thermostat tube
9 glass wool filter
10 test beds
11 bath thermostat
12, 16 safety beds
13 cooler for dehumidizing
17 gamma spectrometer
18 pump
19 pressure cylinder with agent

FIG. 1b. Laboratory apparatus for the determination of charcoal removal efficiency.
bed may be up to 50 cm, stay time and the period of loading can be
adjusted to any realistic value in relation to iodine filters. It is well
known [1, 2] that the charcoal removal efficiency for organic iodine
compounds is influenced very strongly by the high relative humidity of
the sweep gas. For iodine filter systems of water-cooled reactors the
operational range of interest very often is near or at 100% R.H. Small
changes in this region may have a significant effect on the adsorber per-
formance. For comparative laboratory test runs with different types of
charcoal a very accurate control of the humidity of the sweep gas is
needed. Hence, a major effort was taken to achieve accurate control of
the relative humidity in our test apparatus.

Figure 1a is a flow diagram of the test apparatus, Fig. 1b is a photo-
graph of the original set-up in the laboratory and Fig. 1c shows the
thermostat tube and the test beds. The sweep gas enters the equipment
through a particle filter (1) and the gas flow is measured (2). Then the
sweep gas is mixed with steam (3) and transported through a heated tube (4)
to a special cooler (5). This cooler is double-walled and has a very
narrow coil. Through wall and coil there is a constant flow of coolant
from a thermostat. In this 'dew point cooler' the dew point of the sweep
gas is fixed in a range of ±0.1 degC. The condensate from excess steam
is sampled in (6). The sweep gas is taken from the lower third of the
dew point cooler and sucked through a double-walled heated tube (7). The
temperature of the outer tube wall is only 1-2 degC above the dew point
to avoid heat flow to the dew point cooler. Then the sweep gas is sucked
through a long 'thermostat tube' (8) inside a water-filled thermostat (11).
The test agent, mostly CH\textsubscript{3}\textsuperscript{131}I + CH\textsubscript{3}\textsuperscript{127}I in air, is added to the sweep gas
at the central part of the thermostat tube. Inside the thermostat tube the
gas is controlled within ±0.03 degC. The gas is then sucked through a
deep glass wool filter (9) and beds of the adsorber material under test (test beds (10)) inside the thermostat (11). The off-gas from the test beds is heated so that the relative humidity will drop below 30% and is sucked through heated charcoal beds (safety beds (12)). The remaining activity of the gas stream is removed by the first section of the safety beds. Then, most of the humidity in the off-gas is removed by a cooler with exactly controlled temperature (13), filtered by an additional charcoal trap for safety (16) and discharged to the exhaust through a membrane pump (18). The relative humidity in the apparatus can be measured directly by psychrometric methods and can be calculated from the volume of the condensate (14). The dew point method is used as well. Different temperatures in the dew point cooler (5) and the thermostat (11) allow the humidity of the gas to be varied from 5 to 100% R.H. The whole apparatus works almost fully automatically. We have performed runs up to 98 h at 99-100% R.H. without condensation in the test beds.

As slight condensation in the adsorber material would obscure the results of high humidity runs, the gain in weight of the subsequent charcoal beds by water adsorption is measured after each run. The time dependence of the water adsorption and the total adsorption in equilibrium with the humidity of the sweep gas is measured in a run without any activity.

Figure 2 indicates the results of a water adsorption experiment with a total bed depth of 50 cm. The charcoal was divided into three subsequent beds and the time dependence of the water adsorption of each bed was measured. Air at 30°C and 100% R.H. was used. Most of the adsorption took place in the first 7 hours, equilibrium was reached in a period shorter than 13 hours in the first charcoal bed. Considering the pressure drop in the charcoal, the H₂O partial pressure will be somewhat lower in each subsequent bed and so will be the total amount of adsorbed water. The exact data of this run are given in Table I.
TABLE I. WATER ADSORPTION OF IMPREGNATED CHARCOAL

Charcoal: Norit 0.5% KI, pellets, diam. 4 mm, length 4-8 mm, 3 successive charcoal beds, total bed depth 50 cm.
Wet air: 30°C, 100% R.H., superficial air velocity 42 cm/s.

<table>
<thead>
<tr>
<th>Duration of air flow (h)</th>
<th>Water adsorbed in wt % of dry charcoal</th>
</tr>
</thead>
<tbody>
<tr>
<td>bed 1</td>
<td>bed 2</td>
</tr>
<tr>
<td>1</td>
<td>23.64</td>
</tr>
<tr>
<td>3</td>
<td>44.61</td>
</tr>
<tr>
<td>7</td>
<td>46.33</td>
</tr>
<tr>
<td>15</td>
<td>46.49</td>
</tr>
<tr>
<td>31</td>
<td>46.49</td>
</tr>
<tr>
<td>37</td>
<td>46.57</td>
</tr>
</tbody>
</table>

Standard test procedure

To compare the efficiency of different types of charcoal we carry out a standard test procedure. Test conditions are: 20 h pre-humidification of the charcoal with wet air at 30°C, 100% R.H., and a loading time of an additional 20 h with a mixture of CH₃¹³¹I + CH₃¹₂⁷¹I in the wet air. After loading, the wet air stream is maintained for an additional 2 h. In Table II the removal efficiency under standard conditions is given for some charcoals. For one non-impregnated and one impregnated charcoal the results of re-runs are also given to demonstrate the reproducibility of tests under extremely high relative humidities for both types of charcoal.

Test procedure under simulated MCA-conditions

For purposes of reactor licensing, the main point of interest lies in test runs under the conditions expected in the MCA. Table III shows the results of tests for the MCA-iodine filter of the Obrigheim reactor. This filter was built for a removal efficiency better than 99.9% for fission-product iodine. Relative humidity may be up to 100% at a temperature up to 31.2°C; at higher temperatures the relative humidity will drop because there is a limited supply of steam resulting from a leak between the first and the second containment. The stay time of the off-gas in the iodine filter with a bed depth of 50 cm will be 1 sec and the total operating period after an accident would most likely not exceed 48 h.

Considering the leak rate between the first and second containments and a total amount of 10% of the iodine converted to methyl iodide, the loading of the charcoal in the iodine filter will not exceed 1.5 µg CH₃I/g of charcoal. With these data in mind we selected the test conditions listed in Table III. In Fig. 3 the penetration of the charcoal beds is shown plotted against the bed depth for those tests (curve b). There is a slight deviation
TABLE II. CH$_3^{131}$I REMOVAL EFFICIENCY OF ACTIVATED CHARCOAL UNDER STANDARD CONDITIONS

Charcoal: 4 successive beds, bed depth 25 mm, diam. 25 mm.
Loading: about 5 µg CH$_3$I/g charcoal, total $^{131}$I activity 0.1 - 0.2 mCi.
Sweep gas: air, temperature 30°C, R.H. 100%, atmospheric pressure, superficial velocity 15 m/min.
Duration of air flow: pre-humidification 20 h, CH$_3$I injection 20 h, air flow continued for additional 2 h, total 42 h.

<table>
<thead>
<tr>
<th>Charcoal</th>
<th>CH$_3^{131}$I removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bed depth (cm)</td>
</tr>
<tr>
<td></td>
<td>Stay time (sec)</td>
</tr>
<tr>
<td>Norit, in pellets, 0.8 mm diam., unimpregnated,</td>
<td></td>
</tr>
<tr>
<td>length 2 - 3 mm</td>
<td>(1)</td>
</tr>
<tr>
<td>As above</td>
<td>(2)</td>
</tr>
<tr>
<td>Average values of (1) and (2)</td>
<td></td>
</tr>
<tr>
<td>Norit RCX 1% KI, 0.8 mm diam. (As above, but impregnated)</td>
<td></td>
</tr>
<tr>
<td>Norit 0% KI, in pellets, 2 mm diam., length 4 - 8 mm</td>
<td></td>
</tr>
<tr>
<td>Norit RX 3210 1% Bal, in pellets, 1 mm diam., length 3 - 6 mm</td>
<td></td>
</tr>
<tr>
<td>SS 207 B 0.5% KI (UK)</td>
<td>(3)</td>
</tr>
<tr>
<td>As above</td>
<td>(4)</td>
</tr>
<tr>
<td>Average values of (3) and (4)</td>
<td></td>
</tr>
</tbody>
</table>

*CH$_3$I injection, 2 h, air flow continued for 20 h, loading (CH$_3$I) 50 ± 10 µg/g of charcoal.*

in the plot from a straight line in the direction of higher removal efficiencies with increasing bed depth. We think this is due to the pressure drop in the charcoal connected with a decreasing H$_2$O partial pressure in the successive layers of charcoal and affecting the amount of adsorbed water. From Fig. 3 it can be concluded that in this region of very low CH$_3$I-loading, over a range of nearly four orders of magnitude, there is no pronounced effect from the total amount of CH$_3$ and CH$_3^{127}$I reaching the successive layers of the impregnated charcoal. The total uptake of water in the first charcoal bed plotted against time for one of the two runs is given in Fig. 4. The diagram shows that condensation was clearly avoided. The total water inventory of the charcoal is the same as in a previous water adsorption test of a much shorter duration, indicated in Table I.
FIG. 3. Penetration of CH$_3$I through impregnated charcoal of the Obrigheim MCA-iodine filter.

TEST CONDITIONS
CHARCOAL NORIT, TYPE 0.5% KI
(a) AIR, 22-23°C, 40-61% R.H
PENETRATION ACCUMULATED OVER 2 hr 25 min
CH$_3$I INJECTION 25 min,
AIR FLOW CONTINUED FOR AN ADDITIONAL 2 hr
(b) WET AIR, 31°C, 100% R.H
PENETRATION ACCUMULATED OVER 50 hr
CH$_3$I INJECTION 48 hr,
AIR FLOW CONTINUED FOR AN ADDITIONAL 2 hr
○ RUN 1
○ RUN 2
○ AVERAGE OF RUNS 1 AND 2


TEST CONDITIONS
CHARCOAL NORIT, TYPE 0.5% KI, DIAM. OF PELLETS 2 mm
WET AIR 31.2°C 100% R.H 3.6 x 10$^3$ AIR CHANGES/h

WATER ABSORBED IN % OF DRY CHARCOAL

0 20 40 60 80 100
0 10 20 30 40 50
TIME [h]
TABLE III. CH$_3^{131}$I REMOVAL EFFICIENCY OF IMPREGNATED CHARCOAL UNDER SIMULATED MCA CONDITIONS

Charcoal: Norit 0.5% KI in pellets, 2 mm diam., 3 successive beds, total bed depth 50 cm, diam. 2.5 cm.
Loading: 3.5 ± 0.5 μg CH$_3$I/g charcoal, total $^{131}$I activity 0.15 ± 0.05 mCi.
Sweep gas: air, temperature 31.2°C, relative humidity 100%, atmospheric pressure, superficial velocity 30 m/min.
Duration of air flow: pre-humidification 48 h, CH$_3$I injection 48 h, air flow continued for additional 2 h, total 98 h.

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>Stay time (sec)</th>
<th>CH$_3^{131}$I removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run 1</td>
<td>Run 2 Average</td>
</tr>
<tr>
<td>6.25 ± 0.4</td>
<td>0.125</td>
<td>54.56 52 18 53 37</td>
</tr>
<tr>
<td>12.50 ± 0.4</td>
<td>0.250</td>
<td>88 21 81 34 83 28</td>
</tr>
<tr>
<td>18.75 ± 0.4</td>
<td>0.375</td>
<td>93 53 91 94 92 74</td>
</tr>
<tr>
<td>25.00 ± 0.4</td>
<td>0.500</td>
<td>97 85 97 90 97 61</td>
</tr>
<tr>
<td>31.25 ± 0.4</td>
<td>0.625</td>
<td>99 32 99 23 99 28</td>
</tr>
<tr>
<td>37.50 ± 0.4</td>
<td>0.750</td>
<td>99 74 99 68 99 71</td>
</tr>
<tr>
<td>43.75 ± 0.4</td>
<td>0.875</td>
<td>99 93 99 92 99 92 5</td>
</tr>
<tr>
<td>50.00 ± 0.2</td>
<td>1.000</td>
<td>99 98 99 97 99 97 5</td>
</tr>
</tbody>
</table>

* The charcoal from the single beds was poured out in fractions. Therefore, the tolerance for one fraction is higher than for the total bed depth.

To avoid overloading the MCA-iodine filters, we perform our tests with at least twice the maximum mass of CH$_3$I per gram of charcoal expected in an accident. However, there is some concern about the validity of experimental results with tracer activities of CH$_3$I for MCA conditions. The specific activity of organic iodine may be higher than in the test runs by a factor of 10$^6$ and more.

Tests with methyl iodide of high specific activity

Today it is generally accepted that the trapping of radioactive CH$_3^{131}$I by impregnated charcoal is mostly due to an isotopic exchange of $^{131}$I in the form of CH$_3^{131}$I in the gas phase with $^{127}$I on the charcoal, mostly as K$^{127}$I or $^{127}$I$_2$. For this isotopic exchange the relation of active organic iodine in the gas stream to inactive iodine on the charcoal will be much more unfavourable in a MCA situation than under the widely used laboratory test conditions. The upper loading limit for activity in the form of organic iodine compounds should be established. We performed some tests with mixtures of CH$_3^{131}$I + CH$_3^{127}$I of higher specific activity. To avoid trapping of CH$_3$I by adsorption on the charcoal as far as possible, we used air.
TABLE IV. CH$_3^{131}$I REMOVAL EFFICIENCY OF IMPREGNATED CHARCOAL ON LOADING WITH METHYLIODIDE OF HIGH SPECIFIC ACTIVITY

Charcoal: Norit, type RCX 1% KI, in pellets, diam. 0.8 mm, length 3 - 6 mm, 10 successive test beds, bed diam. 8 mm.

Loading with CH$_3^{131}$I ($^{131}$I activity per g charcoal, calculated for the weight of the first test bed): run 1: 3 ± 0.6 mCi/g, run 2: 3.5 ± 0.7 mCi/g, run 3: 8 ± 1.6 mCi/g, run 4: 1 ± 0.2 Ci/g, run 5: 0.3 ± 0.06 Ci/g.

Loading with CH$_3^{127}$I: 20 ± 4 µg total for each run.

Sweep gas: air, 30°C, 98 - 100% R.H., atmospheric pressure, superficial velocity 15 m/min.

Duration of air flow: pre-humidification 20 h, CH$_3$I-injection 15 min, air flow continued for 22 h.

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>Stay time (sec)</th>
<th>CH$_3^{131}$I removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average of runs 1, 2</td>
</tr>
<tr>
<td>2.5</td>
<td>0.1</td>
<td>50.16</td>
</tr>
<tr>
<td>5.0</td>
<td>0.2</td>
<td>77.32</td>
</tr>
<tr>
<td>7.5</td>
<td>0.3</td>
<td>88.80</td>
</tr>
<tr>
<td>10.0</td>
<td>0.4</td>
<td>94.49</td>
</tr>
<tr>
<td>12.5</td>
<td>0.5</td>
<td>97.33</td>
</tr>
<tr>
<td>15.0</td>
<td>0.6</td>
<td>98.75</td>
</tr>
<tr>
<td>17.5</td>
<td>0.7</td>
<td>99.36</td>
</tr>
<tr>
<td>20.0</td>
<td>0.8</td>
<td>99.67</td>
</tr>
<tr>
<td>22.5</td>
<td>0.9</td>
<td>99.84</td>
</tr>
<tr>
<td>25.0</td>
<td>1.0</td>
<td>99.91</td>
</tr>
</tbody>
</table>

$^a$ In run 5 the relative humidity of the sweep gas was slightly lower than in runs 1 - 4, only 4 test beds were used in this run.

with 98-100% R.H. for the sweep gas. Therefore, the results of the experiments should reflect the influence of the changed relationship for an isotopic exchange.

To avoid extreme handling and shielding problems we used small charcoal beds with a diameter of 6 mm. The runs were performed with pellets of KI impregnated charcoal of 0.8 mm diameter and a length of 2 - 3 mm. There will be more channelling than in tests with larger test bed diameters, but in the experiments the results were consistent enough to be sure that this effect would not obscure effects of activity overloading.

In Table IV the results of some runs are indicated. For comparison and to test the reproducibility, runs 1, 2 and 3 were performed on an intermediate activity level. The activity (in the form of CH$_3^{131}$I) reaching
the first test bed was between 3 and 8 mCi/g charcoal, mixed with a total of 20 µg CH$_3^{127}$I. In run 4 the activity was increased to 1 ± 0.2 Ci/g charcoal. Considering the somewhat lower reproducibility of experiments with very small charcoal beds, the removal efficiency is nearly the same in all four runs and no overloading effect can be seen. In Table IV one further run (No. 5) is included with a relative humidity slightly lower than that of runs 1-4. The total activity (in the form of CH$_3^{131}$I) reaching the first charcoal bed was 0.3 Ci/g charcoal. The removal efficiency is better than in runs 1-4, which demonstrates the sensitivity of the results to small changes in the relative humidity. Figure 5 shows the penetration of the charcoal beds plotted against bed depth for run 4. Each point represents one of the successive charcoal beds. To the first and the last point are assigned the values for the activity per gram of charcoal reaching that particular charcoal bed. Within the accuracy of the experiment a straight line can be drawn through the points and no sign of a pronounced bend in the region of high-activity loading is observed.

---

**FIG. 5.** Penetration of CH$_3$ $^{131}$I from a methyl iodide mixture of high specific activity through impregnated charcoal.
IN-PLACE TESTS

Test agent and operating conditions

In-place tests should establish the leak rate of the iodine filter system and the condition of the adsorber material. For the test agent, therefore, a mixture of $\text{C}_{3}\text{H}_3\text{I}^1 + \text{C}_{3}\text{H}_3\text{I}^2$ is used where the iodine filter is filled with impregnated charcoal. For filter systems of an older design (and lower removal efficiency, of course) a mixture of $\text{I}^1_2$ and $\text{I}^2_2$ will be used. For technical and financial reasons, the in-place tests are performed under normal operating conditions of the iodine filter system.

Pre-run in the laboratory, activity of test agent

In the test procedure a pre-run in the laboratory is included with the conditions expected for the in-place test. This will indicate the maximum removal efficiency of the iodine filter, excluding mechanical leaks and aged charcoal. Curve (a) of Fig. 3 shows the results of a pre-run for an in-place test of the Obrihein iodine filter. In this case, the removal efficiency is high enough to prevent activity from being detected downstream of the iodine filter without a mechanical leak or badly aged charcoal. The total activity used in the in-place tests is calculated with respect to the removal efficiency of the iodine filter system established in the hazards report of the installation in question. We think that the activity should be high enough to indicate a leak which produces 1% of the maximum allowable penetration.

Arrangement and samplers for in-place tests

The arrangement used for the Obrihein in-place test is shown in Fig. 6. To avoid using an extremely high activity, a relatively high gas flow through the downstream sampler is maintained ($\text{m}^3/\text{h}$). The gas flow through the upstream sampler is normally lower by a factor of $\sim 100$. The volume of the impregnated charcoal in the sampler is sufficiently large to have at least a total stay time of 1 sec in tests performed with methyl iodide. The upstream and downstream samplers are fitted with charcoal beds of the same diameter and bed depth to avoid geometrical problems in quantitative gamma-spectroscopy. To compensate for the higher gas velocity in the downstream sampler, a larger number of charcoal beds is used. Owing to the different superficial gas velocities, the distribution of the activity in the upstream and the downstream samplers is not the same. For measurement the samplers therefore have to be dis-assembled, and the charcoal of each bed has to be mixed very carefully. Each charcoal bed is measured separately to check the quantitative removal of the test agent in the sampler.

Container system for test agent

Figure 7 shows a drawing of the container system for handling and transport of the radioactive test agent and a charcoal sampler. The inner container filled with the test agent is built in form of a U-tube closed with bellows seal valves and quick-connects with double end shut-off. The U-tube
is cast in a lead cylinder for shielding. This inner container is used also as a recipient for the distillation of the methyl iodide. This avoids handling of unshielded radioactive agents. The inner container is transported to the iodine filter to be tested inside a gas-tight transport container which is fitted with additional shielding and a charcoal trap. Before the transport container is opened, it is flushed with air so that gaseous activity will be trapped in the charcoal. The charcoal trap is not shielded; therefore a leak of the inner container can be detected by simple gamma measurement on the outside of the charcoal trap without opening the transport container.

Data on the in-place test of the Obrigheim MCA-iodine filter

Finally, some data on the in-place test of the Obrigheim MCA-iodine filter are given. The activity of the CH$_3^{13}$I was 100 ± 20 mCi, mixed with 5 ± 1 mg CH$_3^{127}$I.

The gas flow through one upstream sampler was 24 litre/h (s. t. p.), through one downstream sampler it was 2500 litre/h (s. t. p.). Two charcoal samplers of each type were used. The charcoal volume of one downstream sampler was 765 cm$^3$. After an injection time of 15 min the air flow through the iodine filter was maintained for 2 h. The temperature was 21.5 ± 0.5°C,
R.H. $55 \pm 2\%$. The removal efficiency $\eta$ of the iodine filter in the in-place test was

$$\eta = 99.9998\%$$

(under simulated MCA conditions the removal efficiency of the charcoal was $99.975 \pm 0.015\%$).
The simple design of the iodine filter (two containers in parallel with a charcoal fill much higher than the perforated sheet metal welded to both ends of the container and a total charcoal volume of 1 m³) made a result as that received from the in-place test likely, because most sealing problems are avoided.

REFERENCES


DISCUSSION

G. BURLEY: Were all your tests run with fresh charcoal?

J.G. WILHELM: Yes.

P.J. LINDER. You made elaborate arrangements to keep the relative humidity constant at 100%. However, in view of the strong decrease in efficiency at a relative humidity approaching 100%, demonstrated by Mr. Adams in paper SM-110/37, would it not be advisable to perform charcoal filter tests with a system ensuring complete cleaning of the air, e.g. using de-misters, coolers, heaters, etc? Conditions during an MCA should either differ distinctly from 100% relative humidity (80% or 90% R.H.) or else be such that it would be impossible to say more than that a water mist could be present. In the latter case, the efficiency should be tested under the conditions obtained with the suggested de-misters, etc. and with an initial wet-air/steam mixture.

J.G. WILHELM: I agree that an in-place test under MCA temperature and relative humidity conditions would be more informative than a test performed under normal environmental conditions. But normally the off-gas systems are not equipped for such a test and it would be extremely costly to build and maintain the additional equipment. Therefore, extensive testing of the adsorber material under simulated MCA conditions is performed in the laboratory. In addition to this, a test rig should be available at one central place for testing single filter elements under MCA conditions.
HIGH TEMPERATURE PROPERTIES OF ACTIVATED CARBON: PART I. DESORPTION OF IODINE; PART II. STANDARD METHOD FOR IGNITION TEMPERATURE MEASUREMENT

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Abstract

HIGH TEMPERATURE PROPERTIES OF ACTIVATED CARBON PART I. DESORPTION OF IODINE; PART II. STANDARD METHOD FOR IGNITION TEMPERATURE MEASUREMENT. The removal of iodine from activated carbon by flowing air was measured at elevated temperatures to evaluate both various carbons and the effects of variables, such as service, partial regeneration, and temperature, on desorption. The preliminary results are reported. A standard method was developed to measure ignition temperature, to evaluate promising new types of activated carbon, and to evaluate the effects of variables, such as air flow, bed properties, impregnants, and plant service, on ignition temperature. The standard method and results of the evaluation are reported.

INTRODUCTION

Confining the radioactive iodine that would be released in the unlikely event of a reactor accident is very essential because iodine is potentially the most hazardous fission product to the surroundings of a nuclear reactor. At the request of the USAEC Division of Operational Safety, a broad program [1, 2] was undertaken in 1965 at the Savannah River Laboratory (SRL) to seek a system that would remove and retain fission-product iodine from air at temperatures higher than the limitations of the present activated carbon systems. Another phase of this program, the effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon, was discussed by Jones at the Tenth AEC Air Cleaning Conference [3].

At temperatures up to about 100°C iodine is adsorbed and retained on activated coconut-shell carbon with efficiencies greater than 99.9% [4-6] under a wide variety of adverse conditions. In the unlikely event of a reactor accident, decay heat from uncooled reactor fuel or from radiiodine adsorbed on uncooled carbon beds could heat the beds to temperatures above 200°C. At such temperatures substantial amounts of iodine may be released. Therefore the amount and rate of iodine desorption from various carbons, the variables that affect desorption, and the ignition temperature of new carbon must be known when designing nuclear reactor confinement systems and back-up emergency cooling systems.

* The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the US Atomic Energy Commission.
Preliminary results on the desorption of iodine from activated carbon are discussed in Part I of this paper, and a standard method of measuring ignition temperature of carbon is discussed in Part II of this paper.

SUMMARY

Part I. Desorption of iodine

The desorption of iodine from activated carbon at elevated temperatures was measured by heating a test carbon bed (loaded with iodine) with flowing air and collecting the desorbed iodine.

An insignificant amount of iodine (~0.02%) was desorbed from new Type 416 carbon (hereafter "new" refers to non-service carbon) when the iodine was loaded in a steam-air mixture at 65°C and desorbed at 200 ± 10°C for 110 min. Iodine desorption from new Type 416 carbon increased exponentially with temperature. Other carbons tested under the same conditions desorbed substantially more iodine (Type 7271, 0.05%; Type 5921, 2%; and Type 1171, ~30%).

The desorption of iodine increases significantly with service time in a confinement system. The desorption after 46 months service was from 0.025 to 0.2% at 200°C.

Part II. Standard method for ignition temperature measurement

A standard method of measuring the ignition temperature of activated carbon was developed from previous tests which measured ignition temperatures with a small-scale stainless steel apparatus [1, 2]. In the standard method a quartz apparatus was used to eliminate any possible catalytic effect of metals on ignition temperature. A test carbon bed 1 in. in diameter by 1 in. thick is heated at a uniform rate by flowing air. At the ignition temperature, there is an abrupt increase in the temperature of the carbon above the temperature of the flowing air. The detailed procedure is shown in the Appendix.

The ignition temperature of Type 416 carbon was 340 to 350°C for a face velocity of 15 to 180 ft/min. The ignition temperature of Type 592 increased from 435°C at a face velocity of 15 ft/min to 535°C at 105 ft/min. At velocities below 7 ft/min complete ignition did not occur in either carbon because of the limited amount of oxygen.

The ignition temperature of Type 117 carbon (specially impregnated by Barnebey Cheney Co. to retain iodine at elevated temperatures) increased from 380°C at a face velocity of 15 ft/min to 405°C at 90 ft/min.

In a co-operative program with Oak Ridge National Laboratory and the Barnebey Cheney Co. ignition temperatures were duplicated for Type 416, Type 592, and Type 117 carbon by the standard method. This method has been submitted to the American Society of Testing and Materials for consideration.

Tests with the standard ignition method showed that the ignition temperature increased with air velocity and impregnation with elemental iodine and decreased with thicker beds. The same ignition temperature for Type 416 carbon was obtained with the quartz apparatus, the stainless steel apparatus [1, 2], and with full-size beds [1, 2].

1 Product of Barnebey Cheney Co
DISCUSSION

Part I. Desorption of Iodine

Apparatus and procedure

The apparatus shown in Fig. 1 measured iodine adsorption efficiency and the desorption of iodine from activated carbon. Only the desorption of iodine is discussed in this paper.

To measure desorption, a test carbon bed (2-in. diam by 1 in. thick) is loaded by adsorbing from flowing air elemental iodine vapour tagged with $^{131}$I. Then purified air at the desired temperature is passed through the test bed and any desorbed iodine is adsorbed on back-up carbon beds. The ratio of the $^{131}$I on the back-up beds to that on the test bed is the fraction of iodine desorbed.

In this desorption apparatus ambient air is purified with a carbon bed and an absolute particulate filter. Part of the air passes through a rotameter and enters a hood where it vaporizes iodine from a glass frit for about 60 min. The iodine vapour enters a heated cabinet (65°C), passes through an absolute particulate filter and is adsorbed on a test carbon bed. Thermocouples measure the air temperature upstream and downstream of the test bed, the pressure upstream of the test bed is measured with a gauge, and the pressure drop across the bed is measured with an inclined manometer. Any iodine that penetrated the test bed during the loading step is collected on the back-up beds and the accumulation of iodine on the back-up beds is monitored continuously with a gamma detector. The first back-up bed contains Type 416 carbon to remove elemental iodine; the second bed contains Type 727 carbon to remove methyl iodide. No methyl iodine was detected in this work. Air is drawn through the apparatus with an air pump and passes into the off-gas exhaust (OGE) system.
In some tests, the test carbon bed was loaded by adsorbing iodine vapour from a steam-air mixture. Steam is filtered and added to air to form a mixture temperature of 65°C, which is the temperature of maximum water entrainment [7]. In such tests, dilution air is added through the second rotameter, heated, and then combined with the main air flow downstream of the test bed to eliminate any condensation as the air leaves the cabinet and enters the back-up beds. To measure iodine desorption after steam-air loading, the main air flow is closed off, the dilution air is passed through the test bed at the desired temperature, and desorbed iodine is collected on the same back-up beds and measured continuously with the gamma detector.

After a test, the desorption apparatus is disassembled and 20 key pieces are counted with the gamma detector which has three counting positions. A computer processes the experimental data to calculate the amount of iodine desorption, the iodine loading, and the material balance.

Sections of the apparatus through which iodine passes were built of glass and Teflon-coated stainless steel. These materials minimize the deposition of radioactive iodine on surfaces for better material balance and easier cleaning. Operating temperatures are limited to about 220°C to avoid decomposition of the Teflon.

Effect of temperature

An insignificant amount of iodine (<0.02%) was desorbed from new Type 416 carbon at temperatures up to 200 ± 10°C with a face velocity of 68 ft/min (Fig. 2). In this test the iodine was loaded on the carbon with

\footnote{Du Pont trademark for fluorocarbon resins.}
dry air at ambient temperature. The rate of desorption from new Type 416 decreased with time at elevated temperature and after about 30 min the rate was negligible. The iodine desorption in two tests at 140°C agreed within 25%.

As also shown in Fig. 2, the total amount of iodine desorbed increased exponentially with temperatures from 90 to 200°C.

Effect of steam-air loading on iodine desorption

New Type 416 Carbon. The presence of steam during the loading hardly affected the desorption of iodine from new Type 416 carbon at 200°C and a face velocity of 68 ft/min. As shown in Fig. 3, <0.01% was desorbed in both tests. The greater iodine desorption from carbon that was loaded from ambient air may be caused by the heavier iodine loading. Additional tests will continue to evaluate the effect of loading on iodine desorption.

New Type 592 Carbon. Penetration of iodine from new Type 592 was insignificant (<0.01%) when the carbon was loaded with either a steam-air mixture at 65°C or dry air at 65°C. Similar results for steam-air tests were obtained previously [1]. However, during the desorption test in dry air at 200°C an unusually large amount of iodine was released. As shown in Fig. 4, there was no significant difference in desorption for the steam-air loading or the air loading. As the bed temperature reached 160 to 170°C, there was a sudden increase in the rate of desorption of iodine from new Type 592 carbon for both loadings. The advantage of the high-ignition temperature of Type 592 carbon is offset by its poor iodine retention at elevated temperatures. Therefore, Type 592 carbon is not recommended for confinement applications.

![FIG. 3. Effect of steam-air loading on desorption of iodine.](image)
Comparison of desorption from different carbons

The desorption from Types 416, 727, 592, and 117 carbon was measured from test beds prepared by loading iodine from a steam-air mixture at 65°C and desorbing it at 200°C with dry air. The face velocity for loading and desorbing was 68 ft/min. Overall, Type 416 desorbed the least amount of iodine (<0.01%) of the four carbons tested.

Figure 5 shows that about 0.05% of the iodine was desorbed in 110 min from Type 727 carbon which is impregnated with about 5% iodine for applications requiring removal and retention of methyl iodide.

About 2.0% of the iodine was desorbed from Type 592 carbon in 110 min.
The greatest amount of iodine (28%) was desorbed from Type 117 carbon even though the iodine loading was much lower (0.30 mg I/g C) than that for the others. Type 117 carbon is impregnated in a proprietary manner to retain iodine at elevated temperatures and to have a relatively high ignition temperature (405°C at a face velocity of 70 ft/min). However, with such a high rate of desorption, this carbon is unsatisfactory for most confinement applications.
The results of the evaluation of the desorption properties of four carbons are summarized in Table I.

**TABLE I**

**DESORPTION OF IODINE FROM VARIOUS CARBONS**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Iodine Loading mg I/g C</th>
<th>Desorbed in 110 Min Test with Air at 200°C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 416</td>
<td>0.77</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Type 727</td>
<td>0.60</td>
<td>0.05</td>
</tr>
<tr>
<td>Type 592</td>
<td>0.62</td>
<td>2.0</td>
</tr>
<tr>
<td>Type 117</td>
<td>0.30</td>
<td>28</td>
</tr>
</tbody>
</table>

Effect of service and partial regeneration on desorption

As would be expected, desorption of iodine from activated carbon increases with service; however, the life of the carbon can be extended by partial regeneration. As seen in Fig. 6, after 46 months service in the SRP confinement system Type 416 carbon desorbed a significant amount of iodine. The desorption from new Type 416 is also shown in Fig. 6 for comparison. Each sample in Fig. 6 had been partially regenerated in the laboratory by heating the sample in a stream of purified air. This treatment simulated the treatment of carbon in the SRP confinement system prior to the on-line Freon® test [8] which is made each year. In the confinement system, the carbon is heated to 60°C for at least 48 h at a face velocity of 5 to 10 ft/min. Table II summarizes the laboratory partial regeneration conditions for test carbons.

<table>
<thead>
<tr>
<th>Test Carbon</th>
<th>Time h</th>
<th>Temperature °C</th>
<th>Velocity ft/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>60</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>96</td>
<td>60</td>
<td>7.5</td>
</tr>
<tr>
<td>3</td>
<td>66</td>
<td>-45</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The desorption of iodine from test carbon 1 (0.0021% after 60 min) was about the same as from new carbon (0.0026%). The desorption of iodine from test carbon 2 (0.013%) was significantly greater than that from new carbon. The reason for the large difference in desorption from test carbons 1 and 2 is being studied.

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* Du Pont trademark
Test carbon 3 had the same history as 2, but was partially regenerated at about 45°C instead of 60°C. As seen in Fig. 6, the desorption from 3 was significantly greater than that from 2 because at lower temperature a smaller fraction of the impurities were released.

Future work

The preliminary results presented will guide future work. The desorption test will be used to evaluate promising new carbons for confine-
ment applications and to determine the effect of inlet iodine concentration, loading, and face velocity.

Tests are planned to identify the impurities that degrade carbon and to determine if partial regeneration will restore the carbon. Such information may lead to the development of accelerated tests of carbon quality by artificially aging carbon through exposure to higher concentrations of these impurities, but for shorter times than found in normal service.

Additional tests are planned to determine (1) if better conditions for partial regeneration can be developed which will extend the service life of activated carbon, (2) the effect of slightly higher temperatures (~80°C) and much longer time (~1 week) of partial regeneration, and (3) the possible advantage of using steam-air mixtures for partial regeneration instead of air.

Part II. Standard method of ignition temperature measurement

Apparatus

A standardized apparatus and procedure were developed to determine the ignition temperature of promising new types of activated carbon, and to evaluate the effects of variables on ignition. The standard ignition apparatus is shown in Fig. 7. Compressed air entering the apparatus is purified by a 1-in. thick carbon bed and an absolute filter (Fig. 8). Flows up to 0.98 ft³/min (face velocity of 180 ft/min) are measured by calibrated rotameters. The temperature of the air flowing through the preheater is increased by adjusting the Powerstat. At low face velocities supplementary heat was added with the oven. The carbon is heated by the hot air passing through the bed. Three 0.025-in. OD thermocouples measure the temperature of the carbon bed (Fig. 9). Similar thermocouples measured the upstream and downstream air temperatures. Carbon beds with depths up to 4 in. can be tested in this apparatus.

Procedure

A dense-packed bed of test carbon is prepared by pouring the carbon through a funnel so there was a free fall of 12 in. When the bed is 1 in.

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4 Trademark of Superior Electric Co., Bristol, Connecticut
deep, a coarse quartz frit is placed on the bed and the thermocouples inserted. The carbon bed is heated rapidly to 150°C with flowing air by adjusting the Powerstats, and then the heating rate is adjusted to 2 to 4 degC/min. At the ignition point, the test is terminated by closing Valve 1 (Fig. 7) and flushing the bed with nitrogen from Valve 2.
Results of co-operative tests

Ignition temperatures of three different carbons agreed within 5 degC (except one was 8 degC) when measured by Savannah River Laboratory, Oak Ridge National Laboratory, and Barnebey Cheney Co. with the standard ignition method (Fig. 10). Each laboratory used identical samples of carbon which were provided by the Barnebey Cheney Co.

Type 416 carbon

The ignition temperature of the Type 416 carbon, a coconut-shell carbon that is used in the SRP confinement system, is 340 to 350°C for a face velocity of 15 to 180 ft/min in the standard quartz apparatus. As shown in Fig. 11, these temperatures are essentially the same as those obtained with the stainless steel apparatus. Similar results also were obtained in the standard quartz apparatus for a sample of Type 416 carbon that was ordered for test purposes.

At velocities of 7 ft/min or less the combustion of Type 416 carbon was so slow that there was no runaway oxidation even though the carbon was heated to 700°C. Apparently at velocities of 7 ft/min or less the combustion was controlled by the limited oxygen supply and the accumulation of oxidation products in the bed.

As the ignition temperature was approached at velocities from 30 to 180 ft/min, the temperature at the downstream face increased above the temperature at the upstream face. This increase was attributed to heat from the slow oxidation of carbon at temperatures below ignition. At velocities from 65 to 180 ft/min a blue flame from the combustion of carbon monoxide was occasionally observed. As soon as the air flow was stopped, combustion stopped.
Type 592 carbon

The ignition temperature of Type 592 carbon from a production lot in the standard quartz apparatus was slightly higher than that for carbon from an experimental lot in the stainless steel apparatus (Fig. 12).

FIG. 11. Effect of face velocity and apparatus on ignition temperature of Type 416 carbon.

FIG. 12. Effect of face velocity on ignition temperature of Type 592 carbon.
As observed previously [1, 2], the ignition temperature of Type 592 carbon increased with increasing face velocity. Eight full-sized beds of this carbon were installed in the SRP confinement system in 1966 to evaluate the effect of service.

The iodine adsorption efficiency of Type 592 carbon was 99.99+% in a stainless steel apparatus [1, 2] with a loading of 0.34 to 1.51 mg I/g C. At velocities less than 7 ft/min the combustion of Type 592 carbon also was so slow that there was no runaway oxidation even though the carbon was heated to 700°C. At these low velocities combustion was controlled by the limited oxygen supply and the accumulation of oxidation products in the bed.

The ignition temperature of Type 592 carbon decreased with increased face velocity from 7 to 10 ft/min (Fig. 12). At velocities above 10 ft/min there was a significant increase in ignition temperature. Similar behaviour was measured in the stainless steel apparatus.

Type 592 carbon burns at a much slower rate than Type 416 carbon because of the special treatment that increases its ignition temperature. Type 416 carbon burns with a bright red-white incandescence. Type 592 carbon burns with a dull glow. Type 592 carbon was not homogeneous because occasionally at about 470°C (velocities > 95 ft/min) a single granule would ignite, but the glow vanished without igniting the bed. The temperature of the bed could then be increased without ignition until ignition point was reached.

Type 117 carbon

The ignition temperature of Type 117 increased from 380 to 410°C as the velocity increased from 15 to 90 ft/min in the standard quartz apparatus (Fig. 13). This newly developed coconut-shell carbon is especially impregnated in a proprietary manner to retain iodine at elevated temperatures and to have an ignition temperature intermediate between Type 416 and Type 592.

The iodine adsorption efficiency of an experimental lot of Type 117 carbon was 99.99+% [5] with a loading of 1.23 mg I/g C. This new carbon, which is made from the same base material as Type 416 carbon, has a surface area of about 1000 m²/g, 10 to 14 mesh size and a hardness of 97%. 
Other carbons

The ignition temperatures of other carbons were measured in both the standard quartz apparatus and a stainless steel apparatus and agreed well (Table III). In the standard quartz apparatus measurements were made on a 1-in. thick by 1-in. diam. bed at a face velocity of 70 ft/min. In the stainless steel apparatus, measurements were made with a 1-in. thick by 3-in. diam. bed at a face velocity of 70 ft/min.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Mesh</th>
<th>Ignition Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard Quartz Apparatus</td>
<td>Stainless Steel Apparatus</td>
</tr>
<tr>
<td>European carbon</td>
<td>1 mm diam. x 3 mm long</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>3 mm diam. x 7.5 mm long</td>
<td>265</td>
</tr>
<tr>
<td>ASC Whetlerite*</td>
<td>12-30</td>
<td>265,270</td>
</tr>
<tr>
<td>Whetlerite*</td>
<td>12-30</td>
<td>240,240</td>
</tr>
<tr>
<td>Type 416*</td>
<td>10-14</td>
<td>345,350</td>
</tr>
<tr>
<td>PBC*</td>
<td>6-16</td>
<td>370</td>
</tr>
<tr>
<td>Type 727*</td>
<td>8-14</td>
<td>380</td>
</tr>
<tr>
<td>Type 348*</td>
<td>6-16</td>
<td>445</td>
</tr>
<tr>
<td>Type 592*</td>
<td>10-14</td>
<td>500</td>
</tr>
</tbody>
</table>

1 l-in. thick by 1-in. diam. bed
2 l-in. thick by 3-in. diam. bed
3 Specification MIL-C-13724A
4 Product of Pittsburg Activated Carbon Co.
5 Product of Barnebey Cheney Co.
6 Product of Whitco Chemical Co.

Effect of face velocity on location of ignition

In measuring ignition temperature, the carbon is heated by increasing the temperature of the inlet air 2 to 4 degC/min. Initially the bed temperature remains below the inlet temperature; however, as the bed temperature reaches 150 to 165°C (at velocities up to 9 ft/min), the temperature of the carbon at the upstream face of the bed becomes greater than the temperature
of the incoming air. The heat that produces this temperature rise comes from the 'slow' oxidation of carbon

\[2 \text{C (excess)} + \text{O}_2 \rightarrow 2 \text{CO} \quad \Delta H = 26.4 \text{ kcal/mole} \ [9]\]

The product of this reaction is carbon monoxide because carbon is present in a large excess. At a face velocity of 9 ft/min the heat produced by 'slow' oxidation was 1.8 pcu/h (a \(\Delta T\) of 20°C). The 'slow' oxidation of carbon did not produce any glowing granules. At >10 ft/min the heat of this reaction was removed so rapidly by flowing air that the temperature of the upstream face was the same as that for the incoming air.

At \(\leq 7\) ft/min the initial combustion in a 1-in. thick bed always occurred at the upstream face. As the carbon granules in the bottom of the bed slowly turned to ashes, granules from above dropped into the ashes and slow combustion continued at the upstream face until the carbon was consumed. This process took about 20 min at a face velocity of 5 ft/min. Temperature measurements were difficult because of granules falling to the bottom of the bed.

The test showed that at low velocity, combustion was at the upstream face because the oxygen was completely converted to carbon monoxide upon the first contact with the hot carbon. Because the atmosphere downstream from the bed was depleted in oxygen, combustion in the downstream areas of the bed was negligible even up to 700°C.

As the bed temperature was increased uniformly at 2 to 4 degC/min at these low velocities, the temperature of the upstream face at the ignition point increased suddenly, but with no runaway oxidation or glow of carbon granules. At about 450°C a single granule showed a dull red glow in the first eighth of an inch of the upstream face of the bed. At 1 and 1.5 ft/min the single granule frequently burned out without igniting additional granules. At 2 to 7 ft/min a single granule ignited adjacent granules and in about two minutes the upstream face of the bed had a dull red glow. At 5 ft/min with a single granule glowing when the velocity was suddenly increased to 70 ft/min the entire bed ignited at once. When the air flow was stopped suddenly after the entire bed had ignited, the glow disappeared instantly.

At these low velocities the temperature of the upstream face of the bed can increase as much as 300 degC above the temperature of the inlet air because of slow combustion without runaway ignition. The temperature increase depends on heat loss from the system.

At 9 and 10 ft/min ignition was midway between the downstream and upstream faces of the bed. The ignition propagated toward the upstream face of the bed because the downstream atmosphere was depleted in oxygen.

At 15 to 180 ft/min the initial ignition in a 1-in. thick bed usually was at the downstream face, occasionally up to one quarter inch from the downstream face. At these velocities, the ignition rapidly propagated upstream and the entire bed burned to ash (about 1.5 min at a face velocity of 70 ft/min).

The effect of velocity as well as other parameters is discussed by Davis in terms of a theoretical model [10].

Effect of bed depth

In the standard quartz apparatus the ignition temperature of Type 416 carbon decreased about 15 degC as the bed depth increased from 1 to 4 in.
FIG. 14. Effect of bed depth on ignition temperature of Type 416 carbon.

at a face velocity of 70 ft/min (Fig. 14). Measurements in a stainless steel apparatus showed < 5 degC decrease in ignition temperature with increased bed depth.

CONCLUSIONS

Part I. Desorption of iodine

An insignificant amount of iodine (< 0.01%) was desorbed from new Type 416 carbon by dry air at temperatures up to 200°C at a face velocity of 68 ft/min.

High temperature (~200°C) desorption of iodine from activated carbon increases with increased service life.

Impregnated activated carbon (to retain methyl iodide or increase ignition temperature) have significantly inferior desorption properties, therefore, these impregnated carbons should be confined to low-temperature applications.

Ignition temperature, without regard to desorption characteristics, is not an adequate indicator of high-temperature effectiveness of activated carbon.

Part II. Standard method for measurement of ignition temperature

A standard method to measure the ignition temperature of activated carbon was developed and used to evaluate promising new types of carbon and the effects of variables.

ACKNOWLEDGMENTS

The valuable guidance of A. H. Peters in the design and operation of the desorption apparatus and in the planning of the experiments is gratefully acknowledged. The author also expresses gratitude to L. R. Jones for the preparation of the computer program and to J. H. Williams who assembled the apparatus and performed the experiments.
APPENDIX

PROPOSED TENTATIVE METHOD FOR MEASUREMENT OF
THE IGNITION TEMPERATURE OF ACTIVATED CARBON

1. SCOPE

1.1 This ignition method measures the ignition temperature of activated carbon up to 600°C and for air velocities to 100 ft/min.

1.2 The method is applicable to granular, activated carbon (6 to 20 mesh range) made from coconut shell, coal, or petroleum. It is applicable to carbon that is new or has been in service.

2. SUMMARY OF METHOD

2.1 The sample is heated by passing air upward through a bed of activated carbon that is supported on a coarse quartz frit (Figure 7). At the ignition temperature, the temperature of the carbon suddenly rises above the temperature of air passing into the carbon.

3. DEFINITION OF TERMS

3.1 For definitions of terms used in this method, refer to American Society for Testing and Materials Definitions D 2652, Terms Relating to Activated Carbon.

4. APPARATUS

4.1 Sample holder. An apparatus made of quartz (Figure 9) is used to hold the test carbon bed.

4.2 Glass funnel, 6-in. diam. with 0.4-in.-ID stem.

4.3 Thermocouples, Chromel-Alumel with a 0.025-in. stainless steel sheath 10 in. long, Thermocouple Products Co., Villa Park, Illinois, or equal, are used to measure the temperature of (a) the inlet air, (b) the upstream carbon-quartz frit interface, (c) the carbon 1/8 in. from the upstream frit, (d) the carbon 1/8 in. from the downstream frit, and (e) 1 in. above the downstream frit.

4.4 Air prefilter (Figure 8), 1-in. thick by 3-in. diam. bed of activated carbon (Barnebey Cheney Co., Type 416 or equal). Barnebey Cheney Co., Columbus, Ohio. The downstream face contains a high efficiency particulate filter, 3-in. diam., flat medium (Cambridge Filter Corp. Type C-30-B or equal). Cambridge Filter Corp., Syracuse, New York.

4.5 Rotameters, 0 to 6.5 scfm air and 0 to 0.65 scfm air.
4.6 Preheater, Type M2018 electric furnace, 1870 watts, Hevi Duty Electric Co., Milwaukee, Wis., or equal. Install 1/4-in.-OD tubing with about 1 ft² of surface area so that air can be heated to desired temperatures.

4.7 Oven, Type M3012 electric furnace, 1650 watts, Hevi Duty Electric Co., Milwaukee, Wis., or equal.

4.8 "Powerstat", variable transformer, Type 3PF136, Superior Electric Company, Bristol, Conn., or equal.

4.9 Compressed air, 60 psig.

4.10 Compressed nitrogen, 20 psig.

4.11 Tubing, 1/4-in.-diam. stainless steel, Swagelok fittings or equal. Crawford Fitting Co., Cleveland, Ohio.

4.12 Valves, 1/4-in. globe, brass or equal.

4.13 Insulation, 1/8-in.-thick asbestos cloth wrapped six layers deep.

5. REAGENTS AND MATERIALS

5.1 Activated carbon, representative sample of new carbon or carbon that has been in service.

6. STANDARDS

6.1 Primary standards are not available. Coconut carbon, Type 416, manufactured by the Barnebey Cheney Co., has shown a consistent ignition temperature of 330 to 340°C in tests with several different batches.

7. PREPARATION OF SAMPLES

7.1 A representative sample of carbon to be tested is placed in a beaker, and the weight of the beaker and carbon is measured and recorded.

7.2 The carbon is poured into the top of the apparatus to form a bed 1 in. deep. Pour the charcoal slowly into a 6-in. glass funnel with a 0.4-in.-ID stem. Allow the carbon to fall 12 in. to insure dense packing.

7.3 The weight of beaker and its contents is measured and recorded.

8. ASSEMBLY OF APPARATUS

8.1 Assemble apparatus as shown in Figures 7 and 9.

8.2 Test all connections to insure absence of leaks. Insulate tubing.
9. TEST PROCEDURE

9.1 Adjust air flow to give desired face velocity. The velocity should not exceed 100 ft/min (the bed becomes fluidized at velocities > 100 ft/min).

9.2 Apply power to the preheater by adjusting the "Powerstat." Heat the inlet air at ~10°C/min to 150°C.

9.3 Apply power to the oven so that temperatures at the upstream and downstream face of the bed are within 20°C.

9.4 Increase the temperature of the bed by adjusting the "Powerstats."

9.5 Adjust the rate of heating of the inlet air thermocouple to 2 to 3°C/min when the temperature is ~50°C below the expected ignition temperature.

9.6 Record the ignition temperature when a sudden rise occurs in the temperature of one of the thermocouples in the carbon bed or the thermocouple above the bed.

9.7 Stop the air flow by closing Valve 1; start the nitrogen flow by opening Valve 2, and turn off power to the preheater and oven.

10. PRECISION AND ACCURACY

10.1 The precision of the ignition temperature measurement is about ±5°C.

10.2 The accuracy of the ignition temperature measurement has not been determined. Data from three laboratories are shown in Figure 10.

REFERENCES

DISCUSSION

R.E. HOLMES: Have any attempts been made to investigate the effect of different bed depths on the rate of desorption?

R.C. MILHAM: To date, we have only measured beds that are 1 inch deep, because this is the thickness of the carbon beds in the Savannah River Plant confinement system.
THE EVALUATION OF THE IGNITION TEMPERATURE OF ACTIVATED CHARCOALS IN AIR, STEAM, OXYGEN AND OXIDES OF NITROGEN

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Abstract

THE EVALUATION OF THE IGNITION TEMPERATURE OF ACTIVATED CHARCOALS IN AIR, STEAM, OXYGEN AND OXIDES OF NITROGEN. The ignition temperature of impregnated and unimpregnated activated charcoals currently used for the adsorption of various forms of radioactive iodine is evaluated in detail. The standardized quartz ignition temperature apparatus was used for the experiments. Atmospheric conditions and gas-charcoal residence times existing in nuclear power reactor containment recirculating filter systems, emergency off-gas filter systems and fuel reprocessing plant filters were simulated for the ignition experiments. A theoretical explanation based on the experimental data is given for the contributing effects of charcoal properties, impregnants and the gas composition. The proper selection of activated charcoals for gaseous iodine filtration is discussed.

Activated charcoal filter systems are extensively used in both impregnated and unimpregnated forms to remove accidentally released gas phase radioiodine from reactor containment atmospheres. In addition to this use, similar filters are employed to purify gaseous exhausts of hot cells and spent fuel reprocessing plants. Current practices are described by Keilholtz, [1] Burchsted [2] and Durant, et al. [3]

Activated charcoals of medium to high surface area containing primarily small micropores have high adsorption and retention capacity for molecular iodine vapor in those concentrations which can occur under accident conditions. Charcoals impregnated with various forms of iodine exhibit good methyl iodide removal capacities by isotope exchange, while charcoals impregnated with organic amines such as triethylenediamine remove methyl iodide by the Menschutkin reaction. [4]

While the iodine removal capacity of activated charcoal under accident conditions exceeds those of other adsorbents, its major disadvantage is the possibility of igniting the charcoal bed at high temperatures in contact with oxidizing gases.

When activated charcoal is used in any fission-gas adsorption system, the ignition of these filters would release all of the retained fission products and contribute a considerable heat load to the containment system.

To avoid the occurrence of fire, several recently installed containment filters include an automatic water spray system which keeps the charcoal filters from rising above a pre-selected temperature.

The inclusion of spray systems for the charcoal filters was necessary because there was insufficient charcoal ignition information available at the time.
Early charcoal ignition work \([5,6,7,8]\) reported the ignition temperature of several carbons, but little correlation was made between the charcoal properties and ignition conditions.

In the last two years more comprehensive work was carried out and reported on the properties of activated charcoal related to ignition temperatures. \([9,10,11,12,13,14,15]\)

This latter work included evaluation of relationships between ignition temperature versus charcoal property parameters (surface area, particle size, ash content) and system parameters (bed depth, gas velocity, radioiodine deposition, gas composition).

Also in the past two years a standard method for ignition temperature measurement was developed as reported by Milham, \([16]\) and several high ignition temperature charcoals were developed, such as Barnebey-Cheney Types 592 and 763 and North American Carbon's Grades G-602 and G-603.

The intent of this study was to evaluate activated charcoal ignition under conditions similar to those existing in large scale applications.

**Description of equipment and test procedure**

The standardized ignition temperature measurement apparatus was used.

The inlet air and charcoal temperatures were increased at a 10°C/minute rate until 150°C was reached. This is a temperature at which thermal derivatographic work did not indicate significant oxidation in dry air. After reaching 150°C the temperature was increased by 5°C/minute. The thermocouple measuring the inlet air temperature was used to regulate heat input.

Standard rotameters were used to measure gas flow. The use of multiple rotameters permitted the control of gas concentration to obtain

1) air at 70% RH at 30°C,
2) air at 100% RH at 75°C,
3) air-steam mixture, where 50% of available oxygen is in the form of air and the other 50% is introduced as steam,
4) air bubbled through concentrated HNO₃ (90% wt.) at 30°C.

The following two materials were evaluated:

1) **Coconut shell charcoal**

   **Particle size:**
   \[
   \begin{array}{ccc}
   \text{On 2380 micron opening sieve} & 0.1\% \text{ maximum} \\
   \text{On 1650} & " & " & 10.0\% \text{ maximum} \\
   \text{On 1168} & " & " & 88.9\% \text{ minimum} \\
   \text{Through 1168} & " & " & 1.0\% \text{ maximum} \\
   \end{array}
   \]

   **Hardness:** 97.8\% (MIL-C-17605B)

   **Ash content:** 3.2\% by wt.

   **Surface area (BET):** 1000 m²/g

   **No impregnants**
2) **Coconut shell charcoal**

**Particle size:**
- On 2362 micron opening sieve: 5% maximum
- On 1680 " " ": 40% minimum
- On 1190 " " ": 40% minimum
- Through 1190 " " ": 5% maximum

**Hardness:** 94.2% (MIL-C-17605B)

**Ash content:** 4.2% (before impregnation)

**Surface area (BET):** 1590 m²/g (before impregnation)

This material contained 5% by wt. KI₃ (KI + I₂)

Both of these charcoals are typical, but not necessarily optimum charcoals of currently existing containment filter systems.

One screening preliminary run was made under all conditions. Thereafter, a duplicate ignition test was run on all samples. A fresh sample was used for each ignition. No reignition studies were made because on impregnated carbon, the iodine loss of the first test would render successive reignition temperatures meaningless.

Tests were performed at 5, 10, 40 and 70 feet per minute (STP) air velocities.

It was found necessary that an additional 3 in. quartz chips bed be put on top of the charcoal bed to eliminate particle movement and/or fluidization.

A blank run was made using quartz chips and no carbon to calibrate the thermocouples from 150°C - 600°C.

**Presentation of the results**

The ignition temperature of the two charcoals tested in air at 70% RH at various velocities is shown on Figure 1. Ignition attempts were made at less than 5 fpm velocities; however, the accurate measurement of actual charcoal bed velocities at these low flow rates is difficult to control due to the chimney effect. It is important to point out that ignition at very low air flows did not produce runaway ignition.

When employing the standard ignition procedure [16] ignition temperature is defined as the point where there is a sudden departure (increase) from the temperature versus time curve of the heat-up cycle. At very low air velocities, this phenomenon does not take place. Similar results were observed by Milham. [17]

The unimpregnated charcoal ignited at a lower temperature at all air velocities than the impregnated charcoal.

Significant iodine release was noted (at 230-240°C) during the heat-up cycle of the impregnated charcoal.

When the relative humidity of the air stream was raised (Figure 2) a slight rise in ignition temperature was observed for the unimpregnated charcoal, while the ignition temperature of the impregnated charcoal did
KOVACH

FIG. 1. Activated charcoal ignition temperature at various air velocities in air at 70% relative humidity (30°C). 

FIG. 2. Activated charcoal ignition temperature at various air velocities at 100% relative humidity (75°C).

not change. The only noteworthy difference is that the iodine release from the impregnated charcoal took place at approximately 275°C.

Very significant differences were observed during the third series of runs performed with steam-air mixtures. No definable ignition took place although the sample lost weight and was oxidized. Also under these conditions, the visual iodine release from the impregnated carbon occurred slightly above 300°C.
The presence of NO₂ in the humid air lowered the ignition temperature of both the unimpregnated and impregnated charcoals. (Figure 3) The iodine release from the impregnated charcoal took place at approximately 275°C; thus the ΔT between ignition temperature and iodine release temperature was the smallest in this series.

Discussion of the results

To evaluate the obtained results it is important to look at the carbon-oxygen reaction in more detail. It is known that the first step of any gas-carbon reaction is the chemisorption of the gas on the carbon surface. These chemisorbed gases in most cases cannot be removed from the carbon surface in the form in which they were chemisorbed. In case of oxygen-carbon interaction, the oxygen can be removed only as the oxides of carbon.

This carbon oxidation can take place in two ways:

\[ 2C(f) + O_2(g) \rightarrow 2C(0) \rightarrow 2CO(g) \]  

\[ C(f) + O_2(g) \rightarrow C(O_2) \rightarrow CO_2(g) \]  

Where \( C(f) \) represents a free carbon site capable of reaction, \( (g) \) represents gas phase and \( C(0) \) represents chemisorbed oxygen atoms or molecules.

Chemisorption of oxygen takes place on the carbon surface because the surface carbon atoms have free valence electrons which form strong bonds with the oxygen. The presence of these electrons can be measured by electron paramagnetic resonance absorption techniques. [18] The number of unpaired electrons at or near the surface is a complex function of the carbon heat treatment temperature and the number and nature of imperfections in the carbon structure.
Heterogeneous reaction rates involving a porous solid such as activated charcoal and a gas may be controlled by one or more of the three major steps:

1) Mass transport of reacting gas and product or products across a stagnant gas film between the exterior surface of the solid and the main gas stream.

2) Mass transport of the reacting gas from the exterior surface to an active site beneath the surface and mass transport of the products in the opposite direction.

3) Chemisorption of reactant, wholly or in part, a rearrangement of the chemisorbed gas species on the surface to a desorbable product, and desorption of product from the surface.

In the temperature zone where most activated charcoal ignition takes place, the reaction rate between oxygen or nitrogen dioxide and carbon is controlled solely by the chemical reactivity of the solid. (Step 3)

Activated charcoals undergo the same oxidation process in a carefully controlled manner during their manufacture. Activated charcoals consist of random agglomerates of contacting hexagonal crystallites, in which the surface carbon atoms do not possess equivalent energy. During the "activation" of charcoals the saturated radicals of the surface cleave or decompose and form broken edges on the hexagonal crystallites or form side chains of carbon atoms. Depending on the degree of activation and whether the charcoal is exposed to oxidizing or reducing gases at the end of the activation process, commercial activated charcoals contain varying amounts of chemisorbed oxygen on their surface.

The degree of activation and the raw material used also determines the number and type of crystallite disorders in charcoals. It is well established that the reactivity of carbon toward oxygen is strongly influenced by the type and distribution of random crystallites in the charcoal. [19, 20] According to Crisdele [20] the rate of oxidation of carbon crystallites is about 17 times faster in the direction parallel to the basal planes (along their edges) than perpendicular to them. Generally, the higher the "activity" of charcoal (increase in surface area) the larger is the number of exposed edges of crystallites. It was shown before that ignition temperature also decreases with increased surface area. [10]

The oxidation of the activated charcoal proceeds at temperatures below the ignition temperature. Differences were noted between the inlet air temperature and the charcoal temperature on all of the tests. The largest $\Delta T$ between air inlet and charcoal temperature was found during the humid air-NO$_2$ runs ($\Delta T$ 75°C) and the lowest during the steam-air runs ($\Delta T$ 10°C).

This latter finding can be explained by the retarding effect of H$_2$ (produced by the H$_2$O-carbon reaction) being chemisorbed on the charcoal surface, making active sites less available for O$_2$ chemisorption. Thus, for ignition to take place it is not enough to chemisorb oxygen on the surface, but the chemisorbed product has to be desorbed. Because the most active sites will be oxidized first, these are sites which retain the chemisorbed species the longest. Therefore, these surface oxides of the carbon can retard the ignition temperature. The longer retention and higher partial pressure of the decomposition products above the
charcoal surface cause the no runaway ignition at the near static gas conditions. At the same time, thermal desorption (in absence of oxidizing gases) of oxygen from the charcoal surface frees the most active sites for reaction with oxygen when oxygen is reintroduced into the system. This subsequent oxidation of the evacuated charcoal surface has higher differential heat of adsorption and causes the bed to ignite at much lower inlet air temperatures than in continuously flowing air. This phenomenon was also observed by Hill and Gizinski. [11]

The presence of steam appeared advantageous for two reasons. It appears to retard the desorption of iodine probably by converting some of the iodine into chemisorbed species and by stopping runaway ignition. This latter is not an unexpected result because charcoal is activated in a similar atmosphere without runaway ignition. It has to be noted that the reaction rate constant for the O2-carbon reaction is much higher than the H2O-carbon reaction and that both H2 and CO, which are products of the H2O-carbon reaction, retard the oxidation of carbon.

The presence of NO2 significantly lowers the ignition temperature of both impregnated and unimpregnated charcoals.

Summary and conclusions

On the basis of previously reported work [10] and this investigation, it is important to realize that "ignition temperature" is not a characteristic property of activated charcoal. Ignition temperature is characteristic only of a system consisting of charcoal, gas flow and composition and charcoal containment.

The ignition of activated charcoals not treated to increase ignition temperature is more likely in low humidity systems, or when NO2 is present (fuel processing plants) in the air stream. Precautions have to be taken if intermittent air flow is used and if possible, this should be avoided.

The presence of large amounts of steam which would occur in PWR containment systems under accident conditions, significantly lowers charcoal ignition hazards.

In all cases, a large percentage of the impregnant iodine evolved from the charcoal before ignition took place.

The presence of impregnant iodine increases the ignition temperature.

REFERENCES

G. BURLEY Are there any measurements of charcoal ignition temperatures at iodine loadings greater than the impregnation levels?

J.L. KOVACH No. The impregnated charcoal discussed in this work contained 5% by weight of KI₂ (KI + I₂) which is typical of impregnated carbons currently used in the USA.

R E KRATEL You gave an explanation of factors responsible for the ignition point of charcoal. It is a known fact that an activated carbon plant, loaded with organic compounds, may produce accidents (i.e. explosions, etc.) even when running under normal operating conditions (ignition temperature of charcoal ~400°C, operating temperature ~50°C). Burning charcoal can be observed at hot points in the charcoal bed. How do you explain this and what is its relationship to the present process, where methyl iodide is present?

J.L. KOVACH The effect of spot overheating is more characteristic of deeper carbon beds. The US Navy has presented results concerning organic solvent loading on carbon beds. At high solvent loadings, the
carbon is only a container and the solvent ignites first, not the carbon. In solvent recovery applications, the use of carbons with oxidizing catalyst ash constituents is known to cause ignition. The effects of these catalysts were reported in the first part of our work (Ref.[10] of the paper). Halogenated solvents do not decrease, but in some cases increase, the ignition temperature of the carbon, thus it is important to know the exact conditions of the system.

F. ABBEY. Have you any information on the effect of carbon particle size on ignition temperature?

J.L. KOVACH. This also was reported in the first part of our work. We found that for identical carbons the ignition temperature decreased with particle size.

W.L. FAITH. Do you believe that low concentrations of NO2 in the gas could cause a build-up on the carbon that might cause an explosion?

J.L. KOVACH. Yes. It is possible to build up a gas complex chemisorbed on the charcoal surface, which may decompose instantaneously. A similar reaction occurs with ozone.
DEVELOPMENTS IN THE REMOVAL OF IODINE AND ITS COMPOUNDS

(Session V, Part 2, and Session VI, Part 1)
Chairmen: K. LEE and J. M. PRADEL
REMOVAL OF IODINE AND METHYL IODIDE
BY A FULL-SIZED CHARCOAL FILTER

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Abstract

REMOVAL OF IODINE AND METHYL IODIDE BY A FULL-SIZED CHARCOAL FILTER. This investigation, performed under conditions simulating those of a reactor accident, was undertaken to evaluate the efficiency of charcoal filters in removing iodine containing minute amounts of methyl iodide. The experiment was run in two series. In the first the efficiencies of small filters, diam. 8.0 cm and thickness from 0.5 to 9.0 cm, were determined under various flow conditions. It was found that the logarithms of the decontamination factors of both iodine and methyl iodide with the filter were approximately proportional to the thickness of the filter. Since the proportionality constant represents the filter efficiency under a given condition, the effects of operational conditions on this constant, such as temperature, humidity, concentration of iodine or methyl iodide, and air velocity passing through the filter, were investigated. From the results of these measurements, equations expressing the efficiency of the filter as a function of the constants were obtained.

The applicability of the equations to large-scale filters was confirmed in the second series of experiments. A full-size filter unit (600 x 600 mm) consisting of prefilter, absolute filter and charcoal filter was constructed for the tests. Humid air containing iodine or a mixture of iodine and methyl iodide was passed through the filter unit, and the efficiency of each filter was determined. The efficiencies for iodine and for the mixture of iodine and methyl iodide agreed closely with those calculated with the equations.

INTRODUCTION

In siting a nuclear power station, it must be guaranteed that the release of radioactive fission products will be below a certain limit even in the event of a reactor accident. One of the ideal ways to control the leakage is to surround the reactor with a containment building. Since it is difficult to keep the atmosphere completely in the container for a long time, a trapping process is usually provided for reducing the concentration of airborne fission products.

As radioactive iodine is considered to be the critical isotope with respect to the health hazard of fission products released, the major efforts have centred on its effective removal.

It is well known that when radioactive iodine is released from fuel, it may take different forms in the atmosphere of a reactor. The principal forms are elemental iodine vapour, particulate iodine, and an organic iodine compound in which methyl iodide is a major component.

Of these, both iodine vapour and iodine particles can be satisfactorily removed by a filter unit combining particulate filters with a charcoal filter. Methyl iodide presents a more difficult problem because it is not trapped well by commercially available activated charcoal. At high humidity, especially, there is a drastic reduction in the efficiency of its removal by charcoal filters. Recent studies, however, have indicated the possibility that methyl iodide can be effectively removed by a charcoal filter, provided that such chemicals as potassium iodide [1] or pyridine [2] are impregnated in the charcoal.
The object of the present investigation is to obtain data on evaluation of the performance of charcoal filters when methyl iodide is present with iodine. The experiments were carried out using two sets of equipment. During the first series of experiments, parametric measurements of the efficiency were made with small-scale equipment, taking into consideration the fluctuation of conditions which may possibly occur in the event of a reactor accident. The principal variables applied were: temperature, relative humidity, concentration of iodine and methyl iodide, and face velocity of the air swept. For the performance tests, a full-size filter unit consisting of particulate filters and a charcoal filter was used in the second series of experiments. The operational conditions were selected to be analogous with those of the previous experiments.

EXPERIMENTS

Small-scale equipment

The equipment used is shown diagrammatically in Fig. 1. It consists, essentially, of the air supply, the iodine and methyl iodide generator, and the filter unit. With the exception of the glass tubes for iodine and methyl iodide generation, all the apparatus is made of stainless steel.

Compressed air is first cleaned by passage through filters. It is then metered by a rotameter and sent through an electric furnace to the filter unit. The air in the other line is passed through a water tank whose temperature is kept constant. By mixing dry air with saturated air coming from the water tank, the humidity of the air can be adjusted to a suitable constant value.

Elemental iodine and methyl iodide labelled with radioactive iodine, $^{131}\text{I}$, are injected into the main air flow at a constant rate. Dry nitrogen used as carrier gas is swept slowly over the iodine crystals maintained at a constant temperature to saturate nitrogen gas with iodine vapour. The rate of iodine injection is controlled by mixing the swept gas into the main air flow. Methyl iodide is introduced into the flow by means of diffusion through a capillary tube in a constant-temperature bath. The diffusion rate of the methyl iodide can be adjusted to a suitable value by varying the diameter of the capillary tube or its temperature. Before starting the experiments, the exact amounts of iodine and methyl iodide introduced by these methods are checked.
The filter unit is composed of a test filter and three identical filters which are installed in series downstream from the test filter at 5 cm intervals, as shown in Fig. 2. These three back-up filters are provided to trap the iodine and methyl iodide which have penetrated through the test filter for the determination of the efficiency of the test filter. The activated charcoal used in this investigation was granular Shirasagi-GCA, in the 6-10 mesh range. The diameter of each of the filters was identical, 8.0 cm, while their thickness was varied from 0.5 to 9.0 cm according to the operational conditions required. After passing the air for 2 hours, the filter unit was disassembled and the amounts of iodine or methyl iodide adsorbed on each of the filters were measured by gamma-counting the radioactive iodine. The efficiency of the test filter was determined by comparing the total amounts of iodine or methyl iodide passing through the test filter, i.e. trapped quantitatively by the charcoal filters in the filter unit, with the amounts adsorbed in the test filter.

Full-size equipment

A flow diagram of the equipment and its layout are shown in Figs 3 and 4. All parts coming into contact with humid air are made of stainless steel. The air entering the system from outside the building is cleaned over two
particulate filters and then sent to a heating duct. Air flow through the system is provided by a blower with a maximum capacity of 25 m³/min, giving a face velocity of 100 m/min at the surface of the charcoal filter. Steam is added to the air flow downstream of the heating duct. The adjustments of the air flow and its humidity can be accomplished by regulating the blower and the flow rate of steam added.

The methods for introduction of iodine and methyl iodide into the main air flow at a constant rate are entirely the same as those described in the previous section. An orifice for mixing was installed downstream of the train for iodine injection. The tests performed prior to initiation of the experiments indicated adequate mixing of iodine with air.

The filter-holding duct measures 70 cm square and 230 cm in length. It houses three filters: a prefilter, an absolute filter, and a charcoal filter. They are each spaced at intervals of about 50 cm. The prefilter is made of mats of glass fibres with an average diameter of 200 μm. The absolute filter, of the same size as the prefilter, is made of cellulose fibres with a thin separator between the two mats. A plate type filter, packed to a density of 0.52 g/cm³ with granular Shirasagi-GCA, is used. These filters are held in place with silicon rubber gaskets and are replaced with new ones after every loading run. For measuring the temperatures and pressure drops across each of the filters, four thermocouples and pressure taps are provided in the filter-holding duct. To determine the efficiency of the filter, four sample trains are also provided at positions upstream and downstream of each filter. Air is extracted continuously through these trains for sampling. Rotameters are used to keep the flow rate constant and the total volume of gas taken is measured by integrating flow meters. During the period of a run, the iodine and methyl iodide trapped by the sampling filters in each of the sampling lines are monitored by NaI crystals. After the run the sampling filters are disassembled for measuring the activity in the filters. The efficiency of each filter can be calculated with the concentration of iodine and methyl iodide in the inlet and outlet gas of the filter.
Preparation of radioactive iodine and methyl iodide

Elemental iodine is prepared in crystalline form by oxidising iodide to iodine with a hydrogen peroxide solution. A few millilitres of 30% hydrogen peroxide solution together with a few drops of concentrated sulphuric acid are added to an aqueous solution containing appropriate amounts of iodine carrier and radioactive iodine (\(^{131}\)I) as iodide. After mixing the solution, a few millilitres of sulphuric acid are dropped into it. Iodine crystallized in the solution is collected on a glass filter and is washed with water several times. Finally, the iodine in the cooled bath is dried by passing dry nitrogen through it for 5 hours.

Methyl iodide is prepared by adding dimethyl sulphate to an aqueous sodium iodide solution. A few millilitres of dimethyl sulphate is added to about one millilitre of an aqueous solution containing the appropriate amounts of both active and non-active iodide. Then about one gram of powdered calcium carbonate is added to maintain the proper pH. When the solution is warmed gently to about 50°C, methyl iodide is evaporated. Dry helium gas is sent through the solution to a condenser at about -20°C. Here the bulk
of the water vapour is removed as ice. The helium gas from the condenser is introduced into a cold trap at about -75°C for collection of methyl iodide as a solid.

RESULTS AND DISCUSSIONS

When the amount of iodine and methyl iodide adsorbed is so small that iodine or methyl iodide is held permanently in a charcoal filter, it is considered that the amount adsorbed per filter thickness will be proportional to the concentration of iodine or methyl iodide in the inlet gas. These relations can be expressed with the following equations

\[ \frac{C_0}{C} = DF = e^{\alpha x} \]  \hspace{1cm} (1)

\[ \frac{C_0'}{C'} = DF' = e^{\beta x} \]  \hspace{1cm} (2)

Here \( C_0 \) and \( C \) represent, respectively, the concentration of iodine and methyl iodide in the passing air at the inlet and outlet of the filter with a thickness of \( x \) cm. Similarly, \( C_0' \) and \( C' \) indicate the concentration of methyl iodide. \( \alpha \) and \( \beta \) are the proportionality constants for iodine and methyl iodide which are associated with the rate constant of the adsorption under a given condition. \( DF \) and \( DF' \) are the decontamination factors of iodine and methyl iodide, respectively.

![FIG. 5. Variation in decontamination factor.](image-url)
This relation was confirmed by the following experiments conducted with the small-scale equipment. In Fig. 5 the decontamination factors of iodine and methyl iodide were plotted against the thickness of the filter. This relation was found in the experiments carried out under other conditions, except where methyl iodide was adsorbed at a high relative humidity. The exceptional behaviour of methyl iodide in such a case could be attributable to the drastic reduction of the loading capacity of charcoal with the increase in the amount of water adsorption.

![Operational Conditions](image1)

**Operational Conditions**
- Relative Humidity 80% for I₂
- Concentration 10 ppm
- Face Velocity 41 cm/s

**Operational Conditions**
- Temperature 80°C for I₂
- Concentration 10 ppm
- Face Velocity 41 cm/s

![Operational Conditions](image2)

**Operational Conditions**
- Temperature 80°C for I₂
- Relative Humidity 80%
- Face Velocity 41 cm/s

**Operational Conditions**
- Temperature 80°C for I₂
- Relative Humidity 80%
- Face Velocity 41 cm/s

The proportionality constant for methyl iodide was extremely small in comparison with that for iodine under the same conditions. This fact must be due to a low rate of methyl iodide adsorption in charcoal. Since the proportionality constants for iodine and methyl iodide changed, more or less, with the varying conditions of the passing air such as temperature, relative humidity, concentration of iodine or methyl iodide and face velocity, systematic measurements of the constants were carried out. The variations in the constants with temperature are shown in Fig. 6. The relative humidity and face velocity were kept fairly constant. As seen in this graph, the constant for iodine increases linearly with the rising temperature, but the rate of increase is not pronounced. In contrast to this, the constant for methyl iodide decreased remarkably when the temperature was raised from 40 to 60°C, becoming almost temperature independent above 60°C.
The constants for both iodine and methyl iodide are affected by the increasing relative humidity. Figure 7 shows the results when the relative humidity was varied from 20 to 100%, while the temperature was kept at 80 and 40°C for iodine and methyl iodide, respectively. The variation in the constant for iodine caused by the relative humidity is quite small in comparison with that for methyl iodide, which is found to decrease remarkably with the increasing relative humidity. The abrupt change noted as the relative humidity was increased from 40 to 60% seems to be correlated with the capillary condensation of water in the pores of charcoal [3].

Considering the mechanisms of iodine and methyl iodide absorption in charcoal, the constants are expected to be essentially independent of the concentration of the adsorbates. There is, in practice, a small variation in the constants within the range of the conditions employed. Figure 8 indicates the dependence of the concentration on the constant in the region from 0.5 to 10 ppm. The lower value of the constant for iodine at a low concentration implies the existence of different forms of iodine.

The relations between the constants and the face velocity under conditions of a temperature of 80°C and a relative humidity of 80% are shown in Fig. 9. The constants for both decrease linearly with the increase of the face velocity. The remarkable decrease for methyl iodide must be due to a low rate of adsorption [4].

The efficiency, as reported by Collins [1], can be represented as a function of the stay time, which is the result of dividing thickness by face velocity. This relationship, however, is not found when the face velocity drops below about 80 cm/s, as seen clearly in Fig. 10. The lower value of the decontamination factor at the low face velocity must be due to a different rate determining factor from that at the high face velocity.

If there is no interaction between iodine and methyl iodide, the overall efficiency of the filter for the mixture of both adsorbates is calculated with the following equation [5]:

$$DF_t = \frac{1}{(1 - P)e^{-\alpha x} + Pe^{-\beta x}}$$  \hspace{1cm} (3)
Here \( DF_t \) is the overall decontamination factor, and \( P \) is the weight ratio of methyl iodide to methyl iodide plus iodine present in the inlet air. \( \alpha \) and \( \beta \) represent, respectively, the proportionality constants for iodine and methyl iodide under a given condition. To confirm the validity of this equation, several runs of the experiments were carried out. Figure 11 shows the distribution profiles of both iodine and methyl iodide when the mixture of iodine and methyl iodide was passed through filters of different thicknesses.

**FIG. 10.** Variation in decontamination factor with face velocity at a constant stay time.

**FIG. 11.** Distribution profile of iodine and methyl iodide.
Lines (1), (2) and (3) in this graph are the results when the concentration of methyl iodide in the air was, respectively, 0.12, 0.07, and 0.02 ppm while the concentration of iodine was kept at a constant value of 2.3 ppm. The black and white circles show the results when iodine was present (white) and when it was absent (black) in the air passing through. The activities obtained by extrapolating the lines to zero of the thickness are proportional to the concentration of methyl iodide. Furthermore, there is no difference between the black and white circles. From these facts it is concluded that no remarkable interaction between iodine and methyl iodide occurred.

The constants calculated using data on the efficiencies of charcoal filters determined by other workers for methyl iodide under conditions of relative humidity below 80% are in the range of about 0.2 - 0.6. The constants with impregnated charcoal filters under similar conditions are in the range of 0.3 - 1.2.

To evaluate the performance of a large charcoal filter, a series of tests with a full-scale filter unit, consisting of two particulate filters and a charcoal filter, were carried out and the data obtained were compared with those calculated with Eq. (1). Figure 12 shows the relationship between the temperature and the removal efficiencies of each filter and filter unit when humid air containing 0.1 ppm of iodine was swept at a face velocity of 40 cm/s. This illustrates that the efficiencies of the particulate filters, the prefilter and the absolute filter vary more or less with the temperature, while the efficiency of the charcoal filter remains almost constant. The fact that some of the iodine was trapped by the particulate filters indicates the presence of fine particles, which are presumably drops of water. There is, however, no reasonable correlation between the amounts trapped by the particulate filter and the operational conditions. In this figure the dotted line shows the efficiencies calculated with Eq. (1) using the proportionality constant determined under the same conditions in the small-scale experiment. The efficiencies obtained by varying the concentration of iodine from 0.2 to 1.0 ppm are shown in Fig. 13. The fact observed in Figs 12 and 13, that the efficiency of the full-size charcoal filter approximates those calculated, suggests the validity of Eq. (3) in the design of filters.

FIG. 12. Iodine removal efficiency of each filter and filter unit.
Table I. Removal Efficiency of the Filters

<table>
<thead>
<tr>
<th>Weight Ratio of CH₃I to CH₃I plus I₂</th>
<th>P (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5*</th>
<th>6*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3.39</td>
<td>3.31</td>
<td>1.76</td>
<td>1.78</td>
<td>1.76</td>
<td>1.89</td>
</tr>
<tr>
<td><strong>For I₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre filter</td>
<td>59.92</td>
<td>78.74</td>
<td>9.80</td>
<td>80.79</td>
<td>29.92</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>Absolute filter</td>
<td>81.63</td>
<td>82.54</td>
<td>90.39</td>
<td>60.03</td>
<td>93.65</td>
<td>68.73</td>
<td></td>
</tr>
<tr>
<td>Charcoal filter</td>
<td>97.10</td>
<td>97.04</td>
<td>95.85</td>
<td>96.89</td>
<td>98.65</td>
<td>99.38</td>
<td></td>
</tr>
<tr>
<td>Filter unit</td>
<td>99.79</td>
<td>99.87</td>
<td>99.64</td>
<td>99.77</td>
<td>99.92</td>
<td>99.81</td>
<td></td>
</tr>
<tr>
<td><strong>For CH₃I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre filter</td>
<td>9.89</td>
<td>8.05</td>
<td>8.32</td>
<td>19.08</td>
<td>40.91</td>
<td>81.33</td>
<td></td>
</tr>
<tr>
<td>Absolute filter</td>
<td>10.26</td>
<td>8.75</td>
<td>4.59</td>
<td>31.82</td>
<td>29.19</td>
<td>10.31</td>
<td></td>
</tr>
<tr>
<td>Charcoal filter</td>
<td>33.08</td>
<td>50.89</td>
<td>33.23</td>
<td>37.50</td>
<td>56.00</td>
<td>63.13</td>
<td></td>
</tr>
<tr>
<td>Filter unit</td>
<td>45.89</td>
<td>58.80</td>
<td>41.58</td>
<td>65.52</td>
<td>89.59</td>
<td>93.37</td>
<td></td>
</tr>
<tr>
<td><strong>Overall (I₂ + CH₃I)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre filter</td>
<td>58.23</td>
<td>76.40</td>
<td>9.78</td>
<td>79.69</td>
<td>30.11</td>
<td>3.09</td>
<td></td>
</tr>
<tr>
<td>Absolute filter</td>
<td>76.40</td>
<td>73.02</td>
<td>89.58</td>
<td>58.02</td>
<td>92.68</td>
<td>68.52</td>
<td></td>
</tr>
<tr>
<td>Charcoal filter</td>
<td>79.31</td>
<td>76.97</td>
<td>86.26</td>
<td>90.06</td>
<td>92.48</td>
<td>95.95</td>
<td></td>
</tr>
<tr>
<td>Filter unit</td>
<td>97.97</td>
<td>98.51</td>
<td>98.62</td>
<td>99.16</td>
<td>99.60</td>
<td>99.68</td>
<td></td>
</tr>
<tr>
<td><strong>Overall efficiency calculated</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>97.77</td>
<td>97.83</td>
<td>98.76</td>
<td>98.75</td>
<td>99.32</td>
<td>99.28</td>
<td></td>
</tr>
</tbody>
</table>

* impregnated charcoal

**Operational Conditions**
- Temperature: 70 °C
- Relative Humidity: 80%
- Face Velocity: 80 cm/s
- Concentration of CH₃I: 1.21 Ppb
The performance tests for the mixture of iodine and methyl iodide were conducted under relatively severe temperature and humidity conditions of 70°C and 80% relative humidity. The data on the removal efficiencies of each filter are summarized in Table I. In these tests, the concentration of methyl iodide was varied with the value of P in such a way that the concentration of iodine was held constant. In tests 5 and 6, charcoal filters filled with charcoal impregnated with 0.7 wt% potassium iodide were used. The overall efficiencies of the filter unit calculated by Eq. (3) are shown in the lowest line of this table.

In these calculations values of 3.0, 0.155 and 0.32 were used as the proportionality constants of iodine and methyl iodide with a charcoal filter, and of methyl iodide with an impregnated charcoal filter, respectively. It is apparent from this result that the data agreed with the results of calculation within the range of measurement errors.

![Operational Conditions Calculated](image)

**FIG. 13. Removal efficiency of the full-size charcoal filter.**

**CONCLUSION**

The removal efficiency of a charcoal filter for iodine, methyl iodide, and a mixture of iodine and methyl iodide can be represented by the proportionality constants, which are defined as the ratio of the logarithm of the decontamination factor to the filter thickness. The constants of both iodine and methyl iodide vary with the operational conditions such as temperature, relative humidity and the face velocity. The constant of iodine is relatively large and less affected by the operational conditions. On the contrary, the constant of methyl iodide is exceedingly small and does vary with the conditions. The overall efficiency of a charcoal filter when a small amount of methyl iodide is present in iodine can be estimated by the constant of iodine and methyl iodide under a given condition. Thus, the constants under various operational conditions give a satisfactory basis for filter design.

The results of the performance tests conducted with a full-size filter indicate no variations in the removal efficiency caused by increased filter size. In addition, it was found that the efficiencies for iodine and for mixtures of iodine and methyl iodide determined experimentally agreed with those calculated with the equations using the constants.

**ACKNOWLEDGEMENTS**

The authors wish to express their thanks to Mr. S. Kawahara and Mr. H. Hujie for their valuable discussions on this work. The present investigation was sponsored by the Science and Technology Agency, Prime Minister's Office of Japan.
REFERENCES


DISCUSSION

G. BURLEY. Do I interpret your Fig.7 correctly as indicating that the efficiency of your charcoal for methyl iodide decreased by 50% at 60% relative humidity?

T. MURATA Yes. In fact it decreases by more than 50%.

J.L. KOVACH. Have you any explanation for the fact that your tabulated results show considerable variations in the efficiency of prefilters?

T. MURATA The variation in the efficiency of the prefilter reflects the existence of particles — which may be water drops — in the stream gas and the fact that the number of particles varies from case to case.
EFFICIENCY OF VARIOUS FILTER PACKINGS FOR REMOVAL OF IODINE-131 AND ITS COMPOUNDS

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Abstract

EFFICIENCY OF VARIOUS FILTER PACKINGS FOR REMOVAL OF IODINE-131 AND ITS COMPOUNDS.
In the course of production of $^{131}$I, a radioisotope produced on a relatively large scale in Hungary, the problem of waste disposal is considered as one of the most important. In spite of careful treatment of waste liquids, the radiation hazard due to volatile iodine compounds present as admixtures of long-lived tellurium activities still demands consideration. Other difficulties have arisen regarding the total capacity and efficiency of the filter system, and all of these problems are related to different valency states of iodine and its compounds. The evaluation of various filters and extensive investigations on the volatility and/or the physical-chemical behaviour of carrier-free radioiodine, as affected by pH, pretreatment and certain chemicals, are described.

1. INTRODUCTION

The most important radioisotope prepared in Hungary is iodine-131.
To ensure the maximum possible yield the method of 'wet distillation' of irradiated tellurium dioxide was chosen. The production is based on the nuclear reaction

$$^{130}\text{Te} (n, \gamma) \rightarrow ^{131m}\text{Te} \rightarrow ^{131}\text{Te} \beta \rightarrow ^{131}\text{I}$$

The block scheme of the technique can be illustrated as follows.

The residue of distillation is $\text{TeO}_2$ in sulphuric acid solution (total solid content being about 250 g/litre).

Besides considerable $^{131}$I activity (of the order of 10 Ci per batch), the residue contains radioactive tellurium isotopes of mass numbers 121m,
125m, 127m, 129m and 131. In the course of air cleaning and waste liquid management, the presence of long-lived tellurium isotopes and of the rather volatile radiiodine raises serious problems. Moreover, the total activity of these types of waste amounts to about 1000 Ci/yr in Hungary. All these problems are certainly related to different valency states of iodine. Therefore in radioactive waste treatment care should be taken to reduce the volatility of radiiodine and to decontaminate aerosols and gases successfully.

2. DEVELOPMENTAL EXPERIENCE IN THE REMOVAL OF $^{131}$I AND ITS COMPOUNDS

Laboratory-scale investigations were carried out to study the behaviour of $^{131}$I in the course of waste management under various chemical conditions, various filter packings were then tested for their efficiency in removing $^{131}$I and its compounds. This investigation was part of our developmental activities and it was also fostered by a research contract with the IAEA.

2.1. Reducing the volatility of radiiodine

In the first part of our preliminary work the aim was to determine those experimental conditions under which evaporation and other thermal treatment of radioactive slurry can be carried out at minimum contamination hazard due to the volatility of radiiodine.

The volatility of iodine was examined in three series of experiments in the course of the distillation process under different conditions: distillation in sulphuric acid medium; distillation in the presence of oxidizing agents, and distillation in alkaline medium.

The experiments were carried out on a laboratory scale, whereby 200ml of the initial solution was poured into a flask which was connected with a cooler and vessel. The distillate was brought through a photo-cell drop-counter into receivers.

When alkaline solutions were used, the distillation was accomplished to dryness, while with acidic solutions distillation was finished when no more water vapour was observed in the flask.

In the course of experiments 5-10 μCi of $^{131}$I were used and the quantity of potassium iodide added was set to maintain $10^{-4}$ moles/litre iodide concentration, avoiding the considerable absorption of carrier-free iodine on the glass surface.

The activities of both the initial solution and the fractions were measured with a well-type NaI(Tl) scintillation detector.

2.1.1. Distillation of iodine in sulphuric acid

The cumulative distillation yields for different initial sulphuric acid concentrations are shown in Fig.1(a). For comparison, the curve obtained for the solution containing 0.1 M sodium hydroxide is drawn in the same figure.

In accordance with data from the literature [1, 2], the curves of Fig.1(a) imply that, by increasing the concentration of the acid more and more
quantities of iodine appear in the first fractions. In addition, some conclusions can be drawn from the shape of these curves regarding whether distillation proceeds in the form of iodine or hydrogen iodide. Assuming that distillation proceeds in the form of hydrogen iodide, we may expect that the shape of the distillation curves would not considerably change by increasing the initial acid concentration. On the other hand, the cumulative yields shown in Fig.1(a) indicate that with low acid concentrations most of the iodine is distilled off into the last fractions, while in more concentrated solutions (10 N or higher) 95-99% of the iodine is contained in the first fractions. The behaviour of the distillation curves is evidence of the fact that the bulk of iodine begins to distill off when the solution is concentrated enough to contribute to the oxidation process iodide $\rightarrow$ iodine. The cumulative distillation curve for the 20 N initial acid concentration indicates that at boiling temperature the oxidation process is perfect while in the 5 N solution this process is negligible. The curve for the 10 N concentration has a distinctive shape: a steep initial slope followed by a section rising only slightly.

Without analysing the processes taking place during distillation in detail, it must be emphasized that the anomalies of the differential and cumulative distillation curves for 10 N acid concentration refer to partial oxidation at boiling temperature, the oxidation is completed when the acid concentration increases to 20 N. Based on these observations, it may be concluded that in the system investigated the iodine content of the distillate is a consequence of reactive distillation.

2.1.2. Distillation of iodine in the presence of oxidizing agents

The effect of two oxidizing agents, ferric sulphate and ceric sulphate, was also investigated. Taking into account the normal potentials of the ferrous-ferric and cerous-ceric redox systems, one would expect that ferric ions promote the oxidation to iodine and the ceric ions to iodate.

Accepting the conclusions drawn from the shapes of the curves shown in Fig.1(a), according to which distillation proceeds in the form of elementary iodine, it is evident that in the presence of ferric ions (at the same concentrations) the iodine content of the first fractions must increase.
The curves in Figs 1(b) and 1(c) confirm this. In Fig.1(b) the cumulative yields obtained at the same acid concentrations as given in Fig.1(a), but in the presence of $5 \times 10^{-4}$ M ferric sulphate, are shown. Comparison of the two figures indicates that the iodine content of the first fractions at low ferric sulphate concentrations is considerably increased. This is especially remarkable when the curves of Figs 1(a) and 1(c) which refer to dilute sulphuric acid concentrations are compared. The distillation curves obtained at constant acid concentrations but at increasing ferric sulphate content are shown in Fig.1(c). The experimental results indicate that the cumulative distillation curve obtained at 0.1 N acid concentration and $5 \times 10^{-3}$ ferric sulphate concentration is practically the same as that obtained at 20 N acid concentration in the absence of ferric sulphate additive.

The distillation yields were also determined in the presence of ceric sulphate additive. It was found that the cumulative yield is considerably lower than that obtained at the same acid concentration but in the absence of ceric ions. Beside this it can be stated that the yield depends on the time after addition of ceric sulphate to the system.

It was found that the cumulative yield decreases in the presence of ceric ions, probably because the iodide is oxidized to iodate and then attains a constant value after about one hour. It should be mentioned that like the other experiments performed, the results refer to $10^{-4}$ M initial iodide concentration. The rate of oxidation is slower for lower iodide concentrations. This observation is in good agreement with the data given in Ref.[2], according to which carrier-free $^{131}$I can be distilled in the presence of ceric ions as well.

It was concluded that in acidic media the yield of iodine in the distillate is considerably decreased when ceric ions in the range of $10^{-3}$ - $10^{-4}$ M are added.

2.1.3. Distillation of iodine in alkaline medium

Figure 1(a) shows the cumulative distillation yield as a function of the distillate in a 0.1 N sodium hydroxide solution. This curve is shown only for comparison with those obtained in the presence of sulphuric acid. It must be emphasized that the yield cannot be given with proper accuracy on a linear scale as the values are of the order of $10^{-2}$ % only.

At such a low distillation rate the possibility of entrainment must also be taken into consideration. To clarify this problem the device was provided with a 200-mm long column and the yields were determined for solutions containing sodium hydroxide in different concentrations and in the presence of 0.5% sodium dicarbonate. The results obtained are shown in Table I.

From the data of Table I it can be concluded that in the course of the distillation of alkaline solutions no entrainment effect should be taken into account, as otherwise the hydroxide content of the solution would have considerably less influence on the yield. Similar results are found in the literature for the extent of entrainment [3]. Under the conditions employed in our measurements (flow rate of vapours, length of the column, etc.) the iodine content in the distillate due to entrainment can be estimated to be about $10^{-4}$ %, a value about two orders of magnitude less than the actual value determined.
TABLE I. CUMULATIVE DISTILLATION YIELDS AT VARIOUS INITIAL ALKALI CONCENTRATIONS

<table>
<thead>
<tr>
<th>Initial alkali concentration of the solution</th>
<th>Cumulative distillation yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N NaOH</td>
<td>$2.4 \times 10^{-2}$ %</td>
</tr>
<tr>
<td>0.01 N NaOH</td>
<td>$5 \times 10^{-2}$ %</td>
</tr>
<tr>
<td>0.5% NaHCO$_3$</td>
<td>$1.7 \times 10^{-2}$ %</td>
</tr>
</tbody>
</table>

From the distillation curves obtained it was concluded that, while in the case of acidic solutions the bulk of iodine can be readily distilled off, in alkaline medium the yield does not exceed the order of $10^{-2}$ %. Though in the case of alkaline solutions the distillation yield is a rather small proportion of the total iodine content, nevertheless it must not be neglected when high-activity wastes are evaporated.

2.2. Investigation of the removal of $^{131}$I from the air stream

Very many types of sorbent media have been studied all over the world from the point of view of the removal of radioiodines. It is generally agreed that the best medium for this purpose is charcoal, even if it poses some problems because of its burning properties and limited efficiency at high relative humidity for some iodine compounds (methyl iodide).

Our investigations were aimed at clarifying the operating conditions of filter packings in the presence of large volumes of iodine and different types of radiotellurium and at finding other filter media for use in radioactive waste management together with their behaviour at higher operation temperatures. The temperatures studied so far in the course of these investigations have not exceeded that of evaporation.

2.2.1. Description and identification of the sorbents used

Two groups of filter media, granular and fibrous sorbents, were tested. Both groups were examined in the untreated state and impregnated with AgNO$_3$. The specifications of the sorbents used are as follows:

Granular sorbents:

<table>
<thead>
<tr>
<th>Charcoals</th>
<th>Nuxit A</th>
<th>Nuxit B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface</td>
<td>1100 m$^2$/g</td>
<td>700 m$^2$/g</td>
</tr>
<tr>
<td>Porosity</td>
<td>120 ml/100 g</td>
<td>80 ml/100 g</td>
</tr>
<tr>
<td>Volume density (dry)</td>
<td>300 g/ml</td>
<td>500 g/ml</td>
</tr>
<tr>
<td>Size</td>
<td>Ø 5×5 mm</td>
<td>Ø 1.8×3 mm</td>
</tr>
<tr>
<td>Base: ZnCl$_2$ actived mixed sawdust</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Molfilit 40 KK** molecular filter

- **Specific surface**: $800 \text{ m}^2/\text{g}$
- **Porosity**: 50% of crystal volume
- **Volume density**: 700 g/litre
- **Thermal stability**: up to 600°C
- **Size**: Ø $3 \times 10$ mm
- **Selectivity**: $< 4 \text{ Å}$
- **Base**: Artificial zeolite

**Varion KS** Cation exchanger resin

- **Volume density**: 800 g/litre
- **Size**: 1 mm
- **Volume capacity**: 1.8 g eq./litre
- **Base**: Styrol-divinyl benzol

**Sodium hydroxide pellets**

Granular commercial product in analytical grade quality

- **Volume density**: 1 g/cm$^3$

**Silica gel**

Dried, sieved commercial product of diameter 1.6-2.5 mm. This sorbent was not impregnated.

- **Volume density**: 0.65 g/cm$^3$

**Fibre-glass**

Ultra-fine product. The diameter of the elemental fibre is 1 µm.

- **Density of filling**: 120 mg/cm$^3$

**Slag wool fibre**

Commercial heat-isolator material. The diameter of the elemental fibres is 10 µm.

- **Density of filling**: 200 mg/cm$^3$

**Polypropylene**

Commercial product: The diameter of the elemental fibre is 20 µm.

- **Density of filling**: 100 mg/cm$^3$
2.2.2. Sorption and desorption of iodine charcoal

The iodine uptake of charcoals of Hungarian make was studied in the system shown in Fig.2. Inactive elemental iodine was sublimated and passed by air flow through the adsorber and the amount of trapped iodine was measured. The iodine was determined by absorption in 0.1 N sodium hydroxide solution.

![Scheme of the experimental unit for the filter efficiency tests and the sorption and desorption experiments for iodine on charcoal.](Image)

**FIG. 2.** Scheme of the experimental unit for the filter efficiency tests and the sorption and desorption experiments for iodine on charcoal.

1 blower  2 rotameters  3 paraffin-oil bubbler
4 aerosol pre-filter  5 iodine generator  6 experimental filter
7 detectors  8 lead shielding  9 chemisorbents
10 heating

**FIG. 3.** Released iodine as a function of the trapped iodine.

Desorption tests were also carried out by changing the test tube for an empty one and the sorbent was leached with fresh air flow. The relation of the trapped and released iodine is shown in Fig.3. It was found that charcoal is capable of retaining amounts of iodine of more than double its own weight.

To study the retention mechanism of spent sorbent filter, an experiment was carried out with a saturated bed, 5.7 g inactive elemental iodine was incorporated in a charcoal bed weighing 2.1 g and loaded with an air flow contaminated with $5 \times 10^{-8}$ Ci/litre $^{131}$I.
Trapping of radioiodine on elemental iodine saturated sorbent was actually based upon the phenomena of isotope exchange. The participation of radioiodine in the whole amount of released iodine was taken to be 100% in the first 20 minutes and to decrease to 6% in the second 20 minutes. After one hour an equilibrium was found in the process, when the iodine released diminished to 1.7-1.8%. This means that the isotope-exchange process on the scale of iodine retention involves some time. After some hours of operation this bed was desorbed by fresh air flow at a speed of 60 m/min for 3 days releasing 73% of the activity.

2.2.3. Activity distribution tests on various sorbents

Distribution tests were undertaken to study the change of activity along the depth of the sorbent bed at various sorbent media and air-flow rates. In these experiments the efficiency of the chemisorbent sampler used was also checked. The aim of these tests was to determine the working depth of the filters for further experiments.

In the experimental unit (Fig. 4) the air-flow blower (1) controlled by needle valve (2) and rotameter (3), pre-cleaned in bubbler (4) and aerosol filter (5) was led into iodine generator (6) from where 15 μCi ¹³¹I and 40 mg elemental iodine in 2 ml CCl₄ solution was evaporated and piped to the adsorber column. The diminishing of the initial activity was measured and recorded by a ratemeter (11) connected to G-M tube (10) in lead shielding (13) and recorder (12). Front and back of the adsorber was bordered by aerosol filters (7). The activity, released by the adsorber was incorporated in chemisorbents (9). Distribution tests were carried out on charcoal, silver impregnated charcoal and silica gel.

After operation the column was surveyed by a scintillation counter in a lead castle provided with a 3-mm gap.

The results of the activity distribution test versus the bed depth at several air velocities and sorbent-media are shown in Fig. 5.
2.2.4. Efficiency tests on various sorbents

The experimental unit (Fig. 2) for studying efficiencies of various filter packings was prepared from quartz and glass. An air-flow rate of 50 litre/h was maintained by a blower (1) and controlled by rotameters (2). Bubbler (3) fitted with paraffin-oil and an aerosol filter (4) were used for pre-cleaning the air supply.

The iodine was generated by a heated (10) test-tube type evaporator (5) in which elemental iodine was dissolved in 2 ml alcohol or carbon tetrachloride and labelled with 10 μCi 131I per batch. The iodine solution was swept and evaporated by the air flow and iodine in molecular and essentially in aerosol form was transferred onto the adsorber bed (6).

For the purpose of HJ generation an aqueous solution of KI was passed through a cation exchanger, regenerated beforehand with hydrochloric acid, where K ions were exchanged for H ions and labelled with 131I.

A 100-mm long and 10-mm diameter glass tube fitted with fibrous or granular media was connected to the elbows with cones. The adsorbent bed was placed in lead shielding (8) with 2 orifices in it for detectors (7).

A 1/10 part of the unfiltered air flow was measured by rotameter (2), then by-passed and trapped by absorbent (9) (NaOH solution) just as the mean air flow which passed through the test filter.

Iodine contaminants accumulated on the upper and lower parts of the test filter were detected and recorded continuously.

To carry out desorption tests, the iodine generator tube (5) was exchanged for an empty test tube, leaching the previously exposed test filter with fresh air flow in the same system.

The efficiencies of the tested filters were calculated on the basis of the ratios of air flows and the specific activities of the chemisorbent samples determined previously. The amount of iodine which escaped from the chemisorbent sample was found to be negligible and uniform for both flasks.
# TABLE II. RESULTS OF THE FILTER EFFICIENCY TESTS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Medium Preparation</th>
<th>Elemental Iodine at density of sorbent (mg/cm³)</th>
<th>Removal of:</th>
<th>Hydrogen Iodide at density of sorbent (mg/cm³)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal</td>
<td>untreated</td>
<td>660</td>
<td>99.82</td>
<td>370</td>
<td>95.4</td>
</tr>
<tr>
<td></td>
<td>silver impregnated</td>
<td>660</td>
<td>99.85</td>
<td>450</td>
<td>92.7</td>
</tr>
<tr>
<td>Nuxit A, B</td>
<td>untreated</td>
<td>26</td>
<td>19.8</td>
<td>26</td>
<td>~55</td>
</tr>
<tr>
<td></td>
<td>silver impregnated</td>
<td>120</td>
<td>99.84</td>
<td>100</td>
<td>93.4</td>
</tr>
<tr>
<td>Fibreglass</td>
<td>untreated</td>
<td>85</td>
<td>24.5</td>
<td>85</td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td>silver impregnated</td>
<td>200</td>
<td>93.15</td>
<td>220</td>
<td>99.84</td>
</tr>
<tr>
<td>Slag wool</td>
<td>untreated</td>
<td>600</td>
<td>79.3</td>
<td>600</td>
<td>~88</td>
</tr>
<tr>
<td></td>
<td>silver impregnated</td>
<td>720</td>
<td>72.2</td>
<td>720</td>
<td>99.6</td>
</tr>
<tr>
<td>Molfilit K 40</td>
<td>untreated</td>
<td>700</td>
<td>25</td>
<td>700</td>
<td>81</td>
</tr>
<tr>
<td>molecular</td>
<td>silver impregnated</td>
<td>1150</td>
<td>14.7</td>
<td>1150</td>
<td>93.1</td>
</tr>
<tr>
<td>filter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varion KS</td>
<td>untreated</td>
<td>700</td>
<td>39.6</td>
<td>700</td>
<td>82.6</td>
</tr>
<tr>
<td>cation</td>
<td>silver impregnated</td>
<td>1130</td>
<td>99.85</td>
<td>1000</td>
<td>99.92</td>
</tr>
<tr>
<td>exchanger</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td></td>
<td>100</td>
<td>20.5</td>
<td>65</td>
<td>63.2</td>
</tr>
<tr>
<td>Silica gel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ø1,6-2,5 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH granulated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results of the iodine and hydrogen iodide removal efficiency tests from the air stream, using various untreated or silver impregnated sorbent media, are shown in Table II. A tellurium removal test on silver-impregnated charcoal was also carried out. The efficiency was found to be 84%.

2.2.5. Results and discussion

A charcoal bed saturated with inactive elemental iodine was studied as a model of spent sorbent filter. It was found that 99% retention was achieved at an iodine content corresponding to its own weight, in spite of using a rather high air velocity. The effect of retention on saturated bed is presumed to be due to isotope exchange. Some time is required to start this effect, while contaminated air with higher specific activities may be released. The saturated bed acts as a buffer. 73% of the whole activity was desorbed from the experimental saturated bed by fresh air over 3 days. It is concluded that an overexposed filter may function adequately if the dilution and/or the chimney-dispersion effects eliminate the hazards of environmental contamination. Nevertheless, in practice this simulation may be altered because the filters are not only exposed to iodine, but are loaded with considerable amounts of dust, smoke, colloidal parts etc.

Regarding the activity distribution experiments, the curves obtained for the various sorbents and air velocities were drawn for comparison in the same diagram (Fig.5). In accordance with the literature [4], the curves imply that dusty sorbents cause an intermediate section in the shape of the distribution curves. This section is accordingly shorter for less dusty, impregnated charcoal beds than the more dusty, untreated ones. This intermediate section is absent in the curves for silica gel which is practically a non-dusty sorbent. The absolute filter, applied at the end of the charcoal bed, trapped the very fine contaminated charcoal aerosols and raised the activity level at the end of the column.

The velocity of the air also interferes with the shape of the activity distribution curves, as may be seen from the different slopes of the curves. Higher air velocity causes a deeper penetration of radioiodine into the sorbent bed.

The initial section of the silica gel distribution curves implies that the first few centimetres of the bed depth are already in a saturated condition. The efficiency tests of our experiments confirmed that both untreated and silver-impregnated charcoals achieved 99% efficiency for the removal of elemental radioiodine. Somewhat worse results were obtained for the removal of hydrogen iodide using other unimpregnated sorbents.

Fibrous sorbents were not effective enough in their natural form, while in the silver-impregnated condition elemental iodine was removed by fibre glass and hydrogen iodide was trapped by slag wool fibres of high selectivity.

Other granular sorbents, such as molecular filters, artificial ion exchangers or silica gels, either in the natural or impregnated form, were found to be less efficient than expected. Solid sodium hydroxide achieved a very high efficiency in the removal of iodine.
3 OPERATIONAL EXPERIMENTS ON REMOVAL OF 131\textsubscript{I} IN IPP

The Hungarian Isotope Production Plant (IPP) which has been operating since November 1966 produces inorganic radioactive products, among them rather large amounts of radioiodine. This operation has provided the experience of radioiodine removal given below.

3.1. Description of waste management systems for 131\textsubscript{I} removal

The semi-hot cells required for the production of 131\textsubscript{I} are provided with a separate ventilation and air-filter system and have double-drainage and waste-management systems for both low and intermediate level radioactive liquid wastes.

3.1.1. Ventilation system for iodine-production cells

The Isotope Production Plant was built on the zone system, corresponding to the contamination hazard. The most dangerous zone of the building is the first one, i.e. the inner part with 21 cells. These are exhausted by fully operated ventilation systems, maintaining a depression of 15-25 mm w.g. relative to the maintenance corridor (2nd zone) and the operating rooms (3rd zone). In the case of the 3 iodine-production cells, the value of the depression is 50-60 mm w.g. relative to the operating zone, maintained by a special fully operated ventilation system which also ensures an air-exchange rate of up to 100 times per hour. The air flow is always directed from the cleanest zone to the more contaminated zones (Fig.6).

The air exhausted from the iodine-production cells is filtered first by a fibrous aerosol filter, then by a twin-connected commercial FP-200 type sorbent filter (Fig.7). These filter bags are made in the Soviet Union and contain three layers in the succession VMT-5 aerosol filter, UP-4...
activated carbon treated with alkaline impregnant and KhP-1 alkaline sorbent based on soda lime. Two twin units of these filters are operated alternately, avoiding the accumulation of high doses on the surfaces of the bags. The initial iodine removal efficiency of this filter type exceeds 99.9%.

3.1.2. Management of the iodine-contaminated medium-level liquid wastes

The medium-level effluents are obtained as residue from the iodine distillation process. After alkalization with NaOH, they are directed into a 300-litre underground, shielded tank for cooling.

The capacity of this tank is sufficient for a period of one year while a considerable part of the radioactivity decays. The slurry of the underground tank is piped to a special concrete incorporator system (Fig.8) containing a 150-litre drum (3) lined by cement powder (4) and pushed up to an infra-red heated hood (5) by a pneumatically operated membrane carriage (13). The liquid from the feed tank (1) (whose volume is half of the weight of the cement) is passed into the cavity of the cement bulk of the drum (2).

After a few hours the liquid is incorporated in the bulk cement (4). If the dose rate is low enough, further liquids can be introduced into the cavity for evaporation. The usual high salt content causes no difficulty because the crystallized part of the residues will never be removed from the drum. Evaporation is effected by infra-red heating.

The equipment is located in the hot area of the laboratory. Nevertheless, operation safety is ensured by a remote-controlled system and the processes may also be observed through a lead-glass window (16).
During the evaporation process the vapour is condensed in a small tank. The distilled water is usually led into the low-level drainage. The equipment is operated under a 200-mm Hg vacuum. The distillate output is about 12 litre/d using a heating power of 900 W. A G-M tube (15) with a signal system is installed for checking the dose rate on the surface of the drum. When this value reaches 500 mR/h and/or the inner cavity is nearly filled with the solid content of the slurry, the operation is stopped and cement-milk is piped onto the residue for closing.

The sludges originating from the chemical precipitator, the slurries of the spent regenerating solutions of the ion exchangers and the backwash of the sand filters are dehydrated in the same infra-red evaporator system but are not incorporated into cement, being merely temporarily stored till the bitumen incorporator equipment is completed.

In the pilot-plant-scale equipment the airborne radioactivity which originates chiefly from the volatile iodine-tellurium components is filtered by special sorbent layers.

3.1.3. Management of the iodine-containing low-level liquid wastes

The low-level radioactive effluents are generally obtained as by-products of decontamination processes performed in the isotope-production cells and their auxiliaries.
These liquids, apart from radiothalliums, are contaminated by short-lived isotopes only. The collecting system of this type of effluent has 3 underground tanks with a capacity of 80 m³ each.

![Diagram](image)

**FIG. 9.** Block diagram of the steam-heated evaporator system.

1 feed tank 2 magnetic anticalcinator 3 preheater
4 dosator 5 evaporator kettle 6 vapour cleaner
7 condenser 8 receiver 9 low-level effluent tank
10 communal sewage 11 vacuum pump 12 emergency tank
13 slurry treatment as shown in Fig. 8

After some months of cooling, the low-level effluents may be purified by the well-known chemical precipitation and/or ion-exchange treatment. The chief isotopes in these liquids are tellurium and some radioiodine residue as a result of its high initial activity. The contaminated regenerating solutions from both the cation and anion exchangers are piped to the feed tank (1) of the steam-heated, vacuum-evaporator system (Fig. 9). Before preheating (3), these liquids pass through a magnetic anticalcinator (2) to eliminate the encrustation hazard in the kettle, then preheated liquids are piped to the dosator (4) to keep a constant level in the evaporator kettle (5). From here the vapours pass through the three-layer filter (6) for purification. The specifications of these filter layers are as follows:

1st layer:
- material: glass wool
- diameter of elementary fibres: 20 µm
- density of filling: 150 kg/m³
- thickness of layer: 150 mm

2nd layer:
- material: glass wool
- diameter of elementary fibres: 1 µm
- density of filling: 20 kg/m³
- thickness of layer: 150 mm

3rd layer:
- material: Teflon chips
- thickness of chips: 0.2-0.4 mm
- density of filling: 50 kg/m³
- thickness of layer: 150 mm

The glass-wool layers are operated either as absolute (aerosol) filters or as sorption filters retaining some volatile contaminants on their surfaces. Since the Teflon in the 3rd layer is quite resistant to heat and has
good hydrophobic properties, it generates large volumes of reflexes, resulting in additional vapour clarification. In an emergency, an underground tank serves as a safety reservoir (12). The clarified vapour is condensed (7) and collected in an evacuated receiver (8).

When the evaporation process is finished, the residue will be charged pneumatically as a slurry into the infra-red heated concrete drum (13) for additional evaporation and/or incorporation into cement.

3.2. Removal of $^{131}$I from air/vapour stream in IPP

3.2.1. Filtration of exhausted iodine contaminated air

To compare the specific activities of the outlet air before and after filtration, a survey was carried out to determine the entrance of radioactivity into air at different steps of the production of radioiodine. The specific activities of contaminated air from the cells were found to be as shown in Table III.

The initial efficiency of the existing sorbent filters was guaranteed as 99.9%. After 20 months of operation, the activity of the air passed was found to be $3 \times 10^{-9}$ Ci/litre at the most volatile process. In this case, the efficiency of the sorbent filter was 99.3%, while the aerosol filter trapped only 6% of the iodine. This peak-value concentration is 140 times higher than permitted by the MPC. Nevertheless, during this operation, the iodine-containing air is diluted by the slightly contaminated air exhausted continuously from the whole building at a ratio of 1:250. In addition, this value

<table>
<thead>
<tr>
<th>No.</th>
<th>Preparative operation</th>
<th>Specific activity (Ci/litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mean value before operation</td>
<td>$6 \times 10^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>Dissolving TeO$_2$ in alkaline</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>Distillation of radioiodine from sulphuric acid</td>
<td>$5 \times 10^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>Disposal of distillation residues from flask</td>
<td>$4 \times 10^{-7} - 2 \times 10^{-7}$</td>
</tr>
<tr>
<td>5</td>
<td>Concentrating iodine by evaporation after alkalization</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>Neutralization process of acidic distillation residues</td>
<td>$4 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
is enhanced by the dispersion effect of the 84-m high chimney up to $10^7$. Apart from peak values, the average air samples have never exceeded the limit of the MPC (Fig.10).

3.2.2. Purification of the iodine-contaminated vapour from the evaporator

The iodine-tellurium contaminated effluents were evaporated in the kettle-type evaporator combined with the vapour purification columns described. The treated water has an initial specific activity of $7 \times 10^{-4}$ Ci/litre and pH 8.5. During the process the concentration of the vapour/air mixture changes as shown in Table IV. The overall decontamination factor of the evaporator is $1.5 \times 10^{-4}$.

![Graph showing specific activity over time](image)

**FIG. 10.** Iodine-131 removed during the period of operation of IPP.

3.2.3. Operational experience with the infra-red heated evaporator

This particular method of dehydrating iodine/tellurium contaminated sludges with or without cement incorporation has led to quite surprising results.

As the evaporation is maintained by dark radiating infra-red heaters, the process temperature is kept below the boiling point of the liquid. In this case the water molecules enter the vapour phase only from the surface layer of the liquid without boiling, while the bulk of the liquid maintains its initial temperature. In this way evaporation of the concentrated radioactive effluents may be carried out under very favourable conditions because very few radioactive ions enter the vapour phase, even if the liquid contains volatile iodine compounds at pH 5.5. No detectable activity was found on the sorbent or chemisorbent filters applied, even when the initial specific activity was as high as 0.5 Ci/litre, while the decontamination factor of the process achieved the value of $10^6$. 
TABLE IV. CHANGE IN THE VAPOUR/AIR CONCENTRATION ON EVAPORATION

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Condensed vapour (Ci/litre)</th>
<th>Air (Ci/litre)</th>
<th>Efficiency of filter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below the filter bags</td>
<td>$4.4 \times 10^{-4}$</td>
<td>$1.1 \times 10^{-14}$</td>
<td>-</td>
</tr>
<tr>
<td>Above the 300-mm thick glass-wool layer</td>
<td>$3.2 \times 10^{-8}$</td>
<td>$4 \times 10^{-11}$</td>
<td>92.3</td>
</tr>
<tr>
<td>Above the 300-mm thick glass-wool layer and 150-mm thick Teflon-chip layer</td>
<td>$5.3 \times 10^{-11}$</td>
<td></td>
<td>93</td>
</tr>
</tbody>
</table>

4. SUMMARY AND CONCLUSIONS

The existing iodine removal equipment of IPP for both the isotope production and waste management systems provides adequate protection against contamination of the environment. Some conclusions may be drawn from the developmental activity carried out.

(1) A reasonable reduction of the volatility of iodine was achieved in acidic media by the oxidation of iodine to iodate. Nevertheless this promising method was not applied in our waste management operations because the solidification processes of the residues obtained by either bituminization or incorporation into cement cannot be performed in the highly acidic form like this. Sulphuric acid forms with cement a thin impermeable layer on the surface preventing further incorporation of the slurry. In the case of bitumen incorporation, the sulphuric acid generates a large volume of foam and results in very poor resistance to leaching out the contaminants.

The oxidation of iodine to iodate may be due to the evaporation process.

(2) Comparing the results of the efficiency tests on elemental iodine and hydrogen iodide it was found that the latter sorbed by silver-impregnated sorbents was removed with better efficiency than with untreated charcoals. Since large volumes of HI are generated during the production of radiiodine, the use of silver-impregnated sorbents seems to be advantageous.

(3) The use of glass-fibre filling as an air/vapour cleaner sorbent during the evaporation process of radioactive effluents containing iodine results in the efficient removal of airborne radiiodine.

(4) An infra-red-heated evaporator was used successfully to decrease the volume of slurries containing iodine. The decontamination factor of this equipment exceeded the value of $10^6$, while no detectable
activity was found on the sorbent filters used despite the rather high initial specific activity.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the valuable assistance of Dr. G. Tóth and O. Pavlik and he also is indebted to Dr. T. Lengyel for his beneficial advice.

REFERENCES


DISCUSSION

J.L. KOVACH. I would like to add a word of caution. Silver salts and alkali salts are the best catalysts for charcoal ignition. It might be useful to investigate ignition at maximum decay heat.

J. HIRLING: Thank you for your remark. So far, our investigations have been carried out at normal temperature only, but we intend to extend them to higher temperatures in the near future and shall keep your remarks in mind.
RESEARCH AND DEVELOPMENT ON COATINGS FOR RETAINING FISSION PRODUCT IODINE

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Abstract

RESEARCH AND DEVELOPMENT ON COATINGS FOR RETAINING FISSION PRODUCT IODINE. It is well known that elemental iodine has the propensity for forming charge-transfer complexes with amines. These complexes are stable at ambient temperatures and retain much of this stability at elevated temperatures. Amines also react with methyl iodide and hydrogen iodide to form the quaternary ammonium salts and amine salts, respectively. These chemical properties of amines provide the basis for the development of retentive coatings for fission product iodine.

Various amine-containing polymers were studied in steam-air environments at elevated temperatures using dilute quantities of tagged iodine. Both non-condensing and condensing steam conditions were investigated. Several of the polymers showed sorption rates and capacities that would be adequate for the chemical removal of accident-released fission-product iodine and were several times more effective than commercial protective coatings currently being used. The removal capabilities for amine polymers also could be enhanced by impregnating the reactant on a matrix material such as asbestos mat, presumably because the impregnation technique leads to enhanced surface area and porosity. The two most promising coating systems found were 1,10-phenanthroline impregnated upon asbestos and a three component composite film of the co-polymer of Genamid 2000 and Epon 828 as a reactive binder with 1,10-phenanthroline as a reactive filler. The use of a reactive coating as a passive safety system should reduce appreciably the airborne iodine half-life and the hazards associated with iodine release during a nuclear reactor accident.

1. INTRODUCTION

The increasing number of power reactors currently being sited has required the development of many types of safety features to protect the general public in the event of a serious nuclear accident. One of the major biological problems arising from such an accident would be the release of 131I vapors and certain compounds such as alkyl iodides (predominantly methyl iodide) and hydrogen iodide containing this isotope. If the released iodine were irreversibly sorbed on the surfaces within the containment vessel under conditions prevalent during an accident, the probability for release to the environment due to leakage would be reduced. Many of the surfaces within the containment shell are fabricated from mild steel or concrete. For protective purposes these surfaces are painted. Laboratory experiments [1] have shown that iodine will deposit on most commercial painted surfaces but the rate of deposition is low and often of little consequence in irreversibly immobilizing the iodine. In addition, the deposition process is reversible, and under some conditions the chemical form of the desorbed iodine is difficult to remove even if active safety systems are operable.

In principle it should be possible to develop a surface coating that would react rapidly and irreversibly with the chemical forms of iodine anticipated to be released under reactor accident conditions. What is required is a chemical compound or group of compounds that can be used either as a vehicle or a pigment and will react, when in the form of a surface coating, with vapor forms of iodine. Coatings of this type would be capable of retaining irreversibly copious quantities of fission product iodine as I\(_2\), CH\(_3\)I, and HI and would thus be capable of functioning as a passive safety system. Such systems would be supplemental to active systems, e.g., sprays and filters, for limiting the potential hazards of a reactor accident. Such a coating would be applied to surfaces within the containment vessel in addition to or in place of protective coatings now used.

2. BASIC ORGANIC AND PHYSICAL CHEMISTRY OF COATINGS USED AS IODINE SCAVENGERS

Most coatings systems are composed of three basic components: (1) the binder or film-forming constituent, (2) the pigment or filler, and (3) the solvent or in the case of emulsion paints an aqueous suspension medium. Invariably small amounts of ancillary materials are also added [2]. The primary function of the binder is, of course, to form a film or polymeric barrier over the substrate and to hold the pigments or fillers in place. Although the binder is usually not thought of as being a reactive material, there is no a priori reason that one cannot be chosen that contains reactive groups in its molecular structure to allow rapid chemical reaction with I\(_2\) and CH\(_3\)I.

On a theoretical basis, the binders which appear most capable of allowing irreversible reactions to occur are polymers which contain tertiary amine groups as part of their basic structures. One example of such a material is the co-polymer of butadiene and vinyl pyridine shown below.

\[
\begin{array}{c}
\text{CH}_2-\text{CH}=\text{CH}_2-\text{CH}_2-\text{CH} \\
\text{N}
\end{array}
\]

There are two reasons for choosing binders of this type. They should react with elemental iodine by formation of so-called charge transfer complexes. A typical reaction between a tertiary amine and iodine leading to the formation of a charge transfer complex may be represented by the general equation.

\[
\text{R}_3\text{N} + \text{I}_2 \rightarrow [\text{R}_3\text{NI}]^+ + \text{I}^-
\] (2.1)

This type of reaction results from the interaction of an electron donor, in this case the tertiary nitrogen atom, and an acceptor, the elemental iodine. The donor has filled orbitals of relatively high energy and the acceptor has empty orbitals of relatively low energy. The main interaction is therefore between the filled orbitals of the donor and the empty orbitals of the acceptor leading to a net transfer of negative charge from the donor to the acceptor. The use of polymers containing tertiary amine
groups has the additional advantage of being able to react with methyl iodide through well known quaternarization reactions. Such reactions result in the formation of the quaternary ammonium salts and may be represented by the equation

\[ R_3N + CH_3I \rightarrow [R_3NCH_3]^+ I^- \]  

With HI, similar reactions lead to the amine salts

\[ HI + R_3N \rightarrow [R_3NH]^+ I^- \]  

Only tertiary amines react with alkyl halides directly to yield the corresponding halide salts. With CH₃I, primary and secondary amines react first to form hydrogen iodide and a substituted amine that is a stronger base than its precursor. The hydrogen iodide that is formed can and probably will react with the new base that is formed and thus prevent further reaction with methyl iodide by making the amine a relatively poor nucleophile. All of the methylation reactions are pH sensitive but only the primary and secondary amines have built-in retarders in their reaction mechanisms. Normally, all amines should have a capacity of 1 mole of methyl iodide per mole or reactant. However, if a strong base is used in conjunction with the amine to react with the by-product hydrogen iodide, the molar capacity of primary and secondary amines for methyl iodide can be increased to 3 and 2 moles of CH₃I per mole of amine, respectively.

Based on the above chemistry, numerous amines were selected and used to formulate coating candidates. In most cases, the amines were used as binders but in several instances they were incorporated as reactive fillers as well. No attempt will be made here to discuss the chemistry and structure of each individual candidate, rather a brief description of the most promising materials is given in Appendix A.

The basic physical chemistry of a coating scavenger system and its relationship to iodine deposition may best be explained in terms of a simultaneous solid phase diffusion with chemical reaction process. The equations governing fission product iodine deposition from either the homogeneous vapor or aqueous phases may be expressed using a modified form of Fick's second law [1]

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \Phi_R \]  

where \( \Phi_R \) refers to the rate of chemical reaction occurring within the coating, \( D \) is the iodine diffusivity, and \( C \) is the local iodine concentration in the condensed phase. Since the rate of reaction depends on the chemical composition or chemical nature of the coating, the function \( \Phi_R \) depends upon the local iodine concentration \( C \) and the number of active sites \( N \) within the coating capable of reaction. For many commercial coatings and iodine scavengers in particular, the reaction rate \( \Phi_R \) can be adequately represented by irreversible second-order kinetics in the form

\[ \Phi_R = kCN \]  

where \( k \) is an arbitrary proportionality constant and \( k \) is the second order rate coefficient for the reaction [1]. The total number of mole-
cules, both sorbed and reacted per unit area, $N_t$, at any time $t$ is given by the integral equation

$$M_t = \int_0^L Cdx + \int_0^L u_0 (N_0 - N) dx$$

(2.5)

where $L$ is the coating thickness and $N_0$ is the total concentration of active sites within the coating.

This analytical model may be used to visualize the manner in which a reactive coating traps fission product iodine. As the fission product comes into contact with the paint, it penetrates into the pores of the binder and reacts with the reactive constituents (amine groups) of either the binder or the filler or both. The reactions between the amine groups and the iodine are for the most part irreversible and lead to either charge transfer complexes or salts. It is in this manner that the iodine is immobilized and unavailable for desorption back into the containment vessel.

3. CRITERIA FOR REACTIVE COATINGS

The criteria required of a coating to function as a passive safety system may be stated as follows:

1. Irreversible reactions with fission product iodine from ambient temperature to $175^\circ$ C

2. A minimum required coating capacity for $I_2$ and CH$_3$I of 0.2 and 0.04 mg/cm$^2$ of geometric area respectively

3. High deposition rates for fission-product iodine, i.e., wall coefficients or deposition velocities, $k_w$, of approximately 1 to 10 cm/sec

4. Functionality in steam and under condensing steam conditions

5. Thermal and radiation stability

6. Solvency in common solvents

7. Compatibility with active safety systems such as containment spray solutions.

Although the parameters $D$, $k$, and $N_0$ in equations (2.4) through (2.6) can be used to describe adequately the iodine deposition process on painted surfaces, they prove to be impractical to use as a standard by which to judge the relative merits of candidate iodine scavengers. Rather one must resort to semi-empirical techniques to obtain a quantitative measure of the effectiveness of candidate materials. For simplicity in criterion 3 the wall factor or deposition velocity concept, $k_w$, has been introduced [3]. The above seven criteria do not include all conditions that a containment vessel coating must meet and additional requirements have been listed elsewhere [4]. Only requirements 1 through 5 will be considered here.
4. EXPERIMENTAL TECHNIQUES

Chemical reactions between candidate coatings and I\(_2\) and CH\(_3\)I were studied in both the vapor state and under condensing steam conditions noting deposition rates (deposition velocities or wall factors, \(k_w\)), capacities, and degrees of irreversibility. Radiation and thermal stability measurements were also taken.

4.1 Non-condensing conditions

An apparatus was designed to obtain iodine deposition rates and capacities for candidate coating materials under non-condensing conditions (Fig. 1). A detailed description of this apparatus is given elsewhere [5]. A steam-air-I\(_2\) mixture (tagged with \(^{131}\)I) having a constant iodine concentration was generated in the flow train using the steam generator, air flow system, and iodine trap. The air-steam-iodine mixture having the desired concentration entered the sample chamber and passed over a 25 mm by 25 mm glass test specimen coated with the material of interest. The mass of iodine deposited was continuously monitored by a scintillation probe located directly under the specimen. The iodine concentration in the gas phase was intermittently measured by collecting small samples of gas in a CCl\(_4\) scrubber and analyzing for its radioactive iodine content. The air-steam-iodine mixture left the sample chamber and entered a steam condenser which removed the moisture from the gas stream and provided a quantitative measurement of the moisture content of the gas stream. The mass of iodine sorbed and reacted by the coating specimen was obtained from the scintillation probe measurement as a function of time. This same apparatus was also used to measure CH\(_3\)I deposition rates by simply placing \(^{131}\)I tagged CH\(_3\)I in the iodine trap and maintaining the trap at dry-ice temperature.

![FIG. 1. Flow train for iodine deposition.](image-url)

To facilitate screening a large number of candidates, a special chamber was used to evaluate several materials simultaneously [6]. This chamber was designed to fit into the flow train described above and consists of a 12-inch cylinder fitted with a rotating glass shaft to which twelve coated panels can be attached by means of platinum wire hooks. The coatings were rotated at a very rapid angular speed in the flowing steam-air-iodine mixture. At various time intervals the twelve panels were removed and radioassayed to determine the amount of iodine deposited. In those cases in which very accurate deposition data were required for materials possessing extremely high values for the wall factor, \(k_w\), the deposition
## TABLE I

THE SORPTION OF ELEMENTAL IODINE\(^{(a)}\) BY VARIOUS COATINGS\(^{(b)}\) AT 115° C IN 50 VOL. % AIR-50 VOL. % STEAM AT 1 ATM

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>(\text{I}_2) Sorption at Indicated Exposure Time, mg (\text{I}_2) per cm(^2)</th>
<th>Percent (\text{I}_2) Irreversibly Retained</th>
<th>Ratio of 20 h Sorption to that of Phenoline 302</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenoline 302</td>
<td>(6.33 \times 10^{-2})</td>
<td>77.4</td>
<td>1</td>
</tr>
<tr>
<td>Poly (aminopropylmethyilsilane)</td>
<td>(6.65 \times 10^{-3})</td>
<td>81.6</td>
<td>1</td>
</tr>
<tr>
<td>Versamid 125 bubble coating</td>
<td>(1.41 \times 10^{-1})</td>
<td>55.6</td>
<td>2</td>
</tr>
<tr>
<td>Versamid 125-30 wt. % Epon 828</td>
<td>(1.64 \times 10^{-1})</td>
<td>67.4</td>
<td>7</td>
</tr>
<tr>
<td>Polyvinyl alcohol-60 wt. % dipiperidylpropane</td>
<td>(3.39 \times 10^{-2})</td>
<td>92.9</td>
<td>2</td>
</tr>
<tr>
<td>Epon 1001-20 wt. % dipiperidylpropane</td>
<td>(2.06 \times 10^{-1})</td>
<td>80.1</td>
<td>7</td>
</tr>
<tr>
<td>Gentac</td>
<td>(1.12 \times 10^{-1})</td>
<td>71.6</td>
<td>8</td>
</tr>
<tr>
<td>TBAM-50 wt. % nickel</td>
<td>(7.73 \times 10^{-2})</td>
<td>87.6</td>
<td>6</td>
</tr>
<tr>
<td>TBAM</td>
<td>(9.49 \times 10^{-2})</td>
<td>93.6</td>
<td>6</td>
</tr>
<tr>
<td>DMAM</td>
<td>(1.66 \times 10^{-1})</td>
<td>93.9</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^{(a)}\) The \(\text{I}_2\) concentration was 203 mg per m\(^3\).

\(^{(b)}\) The coatings were about 2 mils thick.
chamber shown in Fig. 1 was replaced with a chamber in which the gas stream impinged directly upon the sample. Details concerning this technique have been reported by the authors [4].

4.2 Condensing Steam Conditions

To study the deposition process under condensing steam conditions, a 20 liter, right circular cylinder constructed of Type 304 stainless steel was used [3]. The vessel was coated on the inside with Amercoat 33HB and fitted into the flow train. The atmosphere inside the chamber was stirred with a 7-inch diameter teflon propeller at 500 rev/min to insure that gas phase mass transfer effects did not control the deposition process. A steam-air-I₂ mixture at approximately 115 °C was fed into the chamber which contained several 25 mm by 25 mm specimens of the coating of interest. The specimens were attached to the walls of the chamber at various positions using an adhesive. The amount of steam condensing in the chamber was regulated by controlling the temperature of the chamber walls with a heating mantle. A portion of the gas-phase iodine partitioned between both the water and the specimens while the remaining iodine left the chamber in the outgoing gas stream. Provisions existed for monitoring the iodine concentration in the inlet and outlet gas streams and in the condensate. In addition, the deposition of iodine on one of the 25 mm by 25 mm specimens was monitored continuously with a scintillation probe. Amercoat 33HB was chosen as the chamber coating because iodine deposition on this paint was found to be extremely low.

5. RESULTS AND DISCUSSION

Numerous candidates were evaluated initially in the screening apparatus at 115 and 170 °C to determine their iodine capacities, degrees of sorption irreversibility, and iodine affinities relative to a typical commercial coating (Phenolmer 302). All experiments were performed in approximately 50 vol. % steam-50 vol. % air atmospheres containing about 175 mg per m³ of either I₂ or CH₃I. The results of these studies are presented in detail in references [1 and 7]. A partial list of polymers studied and their sorption and desorption characteristics at 115 °C is given in Tables I and II for I₂ and CH₃I, respectively. The mass of I₂ or CH₃I sorbed is presented after 1 hour and 20 hours exposure together with the percentage of iodine sorbed irreversibly. Also included is the ratio of the mass of iodine sorbed after 20 hours by the candidate to that of the standard. Inspection of this table reveals that several of the materials are promising as I₂ scavengers. Many candidates have capacities for I₂ many times greater than the minimum capacity of 0.2 mg/cm² and the reactions produced are quite stable. After 20 hours exposure, none of the experimental scavengers had reached saturation using 2-mil thick specimens.

Relative to I₂ sorption, the candidates invariably did not perform as well with CH₃I. In an effort to increase the capacity for CH₃I sorption, many of the most promising I₂ scavengers were impregnated into asbestos mat to increase the reactive surface area. This technique permitted the use of non-film-forming reactants suspected of having high affinities for CH₃I, for example, 1,10-phenanthroline. The impregnated asbestos candidates were also evaluated in the screening apparatus for I₂ and CH₃I sorption under conditions similar to those used in evaluating the films. The results are partially summarized in Table III for CH₃I and
TABLE II
THE SORPTION OF METHYL IODIDE\(^{(a)}\) BY VARIOUS COATINGS\(^{(b)}\) AT 115°C
IN 50 vol. % AIR-50 vol. % STEAM AT 1 ATM

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>CH(_3)I Sorption at Indicated Exposure Time, mg CH(_3)I per cm(^2)</th>
<th>Percent CH(_3)I Irreversibly Retained</th>
<th>Ratio of 20 h Sorption to that of Phenoline 302</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenoline 302</td>
<td>7.47 \times 10^{-4}</td>
<td>6.42 \times 10^{-3}</td>
<td>84.6</td>
</tr>
<tr>
<td>Poly (aminopropylmethysilane)</td>
<td>1.85 \times 10^{-2}</td>
<td>5.74 \times 10^{-2}</td>
<td>83.0</td>
</tr>
<tr>
<td>Versamid 125 bubble coating</td>
<td>1.01 \times 10^{-2}</td>
<td>4.66 \times 10^{-2}</td>
<td>96.5</td>
</tr>
<tr>
<td>Versamid 125-30 wt. % Epon 828</td>
<td>1.41 \times 10^{-2}</td>
<td>1.57 \times 10^{-1}</td>
<td>100.0</td>
</tr>
<tr>
<td>Polyvinyl alcohol - 60 wt. % dipiperidylpropane</td>
<td>2.30 \times 10^{-3}</td>
<td>4.69 \times 10^{-3}</td>
<td>92.1</td>
</tr>
<tr>
<td>Epon 1001 - 20 wt. % dipiperidylpropane</td>
<td>3.64 \times 10^{-3}</td>
<td>5.29 \times 10^{-2}</td>
<td>98.1</td>
</tr>
<tr>
<td>Gentac</td>
<td>2.70 \times 10^{-3}</td>
<td>1.18 \times 10^{-2}</td>
<td>66.5</td>
</tr>
<tr>
<td>TBAM-50 wt. % nickel</td>
<td>5.59 \times 10^{-3}</td>
<td>5.27 \times 10^{-2}</td>
<td>97.2</td>
</tr>
<tr>
<td>TBAM</td>
<td>6.12 \times 10^{-3}</td>
<td>7.29 \times 10^{-2}</td>
<td>98.6</td>
</tr>
<tr>
<td>DMAM</td>
<td>1.64 \times 10^{-2}</td>
<td>7.62 \times 10^{-2}</td>
<td>100.0</td>
</tr>
</tbody>
</table>

(a) The CH\(_3\)I concentration was 174 mg per m\(^3\).

(b) The coatings were about 2 mils thick.
<table>
<thead>
<tr>
<th>Reactant</th>
<th>CH₃I Sorption at Indicated Exposure Time, mg CH₃I per cm²</th>
<th>Percent CH₃I Irreversibly Retained</th>
<th>Ratio of 20 h Sorption to that of Phenoline 302 Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.43 x 10⁻³, 2.28 x 10⁻²</td>
<td>95.5</td>
<td>4</td>
</tr>
<tr>
<td>Phenoline 302</td>
<td>5.21 x 10⁻³, 6.86 x 10⁻²</td>
<td>97.3</td>
<td>11</td>
</tr>
<tr>
<td>Versamid 125</td>
<td>3.54 x 10⁻², 2.12 x 10⁻¹</td>
<td>100.0</td>
<td>33</td>
</tr>
<tr>
<td>Versamid 100</td>
<td>1.30 x 10⁻², 1.29 x 10⁻¹</td>
<td>98.5</td>
<td>20</td>
</tr>
<tr>
<td>Dipiperidylpropane</td>
<td>1.11 x 10⁻¹, 8.87 x 10⁻¹</td>
<td>100.0</td>
<td>137</td>
</tr>
<tr>
<td>Epon 1001 - 20 wt. % dipiperidylpropane</td>
<td>1.88 x 10⁻², 2.75 x 10⁻¹</td>
<td>100.0</td>
<td>43</td>
</tr>
<tr>
<td>Gentac</td>
<td>3.04 x 10⁻³, 2.94 x 10⁻²</td>
<td>100.0</td>
<td>46</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>3.44 x 10⁻², 8.14 x 10⁻¹</td>
<td>100.0</td>
<td>127</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>3.18 x 10⁻³, 1.41 x 10⁻²</td>
<td>100.0</td>
<td>2</td>
</tr>
<tr>
<td>TBAM</td>
<td>1.28 x 10⁻², 2.18 x 10⁻¹</td>
<td>100.0</td>
<td>34</td>
</tr>
<tr>
<td>DMAM</td>
<td>3.69 x 10⁻², 6.82 x 10⁻¹</td>
<td>100.0</td>
<td>106</td>
</tr>
<tr>
<td>Genamid 2000</td>
<td>3.61 x 10⁻², 4.80 x 10⁻¹</td>
<td>100.0</td>
<td>75</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>1.02 x 10⁻¹, 1.22</td>
<td>92.6</td>
<td>190</td>
</tr>
</tbody>
</table>

(a) The CH₃I concentration was 173 mg per m³.

(b) The asbestos mats were about 28 mils thick and the composites contained about 25 wt. % reactant.
indicate that certain of the impregnated asbestos mats are promising CH$_3$I scavengers. The four most promising candidates, based upon both I$_2$ and CH$_3$I sorption, appeared to be poly(t-butylaminoethylmethacrylate) (TBAM), poly(dimethylaminoethylmethacrylate) (DMAM), Genamid 2000, and 1,10-phenanthroline, all impregnated on asbestos. These four materials were then evaluated in the impinging flow apparatus under non-condensing conditions to obtain values for the wall factor, $k_w$. For these experiments, the sorption versus time curves are shown in Figs. 2 and 3. The initial slope
of the deposition curves were used to calculate wall factors for I₂ and CH₃I on the candidate coatings and the Phenoline 302 control (Table IV). The best material appeared to be 1,10-phenanthroline on asbestos, which had a deposition velocity of 2 cm per sec for I₂ and 0.3 cm per sec for CH₃I. All candidates were about one order of magnitude better than the control.

The four best candidates and the Phenoline 302 control were then evaluated to determine their stability when exposed to 1 x 10⁸ rads of gamma radiation. For these experiments the candidates were impregnated on asbestos mat and the composites attached to glass using a contact adhesive. A 5000-curie Co source was used for the irradiations. No weight change or physical degradation (embrittlement, yellowing, or flaking) was observed for any of the specimens. Following irradiation, the specimens were evaluated as scavengers for CH₃I and I₂ in the screening apparatus. For purposes of comparison, unirradiated specimens were also exposed to iodine simultaneously with the irradiated specimens. The results are shown in Table V in the form of deposition velocities, k_w. With the exception of TBAM, the deposition velocities of the scavengers were not appreciably affected by exposure to gamma radiation. The reactivity of TBAM with I₂ was apparently unchanged by exposure to gamma radiation, but the deposition velocity with CH₃I decreased from about 0.06 to 0.03 cm/sec.

From the standpoint of practicality and ease of application, it would be much more desirable to have a film-former as a scavenger rather than an asbestos impregnate. Accordingly, attempts were made to design film forming systems having iodine affinities equivalent to those exhibited by the best asbestos composites (Table IV). Since 1,10-phenanthroline appeared to be the most reactive candidate, but was not a film former, it was added to various binders as a reactive filler. The most successful coating obtained using this technique was a three component system of 30 wt. % 1,10-phenanthroline, 35 wt. % Genamid 2000, and 35 wt. % Epon 828.

### TABLE IV

A COMPARISON OF DEPOSITION VELOCITIES OF CANDIDATE COATING MATERIALS AT 115°(a)

<table>
<thead>
<tr>
<th>Material</th>
<th>I₂</th>
<th>CH₃I</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMAM</td>
<td>1.10</td>
<td>0.080</td>
</tr>
<tr>
<td>TBAM</td>
<td>1.19</td>
<td>0.066</td>
</tr>
<tr>
<td>Genamid 2000</td>
<td>1.13</td>
<td>0.166</td>
</tr>
<tr>
<td>1,10-phenanthroline</td>
<td>2.13</td>
<td>0.368</td>
</tr>
<tr>
<td>Phenoline 302</td>
<td>0.182</td>
<td>0.00397</td>
</tr>
</tbody>
</table>

(a) The concentration of CH₃I and I₂ was approximately 175 mg per m² and the environment was 50 vol. % steam-50 vol. % air.

(b) All materials impregnated upon asbestos.
TABLE V

THE EFFECT OF GAMMA RADIATION ON THE AFFINITY\(^{(a)}\) OF THE MOST PROMISING MATERIAls FOR METHYL IODIDE AND ELEMENTAL IODINE VAPOR\(^{(b)}\) AT 115°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition Velocity for Indicated Vapor, cm per sec</th>
<th>Dose of Gamma Radiation Prior to Exposure to Methyl Iodide or Iodine, rad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenoline 302 (2-mil film)</td>
<td>0.189, 0.00318</td>
<td>0.0, 1.0 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>0.271, 0.00412</td>
<td></td>
</tr>
<tr>
<td>1,10-phenanthroline on asbestos</td>
<td>1.108, 0.293</td>
<td>0.0, 1.0 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>0.945, 0.275</td>
<td></td>
</tr>
<tr>
<td>DMAM on asbestos</td>
<td>0.562, 0.0256</td>
<td>0.0, 1.0 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>0.561, 0.0214</td>
<td></td>
</tr>
<tr>
<td>TBAM on asbestos</td>
<td>0.464, 0.0611</td>
<td>0.0, 1.0 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>0.471, 0.0256</td>
<td></td>
</tr>
<tr>
<td>Genamid 2000 on asbestos</td>
<td>0.827, 0.0721</td>
<td>0.0, 1.0 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>0.752, 0.0796</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) These experiments were conducted in the screening apparatus with the coatings rotating at 250 rev/min to minimize the gas-phase mass-transfer process. The deposition velocities reported in this table are somewhat lower than those reported in Table IV, since the values reported here were based upon the 1-h deposition points. Those reported in Table IV were based on the extrapolation of the deposition curves back to zero time, which results in somewhat higher values.

\(^{(b)}\) The concentration of I\(_2\) and methyl iodide for these experiments were approximately 175 mg per m\(^3\) and the atmosphere was steam-50 vol. % air.
FIG. 4. Deposition of elemental iodine on most promising candidate materials under condensing conditions.

FIG. 5. Deposition of methyl iodide on most promising candidate materials under condensing conditions.

The Genamid 2000-Epon 828 co-polymer is an epoxy-polyamide and its structure is described in Appendix A. Note in Table IV that Genamid 2000, in addition to 1,10-phenanthroline, has a high affinity for both I₂ and CH₃I. Currently, the 1,10-phenanthroline on asbestos (25 wt. % reactant) and the film consisting of 30 wt. % 1,10-phenanthroline, 35 wt. % Genamid 2000, and 35 wt. % Epon 828 appear to most nearly fulfill the reactivity criteria for an iodine scavenger.
TABLE VI

DEPOSITION VELOCITIES AT 37° C UNDER CONDENSING STEAM CONDITIONS
FOR MOST PROMISING CANDIDATES MATERIALS (a)

<table>
<thead>
<tr>
<th>Candidate</th>
<th>Deposition Velocity, cm per sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,10-phenanthroline impregnated on asbestos (b)</td>
<td>I₂ 0.816</td>
</tr>
<tr>
<td></td>
<td>CH₃I 0.0413</td>
</tr>
<tr>
<td>30 wt. % 1,10-phenanthroline, 35 wt. % Genamid 2000, 35 wt. % Epon 828 coating (c)</td>
<td>I₂ 0.842</td>
</tr>
<tr>
<td></td>
<td>CH₃I 0.0357</td>
</tr>
<tr>
<td>Phenoline 302 (d)</td>
<td>I₂ 0.006</td>
</tr>
</tbody>
</table>

(a) Inlet I₂ or CH₃I concentration was about 175 mg per m³-in 50 vol. % air-50 vol. % steam.
(b) 25 wt. % phenanthroline on 28 mil thick asbestos.
(c) 2 mil thick coating.
(d) Control.
To evaluate the ability of these two materials to sorb iodine under condensing steam conditions, wall factors were obtained in the presence of condensing steam. In these experiments the condensation rate over the specimens was maintained constant at $5 \times 10^{-6}$ g/cm$^2$/sec. Again, the inlet $I_2$ or CH$_3$I concentration was approximately 175 mg/m$^3$ in a 50 vol. % steam-50 vol. % air mixture. The steam-air-iodine mixture entered the chamber at 115 C, and the steam was made to condense by maintaining the walls of the chamber below 100° C. The deposition velocities for the 37°C (wall temperature) experiments are listed in Table VI while the sorption curves for $I_2$ and CH$_3$I are shown in Figures 4 and 5, respectively. Both materials are excellent scavengers for $I_2$. Indeed the sorption curves for $I_2$ (Fig. 4) appear to be limited either by the partition of $I_2$ into the water or diffusion of $I_2$ through a water film adjacent to the surface. As CH$_3$I scavengers at low temperatures, both materials appear somewhat limited possessing wall factors of about 0.04 cm/sec and capacities of about 0.005 mg/cm$^2$. Additional experiments at elevated condensation temperatures namely 60 and 90° C, indicate significantly higher deposition rates and capacities. Figures 6 and 7 present the results of these experiments and indicate increased effectiveness at higher temperatures. Thus, the 37° C experiment should represent the lower limit of deposition for these materials. Relative to commercial coatings under condensing steam conditions, these materials represent a significant improvement.

6. APPLICATION TO REACTOR ACCIDENTS

The advantages inherent in the use of a reactive coating designed to function as a passive safety system during a nuclear reactor accident have been discussed in detail by the authors[4]. These advantages may be succinctly summarized as follows.
(1) The use of a reactive coating should decrease materially the half-life of airborne iodine under natural effects conditions. For illustrative purposes, Table VII shows representative iodine half-lives expected under accident conditions for a typical commercial paint and the two best experimental coating systems developed during this research.

(2) The use of a reactive coating should negate any detrimental iodine desorption effects even in the event an active safety system is operating; that is, once iodine is sorbed on the coating it would be immobilized and unavailable for desorption back into the containment vessel atmosphere. For most commercial paints, the deposition process is largely reversible and significant desorption of iodine is possible.

(3) A highly reactive coating will decrease the wall resistance such that higher gas phase mass transfer coefficients can be obtained without having the deposition process become significantly wall resistance limited. The use of an active safety system (recirculating air systems, sprays, etc.) should promote high gas phase mass transfer coefficients.

(4) Compartmented regions within a containment vessel could be sites for high local iodine concentrations and gas velocities. Deposition in such regions would be enhanced if these regions were painted with a coating having an extremely high deposition velocity.

![Graph](image_url)  
FIG. 7. $\text{CH}_3\text{I}$ capacities versus temperature under condensing steam conditions.
TABLE VII
SUMMARY OF AIRBORNE IODINE HALF-LIVES
UNDER LOSS-OF-COOLANT ACCIDENT CONDITIONS (a)

Non-condensing Steam Conditions at 115° C

<table>
<thead>
<tr>
<th>Coating</th>
<th>I₂ (min)</th>
<th>CH₃I (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Commercial</td>
<td>43</td>
<td>13</td>
</tr>
<tr>
<td>BMI-Experimental (b)</td>
<td>6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Condensing Steam Conditions at 37° C

<table>
<thead>
<tr>
<th>Coating</th>
<th>I₂ (min)</th>
<th>CH₃I (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Commercial</td>
<td>394</td>
<td>130</td>
</tr>
<tr>
<td>BMI-Experimental (b)</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>

(a) The total gas phase mass transfer coefficient due to bulk flow and molecular diffusion was assumed to be 1.0 cm per second for all calculations.

(b) The half-life values are approximately the same for either the Genamid 2000-Epon 828-1,10-phenanthroline composite film or the 1,10-phenanthroline impregnated upon asbestos.

7. SUMMARY AND CONCLUSIONS

Efforts to date have shown that it is possible to form charge-transfer complexes between amine-containing polymers and both elemental iodine and methyl-iodide under the conditions postulated for serious water cooled reactor accidents. Amine containing polymers have been shown to be amenable for fabrication into film-forming coatings or impregnation upon high surface area substrates. Based upon geometric areas available for coating coverage, several candidates possess sufficient iodine retentive capacity to react with all the fission product iodine anticipated to be released during an accident. For many of these materials deposition rates (deposition velocities) appear satisfactory, although some improvement appears desirable at low temperatures under condensing steam conditions. Although this research is incomplete, the two best coating systems found to date from a reactivity standpoint are 1,10-phenanthroline impregnated upon asbestos and a 3 component film using the co-polymer of Genamid 2000 and Epon 828 as a reactive binder with 1,10-phenanthroline as a reactive filler. By utilizing materials of this type to coat the containment vessel of a nuclear reactor, one would expect significant reductions in the airborne iodine half-life under natural effects conditions relative to half-lives observed with most commercial paints.
APPENDIX A
DESCRIPTION OF THE MOST PROMISING COATING CANDIDATES

To date, the most effective material, especially for CH$_3$I, is not polymeric and therefore does not qualify as a binder. However, it can be impregnated on asbestos matting or utilized as a reactive filler. The compound is 1,10-phenanthroline and its structure is shown below.

![Structure of 1,10-phenanthroline](image)

This aromatic amine has been used as a complexing agent for oxidized transition metals. Its unique structure provides the molecule with a high degree of nucleophilicity (hence enhancing its ability to form quarternary salts with alkyl halides). However, steric factors prevent the formation of the diquaternary salts. The structure of 1,10-phenanthroline as shown above is a fused aromatic ring system containing two tertiary amine groups. The molecule is planar, causing the two amine groups to be fixed in space in such a way as to reinforce their nucleophilic character. At this time it seems possible to use this material as a filler in a reactive binder, and research is currently in progress attempting to synthesize potential film formers (binders) incorporating the 1,10-phenanthroline structure.

Other amine containing polymers that have shown extremely good promise as iodine scavengers are poly(dimethylaminoethylmethacrylate), abbreviated DMAM, and poly(t-butylaminoethylmethacrylate), (TBAM). The repeating units of the polymers are shown below as II and III, respectively.

**II**

![Repeating unit of DMAM](image)

Since III is a secondary amine, it is theoretically capable of reacting with 2 moles of methyl iodide. As pointed out previously, the extent to which this occurs depends on a supplementary base being present to
react with the hydrogen iodide by-product of the methylation of secondary amines. Both of the above materials are film-formers and make acceptable coatings if extreme durability is not the principal criterion.

The most promising materials from a durability standpoint are epoxy-polyamides. An epoxy-polyamide is essentially a two-component system and, when mixed, will react at ambient temperatures to form a highly cross-linked structure. The Genamid 2000-Epon 828 formulation is an example of this type of coating. The epoxy portion is usually formed by reacting epichlorohydrin with bis(2,2-hydroxyphenyl) propane. The simplest possible structure for this type of resin intermediate is shown below.

![Chemical structure diagram]

The polyamide portion results from reacting dimerized monobasic fatty acids with a molar excess of a diamine. This results in a polymer that contains a plurality of amine linkages but which is terminated with primary amine groups. For Genamid 2000 the structure would approximate

![Chemical structure diagram]

The entire system is cross-linked through the reaction of the epoxide radicals with the amine group. Tertiary amines catalyze this reaction and are often used for this purpose. In the Genamid 2000-Epon 828 binder, 1,10-phenanthroline can be incorporated as a reactive filler and makes a very attractive film-forming iodine scavenger.

REFERENCES


DISCUSSION

J. PRADEL (Chairman): Those responsible for reactor safety will welcome the development of a passive, and therefore safe, device to trap iodine and its compounds. In applying these coatings, it will be necessary to avoid any destruction of activated carbon traps by the paint's solvent. This means that ventilation will have to be stopped.

J. BRION: Have you investigated the aging of your coatings, i.e. the change in efficiency with age?

J.M. GENCO. The coatings tend to show a decrease in deposition rate as a function of age, i.e. to pick up less iodine. However, in our experiment, we accelerate curing of the coating to the extent that we test fully cured coatings. In other words, we test the worst possible case, obtaining the deposition velocities after essentially infinite time.

C. PELLETIER. As we apparently do not know all the species of iodine that might be present during a reactor accident, I wonder if you have tested the paints for species other than methyl and elemental iodine.

J.M. GENCO: We have tested only I₂ and CH₃I and feel that this is sufficient at present. These are the only two species (apart from HI) that have in fact definitely been identified. HI presents no problem during an accident, since it should pass into the condensed water. People are at present speculating on the presence of HOI as a penetrating form of iodine, but evidence for this form is inconclusive. Although I have not investigated the electro-magnetic properties of HOI, I think that it probably has an appreciable dipole moment, so that, even if present, it should pass into the condensed water during an MCA.
C.G AMATO: Have you or your colleagues any information regarding the stability of their passive coatings under alkaline conditions?

J.M. GENCO: We have no data for the moment, but we are in the process of determining the compatibility of these passive coatings with borated Na$_2$S$_2$O$_3$, Na$_2$S$_2$O$_3$-NaOH, and NaOH solutions. Tests are being conducted by exposing samples to these solutions for periods of up to 3 months at 65°C. The solution concentrations are those recommended by the reactor vendors.
REACTANTS FOR THE REMOVAL OF IODINE AND METHYL IODIDE AND THEIR APPLICATION IN FOAMS

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Abstract

The encapsulation of contaminated air by stable, reactive foams is potentially an efficient method for cleaning air because of large surface areas and long reaction times. Contained atmospheres encapsulated by foam demonstrate significant reductions in leakage. Addition of hydrazines to water based foams provided high removal rates for elemental iodine. A 0.11 M concentration of unsymmetrical dimethyl hydrazine (UDMH) in foam resulted in iodine reductions of 99 and 99.97% within 12 and 18 minutes, respectively. Screening tests of reactive foam solutions for removal of gaseous methyl iodide were made under static and dynamic (shaking) conditions and included the following reactants: hydrazine, UDMH, piperazine, tri-n-butyolphosphine (TBP), triethylenediamine and thioacetamide. In the dynamic tests, 1/3 to 1/4 molal concentrations of the latter three reactants in an alkaline foam solution containing 1/3 molal UDMH required 7, 14 and 28 minutes, respectively, to reduce methyl iodide to 1% of the initial concentration (1-7 ppm). The other reactants were less effective by comparison. Water-foam encapsulation studies for air containing 0.8-2 ppm methyl iodide showed removal rates not significantly different from those found in the static screening tests for the same reactants, even though reactive surface areas were 20-100 times greater after foaming. This suggests that there is an absence of reactant in the foam bubble film probably caused by displacement by surfactants in the foaming agent. High removal rates of elemental iodine by hydrazine-type foams and of methyl iodide by TBP-containing foams are explained by noting that, in these cases, gas-phase rather than liquid-phase reactions are involved and that the foam bubble surfaces are collecting surfaces for the formed aerosol particles.

INTRODUCTION

The principal fission-product isotopes of iodine produced in reactors total 288 kilo curies/MW(th) with $^{131}$I equal to 25 kilo curies/MW(th). According to Morrison, containment safeguards are essential to control released fission products in case of an accident. In addition, iodine released into the containment space must be reduced to $10^{-3}$ of its maximum concentration in $1/2$ hour to assure adequate safety should containment fail. For a 1000 MW(th) reactor, the allowable leakage rate of 0.1% of the containment volume per 24 hours would result in a loss to the environment of 520 curies of $^{131}$I in the first hour assuming a 50% release of the iodine inventory. Rapid clean-up of released radiiodine is mandatory if nuclear power reactors are to be located near populated areas.

In a case of breached or failed containment, clean-up systems based on exhausting containment air through external iodine removing devices would not have adequate capacity to prevent escape of excessive radiiodine to the environment for...
TABLE I

Relative and Total Surface Areas of Single Spherical Bubbles (Foams)

<table>
<thead>
<tr>
<th>Bubble Diam.</th>
<th>Contained Vol. (ft³)</th>
<th>Surface to Volume Ratio (ft⁻¹)</th>
<th>Total Surface Area in Vol. of 10⁶ ft³ (ft²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 in.</td>
<td>4.8 x 10⁻⁶</td>
<td>288</td>
<td>2.88 x 10⁸</td>
</tr>
<tr>
<td>0.75 in.</td>
<td>1.3 x 10⁻⁴</td>
<td>96</td>
<td>9.6 x 10⁷</td>
</tr>
<tr>
<td>1.5 in.</td>
<td>1.02 x 10⁻³</td>
<td>48</td>
<td>4.8 x 10⁷</td>
</tr>
<tr>
<td>124.1 ft.</td>
<td>10⁶</td>
<td>.048</td>
<td>4.8 x 10⁴</td>
</tr>
</tbody>
</table>

the first half hour following an accident. Even when leakage rates are kept as low as an allowable 0.1% of the unbreached containment volume every 24 hours, excessive loss of radiiodine compounds will not be prevented by external clean-up systems, unless of course such systems have very high capacities. For example, the time required to effect a clean-up to 5% of initial radiiodine concentration (i.e., three complete air changes) would be 50 hours for 1000 and 1 hour for 50,000 CFM systems (neglecting radiiodine decay). This indicates that a means for rapid internal clean-up of contained atmospheres is very much needed to control released fission products of iodine.

APPLICATION OF REACTIVE FOAMS

The application of reactive foams within containment vessels has been studied as a method for rapid trapping and removal of radiiodine and its compounds.

Encapsulation of contaminated air by reactive foams offers many advantages. (1) Large surfaces are available for liquid phase reactions with gaseous iodine and its compounds (I₂, HI, methyl, and other alkyl iodides). This is shown in Table I which relates the ratio of liquid surface to contained gas volume for various foam bubble sizes to the total foam surface area in a 10⁶ cu.ft. spherical containment vessel assuming the vessel is entirely filled with foam. A single foam bubble with an average diameter of 0.75 inches has a calculated surface/volume ratio 2000 times that for a spherical 10⁶ cubic foot containment vessel and total surface area of the foam will be in the same proportion. (2) Aerosols may be formed in foams by gas phase reactions between iodine (and iodine compounds) and volatile reactants in the foaming solution. When this occurs, the particles have relatively small distances to travel under the influence of settling and diffusional processes to make contact.
with a foam film and become trapped. (3) Long and intimate contact time is provided for slow mass transfer reactions. (4) Foams permit concentration of contaminants into a relatively small liquid waste volume. (5) A primary advantage of the use of foams is their potential for reducing containment leakage by trapping contaminated air inside foam bubbles which resist passage through cracks and porosities in the vessel.

A major disadvantage of foam application is incompatibility with spray cooling as foams cannot be produced or maintained in the presence of copious liquid sprays. However, foams can be applied prior to or following cessation of spraying; although the time available for foam application would be reduced accordingly.

Foams are fully compatible with all other cooling systems, e.g. internal recirculation of a contained atmosphere through a cooling device (such as refrigerated coils) followed by a foam generator would offer a system for containment air cooling (by chilled coil and foam evaporation) and rapid contaminant removal. Location of a foam generator upstream rather than downstream of a cooling device may produce more stable foams as condensation occurring in the cooling device would result in thicker foam films and compensate for re-evaporation of foam when released into a containment atmosphere above 212°F. Evaporation of foam and liquid from collapsed bubbles in the immediate region of the hot reactor would provide additional core cooling. Studies undertaken to determine the best mechanisms for the application of foams to contained atmospheres include evaluations of the advantages reactive foams offer for reducing containment leakage and for removing iodine and its compounds.

**FOAM GENERATION**

Foams may be generated by (1) co-current flow of air and foaming liquid through dispersing screens or other mesh-type materials and (2) flow of air through screens wetted with foaming chemicals. For high foam production rates, co-current flow methods are preferred whereas the externally wetted screen technique is more adaptable to bench scale laboratory experiments.

A typical large production foam generator is shown in Figure 1. A solution of foam concentrate (surfactant) in water is sprayed onto the upstream face of a pleated, loosely woven, nylon mesh fabric. Simultaneously, the fan blows air through the surfactant spray and deposits it on the wetted nylon mesh fabric. As the air stream passes through the wetted mesh, foam bubbles are formed. By proper adjustment of the application rates of foaming solution and air flow, a range of foam bubble sizes can be obtained. Bubble size is characterized by the term "expansion ratio" which refers to the volume occupied by the fully formed foam compared to the unfoamed volume of the liquid (surfactant plus water) used to produce the foam. High gas to liquid flow rates produce high expansion, or light density, foams whereas low gas to liquid flow rates produce low expansion, or high density, foams. High expansion foams may have ratios as high as 1000:1 whereas low expansion (fire fighting) foams have expansion ratios of approximately 30:1. Low expansion foams have
small bubble size and high liquid content and, therefore, large surface area per unit volume and good heat exchange capability. Therefore, low expansion, reactive foams are preferred for rapid radiiodine removal in heated containment vessels.

FIG. 1. Schematic diagram of a foam generator.

FIG. 2. Leakage simulation chamber.
Leakage rate studies were made with and without foam under controlled conditions in a 36 liter, cylindrical chamber shown in Figure 2. The chamber wall contained 8 capillary tubes 0.5 mm inside diameter (1.57 mm² total leakage area) and 5 cm long. Leakage rate was evaluated by the amount of air needed to maintain a constant pressure differential between the chamber and the outside atmosphere and expressed as percent of chamber volume per minute. Results are presented in Figure 3. As may be seen, the leakage rate for air alone was considerably higher than when the chamber was filled with foam. It may be noted, also, that as pressure increases, the leakage rate with foam tends to assume an asymptotic value. This may indicate that the blocking of the capillaries and reduction in diameter by the liquid film balances the increase in internal pressure. Leakage rates with foam were approximately 1/3 those without foam over the pressure range studied.

In the apparatus shown in Figure 2, the maximum pressure obtainable was 40 inches water gauge (in.w.g.) (1.45 psig). All tests were performed at room temperature (70°F). A chamber capable of withstanding higher pressures would be required to verify leakage reductions obtainable with foams under realistic conditions, i.e., at pressures up to 40 psig in saturated steam-air environments. It may be assumed that wet atmospheres will show lower leakage rates than dry atmospheres because of wetting of cracked and porous surfaces. This suggests that reduction in leakage rates by foam may not be as large for the hot saturated atmospheres postulated for coolant release accidents as might be the case for a completely dry atmosphere.
REMOVAL OF ELEMENTAL IODINE BY REACTIVE FOAMS

Previous Studies

Silverman, et al.[3][4] reported the use of two reactive foams, one containing 0.5% Na$_2$S$_2$O$_3$ and the other 0.5% AgNO$_3$, for removal of elemental iodine from air. Tests in a 1200 ft$^3$ chamber using Na$_2$S$_2$O$_3$ reactive foam showed a reduction in iodine concentration after 1/2 hour of 92% when the foam generator was shut off as soon as the chamber was filled with foam and up to 96% removal efficiency when the foam generator operated continuously over the entire period, i.e., recirculating the chamber air-foam mixture through the foam generator. Comparative studies of 0.5% Na$_2$S$_2$O$_3$ and 0.5% AgNO$_3$ in foam, using a small 53 ft$^3$ chamber, showed 1/2 hour elemental iodine removal efficiencies of 99% and 98%, respectively, when using continuous foam production with recycled air. The removal of elemental iodine by non-reactive foams with and without uranine particles in the air-iodine test atmosphere, showed greater elemental iodine removal when the aerosol was present, indicating significant adsorption and reaction of iodine on the uranine particles.

Tests made at Oak Ridge National Laboratory in a 6000 ft$^3$ hot cell by Yoder, et al[5] with continuous recycling of Na$_2$S$_2$O$_3$ reactive foams showed an 131I$_2$ removal efficiency of 90% in one hour. Removal of 131I$_2$ without foam (by plate-out and leakage from the dry cell) was found to be 70% during a like period, suggesting that there was a corrected iodine removal efficiency of only 67% by the foam alone. However, losses from the chamber by plate-out and leakage in the presence of foam are greatly reduced and most of the 90% reduction can be attributed solely to the foam used in the tests. Substantial reductions in chamber leakage by the use of foam encapsulation has been noted in other large chamber tests conducted with non-reactive foams. Although variations in efficiency were obtained by these earlier studies it is clear that high removal rates for elemental iodine may be obtained by the use of reactive foams.

Foams Containing Hydrazine and Unsymmetrical Dimethyl Hydrazine

The observed rapid reaction of elemental iodine and formation of iodine-containing aerosols by gas phase reactions with vapors of several hydrazines[6] prompted studies of foams containing these substances. In addition, hydrazine, and particularly unsymmetrical dimethyl hydrazine (UDMH), demonstrated significant removal capability for methyl iodide.

Three reactions can occur in the reduction of iodine by hydrazine[7]:

1. $I_2 + 2N_2H_4 = 2HI + N_2 + 2NH_3$  
2. $5I_2 + 3N_2H_4 = 10HI + 2HN_3$  
3. $2I_2 + N_2H_4 = 4HI + N_2$

1. Foaming agent was 2.5% ether lauryl sulfate plus lauryl alcohol stabilizer.
Liquid phase reactions occur as shown by equation (3) but all three reactions may be possible for gas phase reactions depending on concentrations of the reactants and temperature. The hydrogen iodide reaction product reacts further to form a hydrazinium iodide aerosol:

\[ \text{N}_2\text{H}_4 + \text{HI} = \text{N}_2\text{H}_5\text{I} \]  \hspace{1cm} (4)

UDMH may be involved in similar reactions:

\[ \text{I}_2 + 2(\text{CH}_3)_2\text{N}_2\text{H}_2 = 2\text{HI} + \text{N}_2 + 2(\text{CH}_3)_2\text{NH} \]  \hspace{1cm} (5)

\[ 5\text{I}_2 + 3(\text{CH}_3)_2\text{N}_2\text{H}_2 = 6\text{CH}_3\text{I} + 4\text{HI} + 2\text{HN}_3 \]  \hspace{1cm} (6)

\[ 2\text{I}_2 + (\text{CH}_3)_2\text{N}_2\text{H}_4 = 2\text{CH}_3\text{I} + 2\text{HI} + \text{N}_2 \]  \hspace{1cm} (7)

Iodine removal studies with foams containing 0.053 M and 0.156 M hydrazine and 0.108 M UDMH were made in a 3260 ft\(^3\) chamber. The basic foaming solution contained 1.66 fluid ounces of a common household detergent per gallon of cold water (i.e., 1.3 vol. %). This foam-producing solution was used routinely for the remainder of our studies. The foam generator shown in Figure 1 was equipped with an enclosed 1 HP motor and fan and placed on the floor of the test chamber. The foaming solution was pumped to the unit from a location outside the chamber. Chamber air was drawn into the foam generator from the top of the test chamber through a 3 inch diameter duct connected to the fan inlet. Foam was released at floor level and gradually increased in depth until it fully occupied the chamber in approximately 15 minutes.

Prior to foam generation, iodine (\(\text{I}_2\))-air concentrations in the range of 5 – 25 ppm were prepared by volatilizing iodine crystals on a hot plate located inside the chamber. Mixing was accomplished by a recirculating fan located inside the chamber. Relatively large amounts of iodine were needed to prepare the desired test concentrations because of initial high removal of airborne iodine until the exposed surfaces of the chamber became saturated. Foams were generated only after low wall removal rates were reached, usually 1/2 to 1 hour after all the iodine had been volatilized.

Iodine was sampled 18 inches inside the chamber and 30 inches above the floor through clean glass tubing. The sampling train consisted of a foam beaker (an empty, 1/2 liter flask), two bubblers in series, each containing 15 cm\(^3\) of xylene, a flowmeter, and pump, in that order. Gas sample volume ranged from 5 to 10 liters of air and, after removing the iodine, the gas was cycled back to the chamber. Each of the two bubblers in series were analyzed separately as a check on iodine collection efficiency. Analyses were performed colorimetrically with an 4200 \(\AA\) filter using the intensity of the iodine-xylene color as an indicator of iodine concentration.

Results of these studies are presented in Figure 4. Foam without hydrazine or UDMH reactants was not very effective in removing elemental iodine from the chamber air as it required...
FIG. 4. Removal of iodine from air by reactive foams in 92.3 m³ chamber.

183 minutes to remove 80% of the iodine present at the start of the foam generation. To reduce the iodine present at the start of foam application by 99% required 77 and 74 minutes after foam containing 0.053 M and 0.156 M hydrazine, respectively, was added. Although each foam solution contained a significantly different amount of hydrazine, the equilibrium vapor pressure of hydrazine in contact with the liquid was not greatly different, i.e., vapor pressure is equivalent to 22 ppm (parts of hydrazine per million parts of air) for 0.17% solution at 70°F and 35 ppm for 0.50% solution. Elemental iodine removal from air by foam containing 0.108 M UDMH was very rapid; only 12 minutes was required to reduce the initial concentration by 99% and only 18 minutes to make a reduction of 99.9% (i.e., half-life removal time was 1.8 min.).

The reason for this markedly increased iodine removal rate for UDMH compared to hydrazine foams may be a greater reaction rate with iodine. Preliminary studies of the vapor pressure of UDMH show a vapor pressure equivalent to 12-14 ppm above a 0.108 M water solution at 70°F. Since the vapor concentration of UDMH
(12–14 ppm) was lower than that for hydrazine (22–35 ppm) in these tests, UDMH vapor concentration was not the factor responsible for iodine removal rates that were higher than those obtained with hydrazine. It is likely, therefore, that the principal reaction taking place is (5) and/or (6) rather than (7). Reactions (5) and (6) are associated with different reaction kinetics than reaction (3) for hydrazine (corresponding to (7) for UDMH) which is believed to predominate. Preliminary studies of the reaction between iodine and UDMH indicate that small amounts of methyl iodide are formed. If reaction (5) predominates, methyl iodide formation would be minimum and depend upon the participation of reactions (6) and (7). As the major product of all of these reactions is hydrogen iodide, its removal by reaction with the other product of equation (5), namely dimethyl amine, by formation of a salt aerosol may be responsible for the higher reaction rate of UDMH. This is represented by the following equation:

$$I_2 + 2(CH_3)_2N_2H_2 = N_2 + 2(CH_3)_2NH_2I \quad (8)$$

It should be noted that of all the proposed reactions, (8) represents the minimum number of molecular collisions and this would favor its occurrence in preference to the other reactions.

Since hydrazine and UDMH rapidly form aerosols with iodine, it is believed that application of these reactants in foam for iodine removal involves, first, the formation of an aerosol and then deposition on the bubble film by settling and diffusional processes. The aerosol particles that are formed are highly water soluble. This favors particle size growth at high humidities by water addition and tends to increase the effectiveness of particle collection by foam films.

**REMOVAL OF METHYL IODIDE BY REACTIVE FOAMS**

The presence of methyl iodide in the released iodine fission products makes it important to study its removal by reactive foams.

**Methyl Iodide Reactants**

Methyl iodide may react with hydrazine and methyl hydrazines according to the following equations[6][8]:

$$CH_3I + N_2H_4 = CH_3N_2H_3 + HI \quad (9)$$

$$CH_3I + CH_3N_2H_3 = (CH_3)_2NH_2H_2 + HI \quad (10)$$

$$CH_3I + (CH_3)_2N_2H_2 = [(CH_3)_3N NH_2]I \quad (11)$$

The hydrogen iodide formed will react with the most basic compound present to form the corresponding hydrazinium iodide salt. Other reactions of hydrazines with methyl iodide may result in the displacement of iodine by hydrogen to form methane.[8] Methyl iodide reactions with hydrazine and methyl hydrazine do not result in aerosol formation and they appear to be liquid phase reactions. UDMH is most reactive with methyl iodide.
Thioacetamide is highly reactive with alkyl halides under some circumstances and was included in the foam studies. This substance may exist in two forms depending upon pH of the solution, namely:

\[
\begin{align*}
\text{acidic} & : & S \quad \text{SH} \\
\text{basic} & : & \text{CH}_3 \quad \text{C} = \text{NH}_2 \\
\text{CH}_3 \quad \text{C} - \text{MH}_2 \\
\text{CH}_3 \quad \text{C} = \text{NH}
\end{align*}
\]

The molecular arrangement in basic solution proved to be the more reactive of the two with methyl iodide.

Collins et al.\(^9\) investigated a number of activated charcoal impregnants for methyl iodide removal. The two most successful compounds, triethylene diamine (TEDA) and piperazine, were also studied as foam additions for removal of methyl iodide.

The most active reactant for methyl iodide found in screening tests for paint and surface coatings by Morrison\(^{10}\) at Battelle Memorial Institute was tributyl phosphine, \((\text{C}_9\text{H}_{10})_3\text{P}\). Although this substance was not compatible with paints and coatings, its high reactivity with methyl iodide made it desirable to include it in our studies. Other compounds investigated, but found to be ineffective, were hexamethylene tetramine and triphenyl phosphine.

**Screening Tests - Static Conditions**

To compare the reactivity of the substances noted in the preceding section, air-methyl iodide mixtures were placed in contact with unfoamed solutions containing these compounds under quiescent, or static, conditions. Tests were performed by introducing a known concentration of methyl iodide in air into a dry 300 ml (cylindrically shaped) gas sampling flask and then adding a known volume of reactive foam solution from the bottom with minimum agitation, so that the two fluids were in contact only at the gas-liquid interface. Gas samples of 10 μl volume were taken with a micro-syringe through a rubber septum in a side sampling port prior to and periodically after introduction of the reacting solution. The gas samples were analyzed for methyl iodide with a Varian Aerograph gas chromatograph using a 5 ft. long, 1/8" diameter column packed with Chromasorb-W (60-80 mesh) coated with Silicone Gum SE-30. Dry nitrogen was the carrier gas and detection was made by electron capture using a tritium-impregnated foil. Exact concentrations of methyl iodide were produced by double dilution of saturated methyl iodide vapor using a dynamic flow system, metered air flows, and controlled temperatures as described by Viles and Silverman.\(^6\)

Less precise methyl iodide concentrations were produced by injection of a measured volume of saturated methyl iodide vapor into a flask of known volume to prepare a dilute mixture that could be used to make a desired concentration in the reaction flask by adding a measured quantity with a syringe. Reacting solutions were added after a constant methyl iodide concentration was noted by gas analysis.

Results of three groups of tests are presented in Figures 5, 6, and 7. They show percent of the original methyl iodide concentration remaining at intervals following the addition of each reactive solution. Ratio of liquid surface area to gas
FIG. 5. Screening tests (static) for removal of methyl iodide (Group 1).

Volume and composition of the solution are noted as reaction rates and are dependent on these factors. Initial methyl iodide concentrations ranged from 4 to 22 ppm in Figure 5, were 1 ppm in Figure 6 and ranged between 1.4 and 4.1 ppm in Figure 7. It appears from Figure 5 (Group 1) that alkaline thioacetamide (TA) is better than UDMH and hydrazine at the concentrations used and that UDMH is superior to hydrazine. It was also found that TA in 1.3% sodium hydroxide was as effective as in 2.6% NaOH after the first hour of reaction time. Most reactive solutions in Figure 6 (Group 2) are triethylenediamine (TEDA) and alkaline UDMH. The marked superiority of tributyl phosphine (TBP) over TEDA and UDMH is demonstrated in Figure 7 (Group 3). The superiority of TBP over other reactants may be explained at least partially by its water insolubility. As a consequence, a layer of lighter-than-water (SG = .82) pure TBP is in direct contact with the gas phase. In addition, TBP vapors form an aerosol with methyl iodide (the only reactant tested that was observed to do this), indicating that removal
of methyl iodide may be by both gas and liquid phase reactions. The aerosol formed, tributyl methyl phosphonium iodide, is water soluble. The composition of the TBP solutions are listed but, because of TBP insolubility, two liquid phases were present in all TBP tests.

![Graph showing screening tests for removal of methyl iodide (Group 2).](image)

Accurate comparisons between reactants in different groups is difficult as solution volumes, liquid surface area to gas volume ratio, and flask orientation (geometry of gas volume and liquid surface) were different. It may be concluded, nevertheless, that the most effective reactant for methyl iodide was tributyl phosphine (TBP). Triethylene diamine (TEDA), thioacetamide (TA), and unsymmetrical dimethylhydrazine (UDMH) were capable of rapid reaction rates also.
Screening Tests - Dynamic Conditions

To make better comparisons between the most promising reactants for methyl iodide and to eliminate (or at least minimize) unrealistic factors introduced by static testing, additional studies were made using the same equipment and starting procedures but shaking the flasks vigorously in a vibration machine after introducing the reactive solutions. Foam was produced when a foaming agent was present. Shaking continued during the entire test except for short intervals during gas sampling. Results of these tests are presented in Figures 8, 9 and 10.

Hydrazine proved ineffective, whereas UDMH and TA, with $\text{Na}_2\text{HPO}_4$ as an alkaline buffer, showed good results (Figure 8). The addition of 0.167 M UDMH improved the removal rate of TA with 10.3% $\text{Na}_2\text{HPO}_4$ for methyl iodide. The effect of alkalinity
and TA concentration on removal rate of methyl iodide is shown in Figure 9. No foam was produced in Groups 4 and 5 screening tests (Figures 8 and 9) as no foaming agent was added. In the final screening tests 0.33 M UDMH was added to all solutions except the control. This was of special interest because of the very high reaction rate this material has for elemental iodide which must always be removed at high efficiency if foam application is to be successful. Once again, TBP proved to be the most effective agent for reacting with methyl iodide. A summation of data for the nine most reactive solutions for methyl iodide, determined by dynamic screening tests, is presented in Table II.

**Methyl Iodide Removal by Recirculating Reactive Foams**

Limited tests of methyl iodide removal from air by encapsulation in foam containing one or more reactive agents
(TBP, TEDA, TA and UDMH) were performed in an 8.5 liter chamber. Figure 11 is a schematic drawing of the apparatus. A peristaltic pump recirculated air at 3.7 liters/min. through a 5 mm diameter fritted glass gas diffuser located at the bottom of an 8.5 liter foam chamber. The foam-producing solution containing reactive agents flowed down over the outside of the glass frit while air flowed outward to produce the foam which filled the chamber in approximately 6 minutes. Excess foam flowed from the top of the chamber to a 4.5 liter glass bottle which acted as a foam beaker. The released gas passed to a gas sampling flask and then to the pump inlet for recirculation back to the foam chamber. Ten μl gas samples were withdrawn from the sampling flask with a syringe and analyzed for methyl iodide concentration by gas chromatography, as described previously. Foam solution was replenished continuously from a reservoir connected to the inlet air line to assure equalization.
## TABLE II

Dynamic Screening Tests for Methyl Iodide Reactants

<table>
<thead>
<tr>
<th>Reactant Solution</th>
<th>Vol. (ml)</th>
<th>Initial CH₃I Conc. C₀ (ppm^a)</th>
<th>Time Required for Reaction (min.) to 0.5C₀</th>
<th>0.1C₀</th>
<th>0.01C₀</th>
<th>0.001C₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32 M TBP + 0.33 M UDMH + 0.1% NaOH + 1.3% FA</td>
<td>20</td>
<td>1.2</td>
<td>1</td>
<td>3.5</td>
<td>7</td>
<td>10.5</td>
</tr>
<tr>
<td>0.32 M TEDA + 0.33 M UDMH + 0.1% NaOH + 1.3% FA</td>
<td>20</td>
<td>2.7</td>
<td>2</td>
<td>7</td>
<td>14</td>
<td>28</td>
</tr>
<tr>
<td>0.27 M TA + 0.17 M UDMH + 10.3% Na₂HPO₄</td>
<td>50</td>
<td>7.0</td>
<td>4</td>
<td>14</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>0.27 M TA + 20.6% Na₂HPO₄</td>
<td>50</td>
<td>7.5</td>
<td>6</td>
<td>19</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>0.09 M TEDA + 0.33 M UDMH + 0.1% NaOH + 1.3% FA</td>
<td>20</td>
<td>2.9</td>
<td>9</td>
<td>22</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>0.27 M TA + 1.3% NaOH</td>
<td>50</td>
<td>8.3</td>
<td>8</td>
<td>27</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>0.27 M TA + 5.2% Na₂HPO₄</td>
<td>50</td>
<td>7.0</td>
<td>9</td>
<td>32</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>0.27 M TA + 0.33 M UDMH + 0.1% NaOH + 1.3% FA</td>
<td>20</td>
<td>2.9</td>
<td>15</td>
<td>37</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>0.33 M UDMH + 0.1% NaOH + 1.3% FA</td>
<td>20</td>
<td>3.6</td>
<td>14</td>
<td>45</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

^a-Parts of methyl iodide per million parts of air (vol/vol)
^b-Foaming Agent
^c-Extrapolated data
FIG. 10. Screening tests (dynamic) for removal of methyl iodide (Group 6).

FIG. 11. Recirculating foam apparatus.

1—Foam Chamber (8.5 Liter)
2—Foam Generator (5 mm Diameter Fritted Glass Tube)
3—Foam and Chemical Solution Feed (300 cc Bottle Terminating in Hypodermic Needle)
4—Regulating Valve
5—Solution Pressure Equalizing Connection to Liquid Reservoir
6—Peristaltic Pump (Maximum Gas Flow 372 LPM)
7—Water Manometer
8—Thermometer
9—Foam Breaker (4.5 Liter Bottle)
10—Sampling Flask (300 cc) with Rubber Septum (II)
of pressure and constant solution feed rate for a fixed valve setting. Initially, a measured volume of saturated methyl iodide vapor was injected into the system via the septum in the sampling flask and recirculated with air but without foam production until gas samples showed a uniformly mixed methyl iodide concentration. This took approximately one hour. For these studies, "time zero" was when the first definite change in methyl iodide concentration was noted in the sampling flask. Foam applications containing water-insoluble TBP required frequent mixing of the foam solution to assure uniform proportions in the solution feed line. In these small chamber studies, the foam used had an estimated average expansion ratio of 170:1. This is a fairly dense foam and favors the presence of reactant in the foam film.

Results of tests are presented in Figure 12. For these studies, also, TBP proved to be the most effective agent for methyl iodide reaction and aerosol formation. Alkaline TA, UDMH, and TEDA demonstrated lesser, but significant, removal rates. On the basis of these results, additional combinations of these reactants should be investigated.
Discussion of Results

Comparison of results from screening (static) and recirculated foam studies indicates that the foamed solutions did not increase removal rates of methyl iodide over those observed with the unfoamed solutions. These data are summarized in Table III which lists the average time required to reduce the methyl iodide concentration in air to one half ($t_{1/2}$) by various solutions used in static screening and recirculation foam tests.

Solutions containing TEDA had shorter methyl iodide concentration half-lives under static removal conditions than when foamed, even though liquid surface area to gas volume ratio was 20 times greater with foam. Although the ratio was 100 times greater for solutions containing TA, methyl iodide removal was not even reduced by half by the use of foamed solutions of identical strength. The relative ineffectiveness of the generated foam surfactant is believed to result from displacement of the reactive chemicals from the interface by the surfactant, which is known to concentrate on both surfaces of the bubble. As a result, the reactive chemical concentrates in grops at the junctions of adjacent foam bubbles. To provide more reactant in the interfaces, film thickness must be increased so that the reactant can be retained between the two film surfaces occupied by the surfactant but production of foams with thick films is difficult and may result in poor foam stability.

Recirculated foam and static screening tests involving tributyl phosphine demonstrated equal removal rates for methyl iodide even though foam provided a liquid surface area 80 times greater than was present in the static test. The agreement between these two tests indicates that methyl iodide decay is predominantly by gas phase reaction to form an aerosol. If this is true, after the gas phase is saturated with TBP (which occurs within a short time after introduction of the reacting solution) reaction rate is dependent only on methyl iodide concentration and this results in equal decay rates independent of interfacial surface area. The equivalent equilibrium concentration of TBP, obtained from vapor pressure - temperature data, is shown in Figure 13.[11][12] At 25°C, the vapor pressure of TBP is 0.093 mm Hg. This is equivalent to 122 ppm, the TBP air concentration because TBP is water insoluble and overlays the water component because of its lower density. It appears that the principal advantage foam generation has for methyl iodide removal when using TBP is the shortened diffusional and settling distances the water soluble aerosol particles have to travel to be removed by a collecting surface, i.e., the bubble surface.

Of the chemicals studied, TBP is the most reactive agent with methyl iodide and the only one to form an aerosol with methyl iodide. It also reacts rapidly with elemental iodine vapor in the gas phase to form an aerosol. TBP is insoluble in water, but the methyl iodide aerosol that is formed is water soluble. These characteristics are ideal for methyl iodide and iodine removal in hot, water saturated atmospheres inside a containment vessel. TBP can be used without interference from or interfering with cooling water sprays.
## TABLE III
Removal Half-Life of Methyl Iodide by Reactive Solutions

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>$S/V$ (ft$^{-1}$)$^a$</th>
<th>$t_{1/2}$ (min.)</th>
<th>Solution Composition</th>
<th>$S/V$ (ft$^{-1}$)$^a$</th>
<th>$t_{1/2}$ (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEDA (0.178M), FA, 0.1% NaOH</td>
<td>250</td>
<td>37.3$^b$</td>
<td>TEDA (0.135M), FA, 0.1% NaOH</td>
<td>12.8</td>
<td>17.1</td>
</tr>
<tr>
<td>TEDA (0.33M), UDMH (0.33M), FA, 0.1% NaOH</td>
<td>250</td>
<td>54</td>
<td>TEDA (0.27M), FA, 0.1% NaOH</td>
<td>12.8</td>
<td>10.5</td>
</tr>
<tr>
<td>TA (0.27M), UDMH (0.17M), FA, 10.3% Na$_2$HPO$_4$</td>
<td>250</td>
<td>48</td>
<td>TA (0.27M), FA 1.3% NaOH</td>
<td>2.45</td>
<td>81</td>
</tr>
<tr>
<td>TBP (0.33M), FA, 0.1% NaOH</td>
<td>250</td>
<td>13.3</td>
<td>TBP (0.22M), FA, 0.1% NaOH</td>
<td>3.0</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Note: TEDA = triethylenediamine
FA = 1.3% foaming agent
UDMH = unsymmetrical dimethyl hydrazine
TA = thioacetamide
TBP = tributylphosphine

*a-Liquid surface area to gas volume (calculated)
*b-Values of $t_{1/2}$ in ( ) corrected for time gas phase not in contact with foam
Preliminary reaction studies using TBP indicate that when sufficient liquid surface area is present, liquid and gas phase reactions occur with methyl iodide. Methyl iodide and TBP appear to combine as a first order reaction involving single collisions of the two molecules and under simultaneous liquid and gas phase conditions, reaction rate is accelerated markedly by increases in temperature. For example, methyl iodide half-life decay rates when using 0.25 ml of TBP in a 300 ml flask containing methyl iodide-air mixtures were 10, 4, 1.3 and 0.85 minutes at 1.8, 20.7, 48.5 and 60.5 °C, respectively.

**FIG. 13.** Vapour pressure of tri-N-butylphosphine.

**CONCLUSIONS**

Encapsulation of contained atmospheres in persistent, high expansion foam reduces leakage from containment vessels significantly and, when the foam contains reactive chemical additions, provides a means for rapid removal of iodine and its alkyl compounds.
Foams containing hydrazines, particularly unsymmetrical dimethyl hydrazine, react with elemental iodine in the gas phase and produce iodide aerosol particles which collect on the surfaces of the foam bubbles by settling and diffusion. Effective reactants for methyl iodide, on the basis of screening tests, are triethylenediamine, thioacetamide, unsymmetrical dimethyl hydrazine, but the most reactive is tributylyphosphine. The latter enters into gas and liquid phase reactions with methyl iodide (and also elemental iodine), while the other reactants exhibit liquid phase reactions only.

Speed of removal of methyl iodide from air by foams containing tributylphosphine is dependent on two factors: (1) rapid gas phase reaction rate and the formation of aerosols, and (2) distances particles must travel in tiny bubbles to effect rapid aerosol collection by diffusional and settling processes.

When liquid phase reactants are exposed to methyl iodide-air mixtures as unfoamed liquids, their reaction rates per unit surface area are considerably greater than for the same liquids after foaming, suggesting a loss of reactant in the foam films. This results from displacement of reactive solute from the bubble surfaces by the surfactant compounds used as the foaming agent. Before reactive foams containing liquid phase reactants can be used successfully, a means must be found to obtain high concentrations of reactants in the surface layers of foam films that form the interface between gas and liquid phases.

REFERENCES


DISCUSSION

J. PRADEL (Chairman): What do you plan to do with the foam after an accident?

F.J. VILES: Foams obviously cannot be used with sprays, but they can be used in internal, recirculating, clean-up systems, with the foam generator located downstream of the clean-up unit to re-form the foam, since it would be destroyed during passage through the recirculation clean-up unit.

M.I. GOLDMAN: Have you any information on the radiation stability of the tributyl phosphine?

F.J. VILES: No, we have no facilities for investigating this, although I believe arrangements could be made to have the work done at the Massachusetts Institute of Technology Research Reactor. I recently tried to convince Dr. Zittel of Oak Ridge to include this compound in his radiation studies. He may do this work.

D.A. NITTI: In measuring the reduced leakage rate from the vessel, you used 0.5 mm capillaries and a pressure of 40 inches of water. Did you measure the normal bubble pressure for the 0.5 mm capillary tubes? That is, did you measure the normal back pressure that you would expect just from the surface tension of the liquid?

F.J. VILES: No attempt was made to equate pressure or leakage rate with liquid surface tension or liquid capillary flow rates. Our investigation of reduced leakage rate by foam application was merely a preliminary study.

D.A. NITTI: Would you expect to be able to fill a 200 ft high containment vessel with this foam, i.e., would the foam be able to support the weight of a 200 ft column?

F.J. VILES: I cannot answer your question precisely. A 200 ft static column of foam would contain a large amount of solution and would be quite unstable. Such a column would require the use of high expansion foams, i.e., large gas-to-liquid ratios. If foam generation rates were high enough, it is possible that equal foam generation and collapse rates could be obtained for a confined foam height of 200 ft. If the foam were converged as in an exhaust stack, 200 ft heights could be obtained, and, I believe, have been obtained.
W, SCHIKARSKI: What is the situation with regard to rapid energy release by chemical reactions or combustion, with a consequent risk of explosions?

F.J. VILES: If you mean the presence of combustible reactant in the foam, the amount used would not result in a concentration above the lower explosive limit of the combustible in question. For example, the amount of hydrazine used for gas-phase reactions must be below its lower explosive limit, which I believe is ~4%. If we assume a maximum concentration of 0.2%, thus ensuring a safety factor of 20, with all the hydrazine in the gas phase at maximum temperature conditions, the resulting water concentration following cooling to ambient conditions (and I believe the Malibu reactor was used for this calculation) would be ~0.56%. This would be in equilibrium with 10-15 ppm gas-phase concentration, which is quite low, but adequate for iodine removal. Removal would be a bit slow, but it would be effective. Of course, at elevated temperatures, the gas concentration would be higher and approach the 0.2% concentration (2000 ppm) at peak temperature. Moreover, though heat will destroy the foam, it could still be generated at high temperatures as long as water-saturated atmospheres were involved. In the case of tributyl phosphine, since it is water-insoluble, gas concentration is determined from its vapour pressure-temperature relationship. This implies that the use of TBP is limited to a temperature which does not exceed that producing a vapour pressure corresponding to its lower explosive limit. In air, this is estimated to be 90-100°C.
RECENT DEVELOPMENTS IN SPRAY TECHNOLOGY

(Session VI, Part 2)
COLLECTION EFFICIENCY OF WATER DROPLETS FALLING THROUGH AN AEROSOL: A PRELIMINARY REPORT

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Abstract

COLLECTION EFFICIENCY OF WATER DROPLETS FALLING THROUGH AN AEROSOL: A PRELIMINARY REPORT. The collection efficiency of water droplets falling through a NaCl aerosol is approximately 7%. The modal radius of the aerosol particles ranges from 0.2 to 0.4 μm and the water droplets have radii from 0.06 to 0.11 cm. The droplets emerge from the scavenging tube of 81 or 98 cm at about 0.7 to 0.8 of the terminal velocity. The particle size of the aerosols was determined by light scattering, the analysis of the NaCl collected by the falling droplet was carried out by flame photometry, the weight of the aerosol was determined by direct weighing after collection in a thermal precipitator.

1. INTRODUCTION

The scavenging of aerosol particles by water droplets is a process of vast importance both in industry and in nature. On the one hand it provides a means by which air may be cleaned; on the other, it results in the dumping of the atmospheric and stratospheric radioactive aerosols onto the surface of the earth.

The mechanism is not simple. Firstly, the hydrodynamic flow pattern around the moving droplet must be known, and this is often complicated by the effect of the presence of the aerosol particles on the flow field and by turbulence. Secondly, the diffusion of the particles through the boundary layer must be obtained. Although a general solution does not seem possible, Friedlander [1] has obtained some approximate results for low-speed flows and Zebel [2] has considered the effect of an electrical field for both charged and uncharged particles.

Our approach is experimental and phenomenological. We are interested in the collection efficiency, i.e. the weight fraction of particles, contained in the cylinder swept out by the moving droplet, which actually adheres to the droplet. The aerosols consist of spherical particles with a narrow distribution of radii in the range of tenths of microns. The size distribution may be determined quite precisely either by light scattering or electron microscopy. The water droplets of known size are analysed for aerosol content after falling freely through a column of aerosol.

We plan eventually to utilize radioactive aerosols to obtain maximum sensitivity in detection, but to design such experiments we decided first to obtain an estimate of the magnitude of the collection efficiency. This would permit us to select an appropriate radioisotope and to determine

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how 'hot' each aerosol particle must be. Accordingly, preliminary experiments have been carried out in which sodium chloride aerosol particles captured by falling water droplets were analysed by flame photometry. These experiments had the added advantage of permitting us to cope with the many experimental problems without the need for a 'hot laboratory'. The results were not sufficiently precise to permit definitive statements about the effect of such variables as droplet size, particle size, droplet speed, aerosol concentration, etc., upon the collection efficiency. However, we do believe that the approximate result of a collection efficiency of 7% for this system may be of general interest.

2. PREPARATION AND ANALYSIS OF SODIUM CHLORIDE AEROSOLS

The NaCl aerosols used in this study were prepared by condensation of NaCl vapour upon NaF nuclei in a stream of helium. The equipment is represented schematically in Fig. 1. Three heavy-duty combustion furnaces (3a, b, c) were used to produce the aerosol in stages. The first (3a) served as a generator for NaF nuclei, the second (3b) produced a partially grown NaCl aerosol, and the third (3c) supplied additional NaCl vapour from which the final aerosol of narrow size distribution was formed. The solid salts were placed in combustion boats (4a, b, c) which were inserted in the Coors Sillimanite combustion tubes (5a, b, c). The NaF furnace was maintained at 855°C, the first NaCl furnace at 775°C, and the second NaCl furnace at either 795 or 805°C. The flow of helium was maintained steady at flow rates varying from 0.9 to 2.0 litre/min. Under these conditions the NaF nuclei are too small either to show a Tyndall cone in the viewing chamber or to be observed in the electron microscope (Philips Model EM 75B).

Collection of aerosol for the particle size distribution counts in the electron microscope was performed by thermal precipitation in a Model B

![Fig. 1. Generator for sodium chloride aerosols.](image)

1a - helium source, 2 - flowmeter, 3a, b, c - combustion furnace, 4a, b, c - combustion boats containing NaF (4a) or NaCl (4b, c), 5a, b, c - combustion tubes, 6b - potentiometer, 8 - thermal precipitator, 9 - light scattering photometer, 10 - light scattering cell.
thermopositor (American Instrument Co.). Collection was made directly on collodion-coated electron microscope grids in the thermopositor chamber. The aerosols which had been collected on these grids were immediately examined by electron microscopy. An example of these spherical aerosols is given in Fig. 2. The uneven edges are caused by some evaporation due to heating in the electron beam. The particles appear quite smooth when the beam is first turned on and then they develop the serrations upon continued exposure.
The particle size distribution was also determined by light scattering. These measurements were carried out with a Brice-Phoenix light scattering photometer 1000 Series, which was modified and adjusted as described previously [3]. The intensities of the vertically and horizontally polarized monochromatic light ($\lambda = 0.436 \mu m$) were measured in a specially designed cell [4, 5] at 5° intervals of $\theta$, the angle between the direction of the incident and scattered beam, from 40° to 130°.

The method of particle size analysis is based upon comparison of the experimental values of the polarization ratio of the scattered light at 19 angles with theoretical values corresponding to various size distributions [6]. The polarization ratio is the ratio of the intensity of the horizontally polarized component of the scattered light to that of the vertically polarized component. The size distribution is characterized by the zeroth-order logarithmic distribution function [7]

$$p(\alpha) = \frac{\exp\left(-ln\alpha - ln\alpha_M\right)^2/2\sigma_0^2}{\sqrt{2\pi} \sigma_0 \alpha_M \exp(\sigma_0^2/2)}$$

where $\alpha_M$ is the modal value of the size parameter $\alpha = 2\pi a/\lambda$ ($a$ is the radius of the spherical particle and $\lambda$ is the wavelength of the light). The parameter $\sigma_0$ measures the breadth of the positively skewed distribution and for narrow distributions ($\sigma_0 < 0.20$) is approximately equal to the coefficient of variation

$$\sigma_0 \approx C = \frac{\sigma}{\alpha_M}$$

where $\sigma$ is the standard deviation.

The performance of this sodium chloride aerosol generator has been studied systematically earlier [8] where it was shown that the particle size increased with increasing temperature of the NaCl furnaces, with decreasing flow rate of the carrier gas and with decreasing concentration of nuclei. In this work we found that this general behaviour of the generator could be duplicated and also that a constant output of aerosol of a given size distribution could be obtained over a period of several hours. However, we were unable to produce precisely the same aerosol on different days even when the generator was operated under the same apparent conditions. This is illustrated in Table I where the values of $\alpha_M$ and $\sigma_0$ obtained for various generator conditions are tabulated. Each of these experiments was carried out on different days except the last two runs which were carried out on the same day. The particles were generally larger at the higher furnace temperatures. The flow-rate effect was not apparent except for those two runs carried out on the same day when the size definitely decreased with increasing flow rate. Because of this inability to reproduce the size distribution precisely using the same operating conditions, each aerosol used in a scavenging experiment was analysed either by electron microscopy or light scattering.

In several cases the same aerosol was analysed both by light scattering and by electron microscopy. Similar results were found by both techniques except that distribution obtained by electron microscopy was always about 10 to 20% higher in radius. This effect has been observed by us and by others in a large number of cases.
3. THE SCAVENGING ASSEMBLY

The scavenging assembly is depicted in Fig. 3. The aerosol flows from the generator through the 500-ml round bottom flask. One outlet of this flask leads to the hood where the aerosol is vented, the other to the scavenging assembly. Two scavenging tubes, each of 2.5-cm internal diameter were used, whose effective lengths were 81 or 98 cm, respectively. The scavenging tube, in turn, was connected to a tube in which the droplet falling from a hypodermic needle was accelerated. Four accelerator tubes of different lengths were used.

The aerosol flowed by convection from the 3-necked flask into the scavenging tube, the bottom of which was stoppered. The scavenging tube was filled in this way for 10 minutes after which the aerosol appeared to be uniformly distributed. After filling, the scavenging experiments were carried out in three steps: (a) the three-necked flask was disconnected and the inlet tube stoppered, (b) the stopper from the bottom of the scavenging tube was removed and the collection tube put in place, (c) water droplets (usually 30) were dropped from the syringe through the aerosol into the collection tube. A blank analysis verified that no detectable quantity of aerosol fell into the collection tube by settling or convection.

In several cases samples were obtained for light scattering analysis of the aerosol from various parts of the system, i.e. directly from the generator, from the top of the scavenging tube and from the bottom of the scavenging tube. These demonstrated that there was no significant change in the size distribution upon passing through the system.

The water droplets of different sizes were formed with the micrometer syringe assembly using varying needle sizes. The needle passed through a serum cap (similar to those used in gas chromatography) which closed
the acceleration tube. The apparatus was kept straight in order to prevent droplets from hitting the walls by supporting the apparatus rigidly in steel frames, positioning the individual parts of the assembly with the aid of a plumb line. The drops all fell within a small circle of about 1 cm diameter.

The size of the droplets was determined by weighing from 100 to 200 droplets collected after falling through the system. Acceleration tubes of different lengths were used for each droplet size in order that the droplet emerged from the apparatus at about the same fraction of its terminal velocity. The values were 0.71, 0.72, 0.73 and 0.80 for droplets with radii 0.113, 0.106, 0.098 and 0.089 cm, respectively. We were not able, in our laboratory, to construct an acceleration tube sufficiently high so that the droplets moved through the scavenging tube appreciably closer to the terminal velocity.

The experiments were carried out by releasing 30 droplets at intervals of 10-15 seconds. This was repeated 2 or 3 times.

To determine the amount of aerosol in the scavenging tube, it was flushed with helium into a thermal precipitator (Thermopositor) where it was collected on a piece of aluminum foil. This was weighed on an analytical balance. The chamber was then refilled for another set of runs.

4. ANALYSIS FOR NaCl CONTENT

The droplets collected after falling through the scavenging tube were analysed for NaCl content by flame photometry. Each sample of 30 droplets totalled only about 0.1 ml, an amount which was insufficient for handling.
in the flame photometer. Rather than dilute this, better analyses were obtained if the collection tubes already contained 1 ml of a solution 'doped' with 0.004 M NaCl. The sodium content of the resulting solution was determined by conventional flame photometry using the 589-nm sodium line. A standard luminosity-concentration curve was obtained for each series of analyses in order to maintain optimum accuracy.

5. RESULTS

Seventy runs were carried out using two scavenging columns of 81 and 98 cm and five droplet radii varying from 0.06 to 0.11 cm. The size distributions varied from $a_M = 0.21$ to 0.41 $\mu$m with $\sigma_0$ ranging mainly between 0.14 to 0.18.

The results were quite scattered and we were unable to determine whether there were any significant trends with the various variables. We cannot at this time say whether this was because the effect was insensitive to these variables or because the large experimental errors obscured any such trends. Rather than tabulate a large number of experimental results whose accuracy we hope to improve, we present only the average value. This is sufficiently significant for our purpose and it may be of some general interest.

The average efficiency was 7.1% with a standard deviation of 1.2%. The lowest efficiency value obtained was 4.1%; the three highest values were 10.5, 13.7 and 14.1%. Approximately, this efficiency corresponds to collecting about $10^7$ particles per droplet falling through an aerosol containing about $10^7$ particles per cubic centimetre.

There are several possible sources of error in this preliminary experiment, particularly in the weighing of small quantities of aerosol and the analysis of the small quantities of NaCl by flame photometry. Our efforts now are directed towards improvement of these analytical procedures as well as to the overall design of the scavenging assembly.

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DISCUSSION

J.D. JOUBERT: Have you any idea how much the sensitivity of your method could be increased by using radioactive aerosols?

M. KERKER: I am afraid this is confusing two different procedures. We use light-scattering to investigate the particle-size distribution of the
aerosols in situ. The other analytical techniques are used to determine the amount of aerosol which has been collected by the water droplet, when it is no longer in the aerosol phase.

J.D. JOUBERT: Do you consider droplet evaporation to be of importance?

M. KERKER: We did investigate this problem with our system and came to the conclusion that no appreciable evaporation took place.

W. JACOBI: We made similar experiments, several years ago, but in the inverse way. We used fixed spheres of 1-5 mm diameter, around which the aerosol was streaming at a definite rate. We used $^{212}\text{Pb}$ - activated aerosols, and measured their diffusion coefficient. I recommend this method, because a high sensitivity can be reached. Our results agreed fairly well with Smoluchovsky's coagulation theory.

K. LEE: I have a comment on Mr. Joubert's question regarding evaporation. I carried out some investigations which showed that even in superheated steam, when the degree of superheating is low, considerable time is required for evaporation to take place. I would therefore expect evaporation to be negligible in the present experiment.

I also have a question. What was the Reynolds number of the water droplet? I am asking this because when the Reynolds number is large, the boundary layer may separate, leading to inherently unstable hydrodynamic conditions. This would naturally give somewhat varying results. Even the experimental conditions are assumed to remain unchanged.

M. KERKER: I am afraid I cannot tell you the Reynolds number, but you might calculate it from the fact that the droplets leave the system at 7/10 of the terminal velocity. However, there is probably some turbulence in the wake of the droplet which could cause collection at the rear surface of the sphere.
A SUBMICRON PARTICLE PRECIPITATOR BASED ON WATER VAPOUR CONDENSATION

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Abstract

A SUBMICRON PARTICLE PRECIPITATOR BASED ON WATER VAPOUR CONDENSATION. An aerosol particle precipitator has been built composed basically of a gap where a strong water vapour concentration gradient and supersaturation are established. The main mechanism causing precipitation has proved to be particle nucleation and growth which greatly enhance the settling velocity under gravity. The effects of flow rate and particle concentration at the inlet were studied: the parameter ruling the deposition efficiency is the amount of water available to each particle. The contribution of thermophoretic, diffusiophoretic and gravitational forces is also evaluated. The tests were performed with DOP smoke (median diameter 0.3 μm) and with the aid of an aerosol photometer. The collection efficiency under specific operating conditions is better than 99.97%.

INTRODUCTION

Wet filtration mechanisms have not been studied in so much detail as other deposition mechanisms. This work is intended as a contribution to the study of mechanisms connected with vapour diffusion in air and condensation.

For this purpose a precipitator was built consisting basically of a gap in which a vapour concentration gradient is established by means of two surfaces, one evaporating (source) and the other condensing (sink). Inside the gap vapour diffuses towards the sink. Aerosol particles are dragged towards the sink by Stefan flow [1-3] which is proportional to the vapour concentration gradient. This effect is independent of particle size.

The vapour concentration gradient is obtained by keeping the two surfaces at different temperatures. In this temperature gradient aerosol particles undergo thermophoresis and are dragged towards the cold surface and hence in the same direction as the Stefan flow [2-3].

In addition, due to this particular way of obtaining the vapour gradient there is a high supersaturation ratio between the two surfaces. As a result the aerosol particles act as condensation nuclei [3], thus increasing their size and their settling velocity under gravity.

EXPERIMENTAL APPARATUS

The experimental apparatus (Fig. 1) consists of a chamber measuring 20 cm × 40 cm and 1.5 cm high. The two largest surfaces are set horizontally, the bottom one acting as the condensing surface and the top one as the vapour source.

The vapour sink is made of a machined corrosion-resistant plate equipped with a cooling system which enables the temperature to be varied uniformly
from room temperature to -30°C. The vapour source is an absorbent surface whose temperature may be varied uniformly between room temperature and 80°C by means of electric resistors.

The flow inside the chamber is laminar, along the length, with the inlet and outlet in the smaller sides.

The temperatures of the two surfaces, constant to within 0.5 degC, are measured and recorded by copper constantan thermocouples and by a multi-track recorder.

DOP (dioctylphthalate) smoke was used as the test aerosol. The smoke generator (Royco Model 258) was used at the optimum working conditions, that is with an aerosol of 0.3-μm median particle size (with minimum dispersion) [4]. To obtain the proper aerosol concentration, the aerosol was diluted with filtered air. The aerosol thus produced is heavily charged; hence a charge neutralizer, made of a 12-mCi $^{241}$Am source electrodeposited on a silver band inserted spirally into a Plexiglass cylinder of 6 cm inside diameter, was added at the smoke generator outlet. The resulting ion density can bring to charge equilibrium particles with a concentration much higher than that commonly used during tests.

The precipitator transmission is defined as the per cent ratio between the concentration at the precipitator outlet and that at the inlet. The transmission was determined by measuring the particle concentration above and below the precipitator with a Royco Model 230 Aerosol Photometer which measures light scattered at around 90°.

EXPERIMENTAL RESULTS

The efficiency of the precipitators was studied as a function of the ingoing aerosol concentration, of the flow rate of the aerosol through the chamber, and of the temperature difference between source and sink. These are the main parameters affecting the deposition velocity inside the precipitator.

Figure 2 shows a family of transmission curves as a function of ingoing concentration at a constant flow rate equal to 920 cm$^3$/min. The
sink temperature was kept constant at 6.7°C so that the parameter of the family is the source temperature, ranging between 23.5 and 60°C. At an equal concentration at the inlet the greater the temperature difference, the smaller the transmission. At a temperature difference of 53.3 degC and a concentration $7 \times 10^4$ particles/cm$^3$ the transmission is 0.03% with a corresponding efficiency equal to 99.97%.

The curves show a similar behaviour: the transmission at first increases very rapidly with increasing concentration of ingoing aerosol, then at larger concentration values the increase in transmission becomes much slower. In the first section, where the transmission values are still very low, the main phenomenon is water condensation on suspended particles acting as nuclei. In the supersaturated environment the nuclei grow, increasing the suspended mass and hence the deposition velocity [3].

With increasing concentration nucleation should lose importance. In fact, as the amount of water is limited, only some of the particles can nucleate effectively and grow into droplets.

In the high transmission value zone the gravity forces on dry particles (i.e. on the nuclei themselves), thermophoresis and Stefan flow (all of which are obviously independent of particle number concentration) should make a marked contribution to particle precipitation. This contribution is also indirect, due to the higher quantity of water captured by the nuclei and therefore to an increasing settling velocity as the particles approach the sink.
The behaviour of the precipitator in the low transmission region is shown also in Fig. 3. In the horizontal axis the theoretical supersaturation ratio (i.e. the ratio of the water vapour pressure at the source to that at the sink) is given, while in the vertical axis the ingoing concentration corresponding to transmissions of 0.2% (curve A) and 1% (curve B) respectively, as from Fig. 2, is given.

The graph is a straight line, i.e. if the ingoing concentration is doubled, the supersaturation ratio must be nearly doubled to maintain the same transmission. As a matter of fact the amount of water collected on the sink cooled at a constant temperature (Fig. 4) is directly proportional to the supersaturation ratio, which supports the interpretation based on nucleation.

Further tests were carried out maintaining a constant temperature difference $\Delta T = 27$ degC and varying the air flow rate through the precipitator from 1710 to 750 cm$^3$/min. The shape of the transmission plotted against concentration curves shown in Fig. 5 is strictly similar to that obtained when the same curves are taken with $\Delta T$ as the family parameter.

If instead of the concentration we then plot on the horizontal axis the concentration by flow rate product (i.e. the particle number per unit time through the precipitator), the four curves of Fig. 5 overlap in the low transmission region (Fig. 6), proving once more that the leading parameters are

![Fig. 3. Ingoing concentration as a function of the supersaturation ratio for two different transmission values.](image-url)
FIG. 4. Amount of water collected on the sink as a function of the supersaturation ratio.

FIG. 5. Curves of transmission plotted against ingoing concentration (parameter: flow rate).
the total number of particles and the amount of water available for condensation. For high transmission values (or high concentration by flow rate), however, the curves no longer overlap but slowly separate out. This is because gravitational settling, Stefan flow and thermophoresis (which are independent of concentration) should play a more important direct or indirect role in deposition. In this region the higher the flow rate, the greater the transmission.

The effects which cannot be ascribed to nucleation were measured separately from the nucleation effects and their contribution to the overall efficiency (which is the complement of the unity of transmission) was assessed.

First, the efficiency for gravitational settling plus Brownian diffusion was evaluated by measuring the ingoing and outgoing concentration in an isothermal environment. The transmission goes from 89 to 95% as the flow rate rises from 750 to 1710 cm³/min, in agreement with the combination of the two effects.

Figure 7 (curve A) gives the behaviour of the transmission as a function of $1/\phi$ (the inversion of the flow rate). As this quantity is directly proportional to transit time through the precipitator, the graph is a straight line, as expected.

The thermophoresis contribution was evaluated by establishing only a temperature gradient ($\Delta T = 27$ degC) across the gap. In this case the resulting thermophoretic forces are parallel to and work in the same direction as gravitational forces. Curve B of the same figure shows the transmission in this instance: the graph is again a straight line. The contribution to efficiency of thermophoresis alone ranges between 3.5 and 8% when the flow rate goes from 1710 to 750 cm³/min, that is, when $1/\phi$ varies from 0.035 to 0.08 sec/cm³. The contribution of thermophoresis alone for such a
FIG. 7. Transmission as a function of the inverse of the flow rate for gravitational settling plus Brownian diffusion (curve A) and plus thermophoresis at 27 deg C temperature difference (curve B).

temperature difference is about 80% of the gravitational settling plus the Brownian diffusion contribution. The contribution of the thermophoretic forces alone, with constant flow rate of 920 cm³/min and varying temperature differences is given in Fig. 8.

The transmission is plotted as a function of the parameter $300 \Delta T / T$ [3] which is directly proportional to the thermophoretic settling velocity, where 300 is a reference temperature and $T$ is the mean temperature between the two plates expressed in degrees Kelvin and $\Delta T$ is the temperature difference.

If, besides the temperature gradient, a water vapour concentration gradient is established across the chamber and nucleation either does not take place or is only partial, the aerosol particles are dragged along with the Stefan flow from the source to the sink. The deposition velocity is $1.9 \times 10^{-4} \Delta P / \Delta x$ cm/sec, where $\Delta P / \Delta x$ is the vapour concentration gradient in mbar/cm, and in this range is of the same order of magnitude as the thermophoretic velocity.

In view of this, it is interesting to observe the behaviour of the precipitator at high ingoing concentration where the concentration versus


**FIG. 8.** Transmission as a function of the normalized temperature difference.

Transmission (%)

Flow rate = 920 cm$^3$ min$^{-1}$
Constant vapor concentration
Gravitational and Brownian effects subtracted

**FIG. 9.** Effect of temperature gradient direction on transmission.

Transmission %

Temp. gradient: Downward (A), Upward (B)

Ingress Concentration
transmission curve shows a plateau. In this region the transmission ranges from 10 to 40%. It is apparent that the composition of the effects mentioned cannot completely account for the transmission observed and that nucleation must still play a part which cannot be neglected. Most probably the drag effects observed are important in so far as they transfer particles originally close to the vapour source toward the regions of the gas where the nucleation critical radius is smaller.

In all of the experiments described so far the precipitator was run with the temperature gradient directed upward (source above sink). Thus all the forces causing deposition are directed toward the sink and in addition the gas inside the gap is thermodynamically stable; the flow is laminar and no convective cells develop there. If we invert the system, we get results which are quite different (Fig. 9, curve A) from those previously described (curve B). In the low ingoing concentration range the transmission is higher, while at high concentrations the transmission is lower.

It can be said that apart from the different directions of some of the forces in play, convective cells formed inside the gap produce conditions which are difficult to determine experimentally.

**CONCLUDING REMARKS**

The apparatus described above has enabled us to study individually or cumulatively some of the mechanisms favouring the deposition of aerosol particles. Nucleation of particles and ensuing droplet growth seem to be the decisive phenomena for deposition.

In this respect it is worth emphasizing the importance of using the charge neutralizer which makes it possible to improve the performance of the precipitator. Otherwise the transmission would be as high as \( \frac{1}{3} \) to \( \frac{1}{4} \) with a much less marked dependence on ingoing concentration. In the range of supersaturation present in the gap the electric charge should have negligible effects on nucleation. If this is accepted as the main deposition mechanism, the efficiency observed could be explained by the radiolytic production of condensation nuclei [5, 6]. In air with the usual concentrations of \( \text{SO}_2 \) radiations of suitable energy and dose provoke oxidation of \( \text{SO}_2 \) to \( \text{SO}_3 \). Sulphates then form which have been identified as ammonium sulphate. The energy required for the production of a molecule by radiolytic action is around 400 eV [6] and there is evidence of a threshold dose around 5 rad [5, 6].

In our case, at a flow rate around 1 litre/min the dose to air in the neutralizer is of the order of 800 rad. Hence there should be a plentiful production of new condensation nuclei. These nuclei, aggregates of a few molecules, diffuse very rapidly toward aerosol particles and deposit there, thus decreasing the nucleation threshold considerably. In fact, unlike ammonium sulphate, DOP has a high nucleation threshold.

With the charge neutralizer, under suitable conditions of flow rate, concentration, temperature and vapour concentration gradient, the precipitator yields a deposition efficiency of better than 99.97%. It can thus be employed as an absolute aerosol particle sampler for mass concentration, specific activity, size spectrometry of the insoluble component, etc. If suitably developed, these mechanisms might also be applicable to filtration problems.
ACKNOWLEDGEMENTS

The Authors wish to express their appreciation to Prof. O. Vittori for stimulating discussions and to Mr. G. F. Bompane and Mr. A. De Zaiacomo for helpful technical assistance.

REFERENCES


DISCUSSION

J. PRADEL (Chairman): Did you seek some confirmation for your hypothesis by varying the concentration of SO$_2$? You might also investigate the effect of light and try to remove the condensation nuclei by means of a diffusion battery.

V. PRODI: We have not yet studied the radiolytic process you mention, but I think we shall be doing so. Light had no effect in this case because the aerosol was practically in the dark inside the apparatus and in the piping. I have the feeling that, if the hypothesis put forward is correct, ammonium sulphate particle diffusion is too rapid for the nuclei to be removed by a diffusion battery before they reach the DOP particles. However, we shall look into this also.

J.D. JOUBERT: Have you any idea of the Stephan and thermophoretic velocities?

V. PRODI: In our equipment, both these velocities are of the same order of magnitude, i.e. ~0.01 cm/sec$^{-1}$. 
ABSORPTION BY REACTIVE SPRAYS WITH APPRECIABLE LIQUID PHASE MASS TRANSFER RESISTANCE: THE WASHOUT OF METHYL IODIDE BY REACTIVE SPRAYS*

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Abstract

ABSORPTION BY REACTIVE SPRAYS WITH APPRECIABLE LIQUID PHASE MASS TRANSFER RESISTANCE: THE WASHOUT OF METHYL IODIDE BY REACTIVE SPRAYS. A study was made of the washout of organic iodides by reactive liquid sprays. Although the reactive additive used in this study was hydrazine, the results would be applicable to other additives. Falling drop absorption was calculated, assuming surface saturation and first order reaction rates, for stagnant and well mixed drops. For drops having diameters smaller than about 500 \( \mu \)m, and for reaction velocities less than 100 sec\(^{-1}\), the two models gave predicted removal rates which were similar. Computer evaluation of the infinite series solution to the absorption equation was carried out for a range of drop sizes, temperature, fall heights, and reaction velocities. Absorption by liquid wall films is an important part of the overall absorption for the spray systems described in this work. The penetration theory model of absorption into flowing films was used in this study to predict wall film absorption. The overall absorption model thus accounts for absorption by drops and wall film.

The washout of methyl iodide by aqueous hydrazine sprays was measured in spray chambers approximately 4 ft in diameter by 10 ft tall. Measured washout half-times ranged from 8 minutes to several hours, depending on the spray rates, hydrazine concentrations, and temperatures. Collection of the drops and wall liquid permitted measurement of the relative importance of wall and drop absorption in these experiments. Based on the absorption model developed and the experimental results, the removal rate of methyl iodide in larger containment systems was predicted for a range of drop sizes, reaction velocities, temperatures, and vessel heights.

INTRODUCTION

Sprays hold promise of efficiently and rapidly removing airborne fission products following loss-of-coolant in a reactor and release of fission products to the containment vessel. Although reactive sprays have been demonstrated for removing elemental radioactive iodine, the application of sprays to the less reactive methyl iodide known also to be present has received less attention. The authors have studied the washout of organic iodides by reactive liquid sprays and this work is here reported. Although the reactive additive used chiefly in this study was hydrazine, the results would be applicable to other additives.

Liquid phase mass transfer resistance plays an important role in the absorption of relatively insoluble substances such as methyl iodide unless the liquid phase reaction rates are very rapid. For the potential spray additives hydrazine and sodium thiosulfate, the reaction rates with methyl-

* This paper is based on work performed under US Atomic Energy Commission Contract No. AT(45-1)-1890.
iodide, though rapid in comparison with rates for many organic chemical reactions, are slow enough so that virtually all of the resistance to absorption resides in the liquid phase.

The object of this paper is to describe the absorption processes which would be expected to control the washout of organic iodides by reactive sprays in a reactor containment vessel. Results of experiments carried out in small engineering scale spray chambers will be presented as data for comparison with the predicted washout rates.

**ABSORPTION OF A GAS BY A REACTIVE LIQUID**

In absorption solute gas diffuses from the bulk of the gas to the surface of the liquid. The rate of this transport is governed by the magnitudes of the concentration gradient and of the diffusional processes (laminar and turbulent) which transport the diffusing substance down the concentration gradient. At the gas-liquid interface the gas dissolves in the liquid. For the dilute solutions and low mass transfer rates of interest here, the interfacial compositions would be expected to obey Henry's law:

$$c_s = H c_{gi}$$

where

- $c_s$ = concentration of absorbed component in liquid at interface,
- $H$ = Henry's law constant (partition coefficient),
- $c_{gi}$ = concentration of solute gas on the gas side of the interface.

The gas dissolved in the liquid will be transported away from the interface by diffusional processes. If a chemical reaction occurs within the liquid, the absorbed substance will be destroyed in the liquid at a rate depending on its concentration and the rate of reaction. If the chemical reaction were sufficiently rapid, diffusional resistance in the liquid phase would be small, and the absorption rate would be governed by diffusional processes in the gas phase.

**ABSORPTION PROCESSES IN A SPRAY CHAMBER**

Absorption in a spray chamber occurs at all gas-liquid interfaces. The overall absorption rate would be the integral of the absorption rates per unit interfacial area for all the wetted surfaces. A schematic representation of the flow paths in a spray chamber is shown in Figure 1. Liquid enters the chamber through a spray nozzle where it is broken into drops moving initially at high velocity. A fraction of the incoming spray drops impinge against the chamber wall and other surfaces. At the bottom of the chamber, liquid is collected for disposal or recycle.

The airborne concentration of a solute gas can be related to the flow parameters by making a material balance on the solute gas in the chamber. For the spray chamber depicted in Figure 1, the resulting material balance equation is

$$L c_{li} + G = c_g (L_W A + L_D B) + \frac{d}{dt} (V c_g)$$

(2)
in which

- \( L \) = total liquid flow rate
- \( C_{li} \) = concentration of solute gas in liquid entering chamber
- \( G \) = generation rate of solute gas within chamber
- \( C_g \) = gas phase concentration of solute
- \( L_w \) = liquid flow rate along wall surfaces
- \( L_d \) = drop flow rate
- \( A \) = solute absorbed per unit volume of wall liquid per unit gas phase concentration
- \( B \) = solute absorbed per unit volume of drop liquid per unit gas phase concentration
- \( t \) = time from spray initiation
- \( V \) = volume of spray chamber.

Equation (2) relates the gas phase concentration to time and the wash-out parameters for the specific system considered. The form of the time solution to equation (2) depends on the values of \( C_{li} \), the inlet concentration, and \( G \), the rate of generation of the solute species.

For spray systems of greatest practical interest, the inlet concentration, \( C_{li} \) would be virtually zero. Unreacted solute would be present only for very slow reaction rates for which no appreciable enhancement of absorption would be achieved.

The generation rate of the solute gas, \( G \), in a reactor system would likely vary with time. Also, the absorption coefficients, \( A \) and \( B \), are temperature sensitive, and hence would vary during the spraying period. For long time periods in which significant changes in \( G \), \( A \), and \( B \) would occur, the time variation of these quantities would have to be accounted for in solving equation (2).
For the special case in which it is assumed that only $C_g$ changes with time, the solution to equation (2) is

$$C_g = \frac{G}{L_{WA} + L_{P}B} + \left( \frac{G}{L_{WA} + L_{P}B} + C_{go} \right) \exp \left( \frac{(L_{WA} + L_{P}B) t}{v} \right)$$

where $C_{go}$ is the gas phase concentration at the beginning of the spray period. As a further simplification, if the generation rate is neglected, the washout becomes exponential with the washout half-time equal to

$$t_{1/2} \text{ (washout)} = \frac{0.693 \cdot v}{L_{WA} + L_{P}B}$$

The absorption coefficients $A$ and $B$ are controlling parameters, and it has been a goal of this work to evaluate the numerical dependency of $A$ and $B$ on the basic physical and chemical parameters of the spray system.

**ABSORPTION BY FALLING DROPS**

The absorption coefficient $B$ represents the total absorption by drops per unit volume per unit gas phase concentration. In this section we briefly consider the theoretical aspects of absorption with simultaneous chemical reaction into falling drops.

Liquid drops formed by spray nozzles result from the collapse of films or jets. The drops oscillate for a time until viscous damping absorbs the energy of oscillation associated with the collapse of a filament or a sheet into drops. Thus initially at least, absorption will take place into the surface of a drop agitated by oscillation and aerodynamic drag.

A solely theoretical treatment of absorption by liquid as it is being formed into spray is not possible because of flow-complexities. For large spray chambers or for small drops, the distance traveled by a drop in coming to terminal velocity is small compared to the total fall distance. Thus for a major fraction of the exposure time, the drop will fall with respect to the air with a velocity close to the terminal settling velocity.

The drop exposure time may be most simply estimated as equal to the fall height divided by the settling velocity. This would be expected to be a reasonable approximation for many practical systems.

At the surface of a drop, the diffusion flux must be the same in the gas and the liquid phases:

$$D_{L} \frac{\partial C}{\partial N} = k_g (C_g - C_{gi})$$

where

- $D_{L}$ = liquid phase diffusivity
- $\frac{\partial C}{\partial N}$ = concentration gradient in liquid at drop surface
- $k_g$ = gas phase mass transfer coefficient
The interfacial concentrations are related according to equation (1). Using equation (1) in equation (5), the boundary conditions may be written as

$$\frac{3C}{3N} = h (C^* - C_g)$$

where

$$C^* = \frac{H C_g}{h}$$

$$h = \frac{k_g}{D_{lg}}$$

If local variations in $k_g$ are neglected, the boundary condition, equation (6), applies for the whole surface of the drop. The drop differential equation for absorption with chemical reaction, accounting for surface resistance of the form shown in equation (6) has been solved by Dankwerts. His expression for the total amount absorbed, $Q$, by a stagnant drop in time, $t$, is

$$Q = \frac{8\pi a^2 D_g a^2}{3} \sum_{n=1}^{\infty} \frac{k_t(k + D_g a_n^2) - D_g a_n^2(\exp[-t(k + D_g a_n^2)] - 1)}{(k + D_g a_n^2)^2[a_n^2 + h(ah - 1)]}$$

where

- $k = \text{first order reaction rate constant}$
- $a_n = \text{nth root of } a_n \cot(a_n) + ah - 1 = 0$
- $a = \text{radius of drop}$.

The absorption coefficient, $B$, of equation (3) may be expressed as

$$B = \frac{Q}{C_g \frac{t}{3} a^3}$$

with $Q$ being evaluated from equation (7). Equation (7) describes absorption by stagnant drops, accounting for mass transfer resistance in both the gas and liquid phases. For many situations, one of the phase resistances is negligible, allowing more simple expressions for $Q$ than represented by equation (7).

For highly soluble gases or where chemical reactions are extremely rapid, liquid phase transfer resistance would be negligible. The total amount of solute absorbed by a drop in time, $t_e$, would be

$$Q_{\text{gas film}} = 4\pi a^2 k_g t_e C_g$$

and the absorption parameter for drops, $B$, would be

$$B_{\text{gas film}} = \frac{3 k_g t_e}{a}$$

Calculations of washout based on equation (9) have been discussed by others. [2][3]
Absorption of slightly soluble substances such as methyl iodide is controlled by liquid phase resistance unless the reaction rates are extremely rapid. For no gas phase resistance, equation (7) may be simplified by taking the limit as \( n \) becomes very large. The resulting equation is:

\[
Q = \frac{8\pi a D C^*}{\sum_{n=1}^{\infty} \frac{a^2}{ka^2 + Dn^2w^2}} \left( \frac{x}{k + \frac{Dn^2w^2}{a^2}} \right)
\]

We have evaluated equation (11) for a range of reaction velocities, drop sizes, fall heights (exposure times), and temperatures. Selected values of the calculated data are shown in Figures 2 and 3. In Figure 2, the amount absorbed per drop per unit surface concentration, \( Q/C^* \), is shown as a function of drop diameter for reaction velocities of 0.01 to 100 sec\(^{-1}\). Also shown on this figure are values of \( Q/C^* \) for no diffusional transfer resistance in either phase. This is a limiting situation in which the whole drop is assumed to contain the equilibrium solute concentration for the entire exposure time. The absorption up to time \( t_e \) would be

\[
Q_{\text{max}} = \frac{h}{3} \pi a^3 (k t_e + 1) C^*
\]

Equation (11) reduces to equation (12) for small \( a \) and large \( t \). From Figure 3 it is apparent for drops less than about 500 \( \mu \) and for reaction velocities less than about 1 sec\(^{-1}\), that diffusional mass transfer resistance does not play a major role. Thus oscillation and circulation within these drops would not appreciably affect the rate of absorption because the drops would be well mixed by diffusion alone.

For larger drops of liquid of high reactivity the degree of mixing would be important in determining the overall absorption. A number of studies of drop absorption have been carried out to assess the effect of drop circulation and oscillation on absorption. Examples of these studies are the works of Garner and Lane\(^4\), Kronig and Brink\(^5\), and Calvert and Const\(^6\). Soldano\(^7\) at ORNL has reported methyl iodide absorption by suspended drops 4.2 mm in diameter. Unfortunately the data available do not permit satisfactory estimation of drop mixing for reactive drops smaller than 2000 \( \mu \) in diameter, which are of prime interest here. A conservative estimate of the absorption may be obtained by considering the drop to be stagnant.

In Figure 3, the effect of reaction velocity on absorption is shown for drops exposed for times equivalent to fall distance of 100 ft. For 1000 \( \mu \) diameter drops the absorption is not appreciably enhanced for reaction rates lower than about 0.1 sec\(^{-1}\). For smaller drops, slower reaction rates give enhancement over physical absorption because of greater contact times. For drops larger than 1000 \( \mu \), the stagnant drop model shows that the reaction rate for appreciable enhancement of absorption is greater than 0.1 sec\(^{-1}\).

From this brief discussion of drop absorption we have concluded that conservative calculation of drop absorption can be achieved using a stagnant drop model. It should be noted that absorption with chemical reaction into drops under conditions where liquid resistance plays a major
FIG. 2. Drop absorption with first order chemical reaction.

FIG. 3. Effect of reaction velocity on absorption by stagnant drops.
role has not been explored sufficiently from an experimental viewpoint. Additional experimental studies are needed.

**ABSORPTION BY LIQUID FILM ON WALL**

For many spray chambers an appreciable amount of liquid sprayed from the nozzle impinges against the wall. The surface area exposed by the wall of a chamber is significant compared to falling drops. For a cylindrical chamber three meters in height, with a height to diameter ratio of two, the wall surface area is calculated to be 3.2 times larger than the surface area for 1000 μ diameter drops, at a spray density of 0.0067 cm³/sec cm² (0.1 gpm/ft²). For a 100 ft. tall chamber, other factors remaining the same, the wall area is only 32% of that calculated for the drops.

The following brief treatment of wall film absorption is an attempt to arrive at predictive equations expected to give conservative results. Indeed a complete treatment of absorption with chemical reaction is not yet available.

The flow characteristics and absorption by liquid flowing down a wall has been extensively studied during the last 25 years. Many of the studies carried out prior to 1964 have been summarized by Fulford. Based on the theoretical and experimental studies, the general characteristics of wetted wall flow may be stated as follows. At low flow velocities, laminar flow persists, the velocity profile is parabolic, and the free surface velocity is 3/2 the average velocity. At Reynolds numbers in the range of 5 - 25, waves begin to appear on the surface, though the flow is still substantially laminar. At Reynolds numbers of 250 - 500 the flow becomes turbulent.

For the laminar flow regime, absorption with a first order chemical reaction is described by

\[
\nu_{\text{max}} [1 - \left( \frac{x}{\delta} \right)^2] \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial x^2} - kC
\]

where

\[
\nu_{\text{max}} = \text{velocity at surface of film}
\]
\[
x = \text{distance from surface of film}
\]
\[
\delta = \text{thickness of film}
\]
\[
z = \text{distance measured along film}
\]
\[
D = \text{liquid phase diffusivity}
\]
\[
C = \text{concentration of dissolved solute}
\]
\[
k = \text{first order rate constant.}
\]

Equation (13) has not been solved for the general case, but several solutions applicable to special situations have been presented.

For short laminar films, the solute does not have time to penetrate far into the film, and hence the absorption takes place as though the film were infinite in thickness. The differential equation for such films may be obtained from equation (13) by setting \( x = 0 \). This is the penetration theory approximation, and the mathematical solution is given by Dankwerts. Most experimental data obtained with short wetted wall columns, for laminar flow, agree reasonably well with the penetration theory solution.
Calculations based on laminar flow theory indicate that the penetration theory would not be applicable because the solute would diffuse all the way through the film. A lower limit to the absorption in thin films can be calculated by considering the steady state solution to equation (13). Solution of equation (13) for \( \frac{\partial C}{\partial z} = 0 \) gives

\[
\frac{dQ}{dt} = C^{*}(\sqrt{k}D)_{\text{tank}} \frac{1}{\sqrt{k}/D_{\delta}} \quad (14)
\]

where \( \frac{dQ}{dt} \) = absorption rate per unit area.

The film thickness, \( \delta \), used in equation (14) may be estimated from laminar flow theory and experimental measurements of the wall flow rate.

Non-idealities in an actual film, such as turbulence and wave effects, would increase the washout over that predicted by equation (14). Based on equation (14), the washout parameter of equation (2) would be

\[
A = \frac{H(\sqrt{k}D)_{\text{tank}}}{\frac{L_{W}}{A_{W}}} \quad (15)
\]

where \( A_{W} \) = wetted wall area.

**EXPERIMENTAL MEASUREMENTS OF METHYL IODIDE ABSORPTION IN SPRAY CHAMBERS**

The purpose of the spray washout experiments was to demonstrate on a small engineering scale the effectiveness of methyl iodide washout by sprays of aqueous hydrazine solution. Most of the experiments were carried out in a cylindrical chamber 4 feet in diameter by 10 feet in height, made from 304 L stainless steel: This vessel was limited to atmospheric pressure, and hence all of the tests performed in this vessel were at temperatures less than 100°C. Spray washout at temperatures to 123°C was carried out in a pressure vessel 3 feet in diameter by 8 feet in height. This vessel was painted to prevent corrosion.

The experiments performed may be divided into three sets. In the first set of experiments the spray liquid was recirculated continuously, and the quantity of methyl iodide remaining airborne was determined as a function of time. These experiments were performed in the 4 foot diameter stainless steel vessel, at temperatures initially close to 100°C. No heat was added during the spray period, hence the temperature decreased with time. The second set of runs consisted of three spray tests carried out at temperatures near 120°C. In two of these runs, once-through spray periods were employed in which wall film liquid and liquid collected in the bottom of the chamber were separately analyzed to permit assessment of wall absorption. The third set of experiments was designed to more precisely measure wall and drop absorption and a drop collector for evaluating drop absorption was used. These latter experiments were carried out in the 4 foot diameter stainless steel vessel, at temperatures near 90°C. All of the experimental runs were conducted using methyl iodide labelled with \(^{131}\)I. Initial airborne methyl iodide concentrations were between 0.1 and 10 milligrams per cubic meter. The results of these experiments will now be briefly discussed.
### TABLE I

RESULTS OF RECIRCULATING SPRAY WASHOUT OF METHYL IODIDE BY AQUEOUS HYDRAZINE SPRAYS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Drop Size (microns)</th>
<th>Liquid Flow Rate (cm³/sec)</th>
<th>Percent Of Liquid Flowing On Wall</th>
<th>Initial Gas Temp. (°C)</th>
<th>Initial Hydrazine Concent. (wt.%)</th>
<th>Duration Of Run (min)</th>
<th>Initial Washout Half-time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>280</td>
<td>56.8</td>
<td>52%</td>
<td>95°C</td>
<td>4.3 wt.%</td>
<td>62 min</td>
<td>82 min</td>
</tr>
<tr>
<td>9</td>
<td>280</td>
<td>56.8</td>
<td>52%</td>
<td>95°C</td>
<td>4.3 wt.%</td>
<td>327 min</td>
<td>82 min</td>
</tr>
<tr>
<td>10</td>
<td>260</td>
<td>33.3</td>
<td>36%</td>
<td>93°C</td>
<td>4.3 wt.%</td>
<td>354 min</td>
<td>125 min</td>
</tr>
<tr>
<td>11</td>
<td>280</td>
<td>56.8</td>
<td>52%</td>
<td>95°C</td>
<td>16 wt.%</td>
<td>350 min</td>
<td>22 min</td>
</tr>
<tr>
<td>12</td>
<td>280</td>
<td>58.0</td>
<td>52%</td>
<td>95°C</td>
<td>17 wt.%</td>
<td>291</td>
<td>21 min</td>
</tr>
</tbody>
</table>
Recirculating Spray Runs in a Stainless Steel Spray Chamber

The goal of these runs was to demonstrate the spray washout of methyl iodide for a system simulating a post-accident containment vessel. Initial temperatures of the spray chamber were near 100°C, and the spray solution was at near room temperature (20°C) initially. The temperature within the chamber decreased with time, simulating behavior anticipated following a postulated reactor accident.

Drop size distributions for all of the nozzle combinations used were measured near the bottom of the chamber. The drops were collected at an oil-kerosene interface after falling through a thin layer of kerosene. The drop sizing was carried out at room temperature, under the nozzle pressure employed in the run. This nozzle pressure was 100 psi in nearly all of the runs.

Liquid flow along the wall was measured by means of a collector ring installed near the bottom of the tank. Wall liquid and liquid collected in the bottom of the tank were mixed in the pipe leading to the liquid reservoir.

The detailed description of the experimental apparatus is given in an earlier report. Methyl iodide traced with $^{131}$I was injected into the tank and allowed to mix before the spray was initiated. Airborne concentrations in these runs were calculated from a material balance, based on liquid samples collected at time intervals throughout the run, and the small residual of methyl iodide remaining airborne at the end of the run.

Ammonium hydroxide (0.75 mols/liter) was used in all of the solutions to provide excess base to react with carbon dioxide initially in the air.

The results of five of the recirculating spray runs are tabulated in Table I. In run 12, boric acid neutralized with ammonium hydroxide was added to demonstrate that the washout rate would not be adversely affected by the presence of borate ion.

The results of the recirculating spray runs listed in Table I show that the washout rate is proportional to the hydrazine concentration and the liquid flow rate. As expected, the washout rate is much slower than the rate predicted for a gas-phase limited process.

Higher Temperature Spray Washout

These runs, three in number, were carried out in a pressure vessel 3 feet in diameter by 8 feet in height. The atmosphere was saturated with respect to one atmosphere of air at 20°C.

In two of these runs, a once through spray period was employed to allow assessment of absorption by the wall film. A wall trough was provided to permit collection of liquid flowing down the wall, and this was analyzed for comparison with liquid falling as drops which accumulated in the bottom of the tank.

The gas phase activity was measured as a function of time using a sampling train consisting of a membrane filter, silver screens, silver membrane filter, activated charcoal filter paper, and activated charcoal beds arranged in series. The methyl iodide was largely collected within the charcoal beds.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Temp. (°C)</th>
<th>Spray Liquid Flow Rate (cm³/sec)</th>
<th>Reactive Spray Solution Composition</th>
<th>Fraction Of Spray Flowing Down Wall</th>
<th>Overall Washout Half-Time (min)</th>
<th>Fractional Absorption Due to Wall Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-1</td>
<td>120</td>
<td>36.6</td>
<td>10 wt.% N₂H₄, 0.06 N NH₄OH, 3000 ppm H₃BO₃</td>
<td>0.28</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>HT-2</td>
<td>120</td>
<td>60.7</td>
<td>6.5 wt.% N₂H₄, 0.06 N NH₄OH, 3000 ppm H₃BO₃</td>
<td>0.28</td>
<td>9</td>
<td>0.58</td>
</tr>
<tr>
<td>HT-3</td>
<td>123</td>
<td>37.8</td>
<td>10 wt.% N₂H₄, 0.05 N NaOH, 3000 ppm H₃BO₃</td>
<td>0.28</td>
<td>7</td>
<td>0.39</td>
</tr>
</tbody>
</table>
The results of the three runs at higher temperature are briefly tabulated in Table II.

Steam was added at a rate high enough to balance the heat loss throughout the runs. Thus the temperature of the system was more nearly constant than in the recirculating runs at atmospheric pressure. In one of these runs the spray solution was heated to the tank temperature, and in the other two runs, the spray liquid was introduced at room temperature.

The drop size was measured for the same nozzles operating at room temperature and one atmosphere of pressure. For 100 psi pressure drop across the nozzles, the drop size measured 8 feet below the nozzle was 340 microns mass median diameter. For a single nozzle of the same type, the drop size was measured to be 140 microns, indicating that for the 9 nozzle spray header, drop coalescence was significant.

From the results listed in Table II, it may be noted that washout half-times of about 8 minutes were realized.

The wall liquid was found to be more effective, on a volume basis, than the falling drops. This is shown in the last column where the ratio of wall liquid activity to bottom liquid activity is shown. The bottom liquid activity includes absorption into the pool, and hence drop activity would be less than indicated by this measurement.

**DROP AND WALL FILM ABSORPTION EXPERIMENTS IN STAINLESS STEEL CHAMBER**

The goal of these experiments was to provide direct experimental measurements of the washout parameters $A$ and $B$ for wall films and falling drops respectively. In each experiment, the wall film flow was collected separately from the drops falling into the bottom of the chamber. Two drop catchers were placed near the bottom of the chamber to collect liquid falling in the form of drops with immediate removal from the chamber atmosphere. These drop catchers were designed to prevent absorption by drop liquid subsequent to impact against the collecting surface. Methyl iodide-free air was continually purged through the flask to prevent airborne methyl iodide from reaching the liquid surface. Ten cc of 10% sodium thiosulfate solution was added to the flask to react rapidly with methyl iodide carried within drops into the catcher in an unreacted form. Drops impacting against the inlet chimney were not collected, but instead drained away at the outside of the flask. Only those drops falling nearly vertically entered the flask. Gas phase concentrations of methyl iodide were measured using beds of activated charcoal operated in series.

The results of these few runs are shown in Table III. The drop absorption coefficient, $B$, shown in Table III is the average of the values obtained for the two catchers used in each experiment.

As noted before, the drop size shown was measured from drops collected near the bottom of the 10 foot tall chamber. Thus, the mass median diameter measured at this position would probably represent drops larger than the average in the chamber, since coalescence would cause an increase in size with increasing distance from the nozzles.

The temperature within the chamber decreased several degrees centigrade over the 7 minute spray period. The spray solution was heated to the tank temperature before each test to reduce temperature variations.
TABLE III
RESULTS OF WALL FILM AND DROP ABSORPTION EXPERIMENTS
IN ONCE-THROUGH SPRAY RUNS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Average Temp. (°C)</th>
<th>Solution Composition</th>
<th>Wall Flow Rate (cm(^3)/sec)</th>
<th>Drop Flow Rate (cm(^3)/sec)</th>
<th>Wall Film Absorption Coefficient</th>
<th>Drop Absorption Coefficient</th>
<th>Mass Median Drop Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>89</td>
<td>2.15 wt.% N(_2)H(_4)</td>
<td>0.138</td>
<td>47.8</td>
<td>6.27</td>
<td>1.06</td>
<td>320 µ</td>
</tr>
<tr>
<td>14</td>
<td>88</td>
<td>1.0 wt.% Na S(_2)O(_3)</td>
<td>0.125</td>
<td>42.4</td>
<td>4.78</td>
<td>1.45</td>
<td>320 µ</td>
</tr>
<tr>
<td>15</td>
<td>86</td>
<td>4.38 wt.% N(_2)H(_4)</td>
<td>0.143</td>
<td>52.4</td>
<td>8.55</td>
<td>1.95</td>
<td>320 µ</td>
</tr>
<tr>
<td>17</td>
<td>87</td>
<td>1 wt.% Na(_2)S(_2)O(_3)</td>
<td>0.151</td>
<td>55.2</td>
<td>4.4</td>
<td>1.23</td>
<td>320 µ</td>
</tr>
</tbody>
</table>
Unfortunately, these runs are few in number, and hence do not permit evaluation over ranges of temperature, flow rates, and drop sizes. They do demonstrate that wall film absorption, on a unit volume basis, may be considerably larger than absorption by the falling drops.

COMPARISON OF EXPERIMENTAL MEASUREMENTS WITH THEORY

The experimental measurements have been compared with absorption theory briefly discussed in this paper. The basic physical data necessary to carry out the numerical predictions based on theory, were taken from literature values, from general correlations, and from measurements performed as part of this study.

The partition coefficient for methyl iodide in water, for the low concentration ranges of interest here, has been measured as part of this study. Unfortunately the measurements do not extend to temperatures above 65°C, hence extrapolation to the temperatures used in the spray experiments was required. Extrapolation was on the basis of the equation

\[
\ln H = -11.13 + \frac{3680}{T}
\]  

(16)

in which

\[
\ln H = \text{natural logarithm of partition coefficient}
\]

\[
T = \text{absolute temperature, °K.}
\]

The line represented by equation (16) is a best fit of the data obtained over the measured range of 4.8°C to 65°C. Extrapolation of these measurements to higher temperature according to equation (16) is justified only because no alternative exists.

The liquid phase reaction rates between methyl iodide and hydrazine and sodium thiosulfate have been measured. For hydrazine, the second order rate constant at 25°C is \(1.1 \times 10^{-3} \text{ sec}^{-1} \cdot \text{M}^{-1}\) with an activation energy of 20.2 KCal/mole. For sodium thiosulfate, the second order rate constant at 25°C was taken as \(2.84 \times 10^{-2} \text{ sec}^{-1} \cdot \text{M}^{-1}\), and the activation energy was taken as 18.88 KCal/Mole. The pseudo first order reaction rate at the temperature of interest was calculated by multiplying the second order rate constant by the reactant concentration, moles/liter. The temperature correction was based on the standard Arrhenius equation,

\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \frac{T_2 - T_1}{T_1 T_2}
\]

(17)

where

\[
k_2 = \text{rate at temperature } T_2
\]

\[
k_1 = \text{rate at temperature } T_1
\]

\[
E_a = \text{activation energy}
\]

\[
R = \text{gas constant.}
\]

The liquid phase diffusivity of methyl iodide in water was calculated from a correlation presented by Wilke and Chang.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>A Wall Film Absorption Coefficient</th>
<th>B Falling Drop Absorption Coefficient</th>
<th>Calculated Drop Abs. Wall Film Abs.</th>
<th>Predicted Washout Half-Time (min)</th>
<th>Measured Washout Half-Time (min)</th>
<th>Theoretical Half-Time Measured Half-Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>4.97</td>
<td>0.76</td>
<td>0.15</td>
<td>295</td>
<td>82</td>
<td>3.6</td>
</tr>
<tr>
<td>9</td>
<td>4.68</td>
<td>0.72</td>
<td>0.15</td>
<td>313</td>
<td>82</td>
<td>3.8</td>
</tr>
<tr>
<td>10</td>
<td>9.26</td>
<td>0.92</td>
<td>0.18</td>
<td>379</td>
<td>125</td>
<td>3.0</td>
</tr>
<tr>
<td>11</td>
<td>13.60</td>
<td>1.37</td>
<td>0.09</td>
<td>113</td>
<td>22</td>
<td>5.1</td>
</tr>
<tr>
<td>12</td>
<td>12.93</td>
<td>1.38</td>
<td>0.10</td>
<td>115</td>
<td>21</td>
<td>5.5</td>
</tr>
<tr>
<td>HT-1</td>
<td>42.8</td>
<td>1.21</td>
<td>0.07</td>
<td>37.7</td>
<td>8</td>
<td>4.7</td>
</tr>
<tr>
<td>HT-2</td>
<td>20.5</td>
<td>0.90</td>
<td>0.11</td>
<td>45.9</td>
<td>9</td>
<td>5.1</td>
</tr>
<tr>
<td>HT-3</td>
<td>46.5</td>
<td>1.33</td>
<td>0.07</td>
<td>33.7</td>
<td>7</td>
<td>4.8</td>
</tr>
</tbody>
</table>
### TABLE V
COMPARISON OF ONCE-THROUGH RUNS WITH THEORY

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>2.15 wt.% N₂H₄</td>
<td>2.57</td>
<td>0.580</td>
<td>2.44</td>
<td>1.84</td>
<td>0.20</td>
<td>0.15</td>
</tr>
<tr>
<td>14</td>
<td>1.0 wt.% Na₂S₂O₃</td>
<td>3.39</td>
<td>0.61</td>
<td>1.41</td>
<td>2.38</td>
<td>0.16</td>
<td>0.27</td>
</tr>
<tr>
<td>17</td>
<td>4.38 wt.% N₂H₄</td>
<td>3.37</td>
<td>0.73</td>
<td>2.54</td>
<td>2.67</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>1.0 wt.% Na₂S₂O₃</td>
<td>2.39</td>
<td>0.67</td>
<td>1.52</td>
<td>1.83</td>
<td>0.22</td>
<td>0.27</td>
</tr>
</tbody>
</table>
The fluid dynamics of the flowing wall film were calculated from laminar flow theory, neglecting shear at the gas-liquid interface. For these assumptions, the liquid velocity at the gas-liquid interface is

\[ U_s = \left[ \frac{g \gamma^2 \rho}{\rho_v} \right]^{1/3} \]  

(18)

where

- \( U_s \) = downward velocity at interface
- \( \Gamma \) = flow per length of surface
- \( g \) = acceleration due to gravity
- \( \nu \) = kinematic viscosity of liquid.

The thickness of the liquid layer predicted by the laminar flow theory is

\[ \delta' = \frac{\Gamma}{2U_s} \]  

(19)

where \( \delta' \) = thickness of the liquid film.

For the recycle experiments and the high temperature experiments, the results of which are shown in Tables I and II, only the overall washout half-time was compared to theory. In the theoretical calculation, the contribution of wall film and drop absorption must be each evaluated, and this is shown in Table IV where the experimental results are compared with the theory.

Absorption at the top and bottom of the spray chambers was accounted for theoretically by assuming that the overall absorption per unit area for the top and bottom was the same as at the wall. This represents a correction of about 20% for the chambers used in this study.

From the comparison shown in Table IV, it is evident that the washout is considerably more rapid than predicted by the stagnant film theory. The stagnant film theory gives results quite close to those predicted by the penetration theory for a laminar film. If one assumes that the wall film is well mixed, the predicted washout rate is increased by about a factor of 2 over that shown in Table IV for the stagnant film. The observed rate is still a factor of 2 greater than for the well mixed film.

The results obtained in the once through spray in which drop catchers were employed are compared in Table V to the predictions based on stagnant film and drop theory. It should be noted that the predicted wall film absorption coefficients have not been corrected to account for absorption at the top and bottom of the chamber. For the once through runs, the measured washout rates are 1.5 - 3 times faster than predicted from the stagnant film theory. This ratio of measured to theoretical is somewhat lower than found in the recycle experiments. Absorption into the pool at the bottom of the chamber was not included in these experiments, whereas in the recycle experiments, the bottom pool was a factor. Based on this, absorption into the bottom pool would be considered more effective per unit area than wall film absorption. This was also implied from measurements in which bottom liquid absorption was compared to wall liquid absorption. Contact time and agitation in the bottom pool would likely be greater than for the wall film, which would enhance the absorption.
In comparing the measured washout rates with theory, the dominant feature is that the measured rates are 2 - 5 times faster than the predicted. Part of this discrepancy is no doubt due to the assumptions used in the theory, which were chosen to give conservative predictions of washout rate. For the falling film, it was assumed that ideal laminar flow persisted. Waves, rivulets, mixing at surface irregularities, and turbulence would enhance wall film absorption over that predicted by the theory. For the falling drops, the drop size was measured at the bottom of the spray chambers, hence the measured size is a maximum. The volume average over the whole chamber would be smaller, and this would account for part of the observed enhancement of absorption compared to that predicted theoretically.

The accuracy of the input data to the theory is open to question because it was necessary to extrapolate measurements at lower temperatures, or to predict values from correlations. Measurements of solubility and reaction rate for methyl iodide at higher temperatures are badly needed so that better interpretation of experiments and predictions may be attained.

**PREDICTED METHYL IODIDE WASHOUT IN LARGE CHAMBERS**

Reactor containment vessels are much larger than those used in the experiments reported here. Hence application of the small scale tests to large scale systems of practical interest must be based on knowledge of the scale factors which apply. We have attempted to show the effect of spray chamber size on methyl iodide washout rate by calculating the washout rate expected for cylindrical chambers from laminar flow theory described earlier.

In Figure 4, the washout rate of methyl iodide in spray chambers is shown as a function of chamber size. The spray density was assumed to be 0.0068 cm³/cm²sec, drop diameter was taken as 550 microns, and the wall flow rate was chosen as 0.1 cm³/cm sec. The first order rate constant was chosen as 5.55 sec⁻¹, the value predicted for 5 wt.% hydrazine solution at 120°C.

The increase in washout half-time with increasing chamber size is a reflection of the importance of wall absorption, which is predicted to account for over 50% of the total even for a cylinder 100 ft. in height. The curve shown is not highly sensitive to changes in the assumed conditions. For larger drops, the wall would be relatively more important, and the curve shown in Figure 4 would be steeper. For smaller drops or higher reaction rates, the curve would tend to level out, vessel size being of less importance.

Based on this calculation we would expect a washout half-time of about 60 minutes for a vessel 80 feet in height for 5 wt.% hydrazine, for the nominal spray conditions specified in Figure 4.

**CONCLUSIONS**

The absorption of methyl iodide by sprays of aqueous solutions of hydrazine and sodium thiosulfate is controlled by liquid phase mass transfer resistance. Hence its removal rates are much slower than that of elemental iodine which would be controlled by gas film resistance. For
reactive solutions such as 5 wt.% hydrazine and 1 wt.% sodium thiosulfate, absorption by liquid flowing along the wall is important even for large vessels. Measured rates of absorption are 2 - 5 times more rapid than calculated from a model based on a laminar wall film and stagnant drops falling at terminal velocity. Based on the absorption model developed, the washout half-time would be expected to increase with chamber size, for reaction rates studied here. From measured absorption rates in cylindrical vessels 8 and 10 ft. tall, the washout half time in a cylindrical vessel 80 ft. in height and 32 ft. in diameter would be expected to be about 1 hour for 5 wt.% hydrazine solution, at a temperature of 120°C.

![Graph showing predicted effect of vessel size on washout rate for methyl iodide.](image)

FIG. 4. Predicted effect of vessel size on washout rate for methyl iodide.

LITERATURE CITED


DISCUSSION

J.M. GENCO: Was your vessel painted and what fraction of the iodine was picked up by the walls?

L.C. SCHWENDIMAN: The vessel was of unpainted stainless steel. Wall washing accounted for 40-60% of the iodine in the small tank and for ~50% in the larger tank.

J.M. GENCO: Could you have obtained better wall effects by using droplet condensation phenomena?

L.C. SCHWENDIMAN: Droplet condensation may be more realistic, but I believe that all surfaces will have a film of water. The nature of wall flow would have to be investigated, after which we might be able to develop a more realistic model.

P.J. LINDER: What was the concentration of methyl iodide in the air and did it correspond to MCA conditions?

L.C. SCHWENDIMAN: The methyl iodide concentration dropped as low as 0.1 mg/m³, but generally it was 10 mg/m³. It is estimated that in an MCA, the total iodine released to the containment would range from 50 to 100 mg/m³. The 10 mg/m³ of methyl iodide represents about 10% of the total iodine concentration expected.

R.E. HOLMES: In post-accident conditions, I would expect the radiation dose rate and therefore the rate of radiolytic decomposition of hydrazine to be significant. Has any assessment been made of the consequences of dose rate for use within reactor containments?
L.C. SCHWENDIMAN: Yes, some studies of radiolytic decomposition have been made at ORNL and elsewhere. You may find some data in BNWL 530. Hydrazine is decomposed to hydrogen and nitrogen. Under some conditions, ammonia may be formed also. The radiation sensitivity is likely to preclude the use of hydrazine in reactor sprays.

G. BURLEY: How did you measure the drop size and distribution spectrum and where, along the trajectory, was measurement made?

L.C. SCHWENDIMAN: The drop-size measurements are described in BNWL 530. The drops were passed through a slit which was momentarily held over a shallow dish containing a layer of silicone oil and a layer of kerosene — kerosene to cushion the fall and silicone oil to minimize coalescence. Microscopic sizing was carried out in the oil and the droplets were collected near the bottom of the chamber.

D.A. NITTI: Information in the literature indicates that drops with diameters somewhere between 500 and 1000 microns will shatter or break up when entering a solvent-collecting medium. Thus, your measured median drop size is surely smaller than the actual mean drop size. This may help to explain some of the difference between your calculated and measured values for methyl iodide removal.

L.C. SCHWENDIMAN: If droplets are truly less than 500 microns, their break-up upon entering a light medium like kerosene is probably unimportant. Since all sprays used gave droplets with MMD less than 300 microns, it is quite possible that the droplets were of this size. I agree that any break-up of droplets during size measurement would make experimental spray removal results appear to be more in agreement with larger drop-size predictions than with the apparent drop-size washout predictions.
A STUDY OF CONTAINMENT SPRAYS AND CHARCOAL FILTERS FOR THE REMOVAL OF IODINE FOLLOWING A PWR LOSS OF COOLANT ACCIDENT

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Abstract

A STUDY OF CONTAINMENT SPRAYS AND CHARCOAL FILTERS FOR THE REMOVAL OF IODINE FOLLOWING A PWR LOSS OF COOLANT ACCIDENT. This paper summarizes a study of the radioiodine problem associated with the siting of the current generation of nuclear power stations in the United States, and compares the effectiveness of containment spray systems and charcoal filter systems for the removal of the radioiodine following a PWR loss of coolant accident. The study showed that, based on the present reactor siting criteria in the United States, the ultimate iodine removal system must provide an iodine dose reduction factor (DRF) of 13 in the first two hours and then eventually achieve a DRF of 50. This means that about 2% of the iodine need never be removed from the containment atmosphere if the other 98% is removed sufficiently fast.

The performance of iodine removal systems is shown as a function of operating time and design capacity. For removal systems operated in a recirculating mode, the system’s iodine removal efficiency is relatively unimportant when compared with the effect of the presence of a small quantity of a penetrating component. The slow response time of a charcoal filter system limits the maximum dose reduction factor that can be practically obtained in the first two hours to between 5 and 8. However, the fast response of a containment spray system provides the capability of achieving an iodine dose reduction factor of about 50 within the first two hours after an accident. If a small quantity of a penetrating component is present, the charcoal filter system will eventually catch up to the spray system, and both systems will approach the same dose reduction factor.

1. INTRODUCTION

One of the major factors to be considered when evaluating sites for power reactors is the consequences resulting from the leakage of radioactivity to the environs should an accident occur. In the United States all power reactor sites are evaluated based on the siting criteria set forth in the Code of Federal Regulations, 10 CFR 100 [1]. Briefly, these criteria require that:

(a) A reactor site be sized large enough to provide an "exclusion area" of such a size that an individual at the exclusion area boundary for two hours immediately following the postulated fission product release would not receive radiation doses which exceed 25 rem to the whole body or 300 rem to the thyroid from iodine exposure.

(b) A reactor site be located in a "low population zone" of such a size that an individual located on the outer boundary of this zone and exposed to the radioactive cloud for the duration of the accident would not receive radiation doses which exceed 25 rem to the whole body or 300 rem to the thyroid from iodine exposure.
(c) A reactor site's proximity to population centers of about 25,000 or more residents must be at least one and one-third times the distance from the reactor to the outer boundary of the "low population zone."

The conformance of a specific reactor site to the siting criteria is greatly dependent upon the basic assumptions and the calculational procedures; therefore, 10 CFR 100 recommends that the report TID-14844 [2] be used as a guide and "as a point of departure" for evaluating a particular site. Unfortunately, this report does not address itself to the use of engineered safeguard systems for the removal of iodine; therefore, the performance of iodine removal systems must be evaluated by each reactor applicant using an iodine removal system. The lack of standard evaluating procedures often leads to confusion, yet there is surprisingly little written on this subject. This paper summarizes the results of a study on the performance of containment spray systems and charcoal filter systems for removing iodine following a loss of coolant accident in a PWR type power reactor.

2. EVALUATION OF THE IODINE PROBLEM

To evaluate a site's ability to meet the siting criteria, the thyroid dose and the whole body dose must be calculated as a function of distance from the reactor. The iodine dose, $D_T$, was calculated using the method suggested in TID-14844 [2]. The whole body dose from the radioactive cloud or plume was calculated using the method in WASH-740 [3]. Since most modern power reactors of the PWR type are using thick wall, concrete containments, the direct gamma dose is negligible.

The dose equations from references [2] and [3] were modified slightly to include the effectiveness of the iodine removal system of the recirculating (internal) type. The results are shown in equations (1) and (2). Since the meteorological dispersion factor $(\chi/Q)$ is a function of distance, these equations can be used to calculate the thyroid dose and whole body dose as a function of distance and time.

\[
D_T = B \cdot P \cdot F \left( \frac{\chi}{Q} \right) \sum_{i=1}^{1} \left( q \cdot D_e \cdot \frac{\lambda_L}{\lambda_D + \lambda_L + \varepsilon \lambda_R} \right) \left[ 1 - e^{-\left( \lambda_D + \lambda_L + \varepsilon \lambda_R \right) t} \right]
\]

(1)

\[
D_W = 0.261 \cdot P \cdot \left( \frac{\chi}{Q} \right) \sum_{i=1}^{1} \left( q \cdot F_r \cdot E\left( \frac{\lambda_L}{\lambda_D + \lambda_L + \varepsilon \lambda_R} \right) \right) \left[ 1 - e^{-\left( \lambda_D + \lambda_L + \varepsilon \lambda_R \right) t} \right]
\]

(2)

Figures 1 and 2 summarize the results of calculations using these equations. These calculations were based on a fission product source which contained 25 percent of the iodine and 100 percent of the noble gases in the fuel. They also assumed a well mixed containment atmosphere, a containment leak rate of 0.1 percent per day, and a conservative meteorological dispersion factor. These assumptions are consistent with those in TID-14844.

The figures show that for large PWR's without iodine removal systems the thyroid dose controls the site size and location. The figures also show the large reductions in the exclusion area and low population zone sizes which can be obtained by iodine removal systems which yield iodine dose reduction factors (DRF) between 10 and 40.
FIG. 1. Exclusion area size as a function of reactor power and iodine dose reduction factor.

FIG. 2. Low population zone size as a function of reactor power and iodine dose reduction factor.
If the dose reduction factor (DRF), which is the iodine dose obtained without an iodine removal system \( (\lambda_R=0) \) divided by the dose obtained with an iodine removal system, is plotted versus the ratio of \( D_T/D_W \), an interesting result can be observed. As shown in Figure 3, if an iodine removal system can provide a dose reduction factor of 13 in the first two hours, the whole body dose will control the size of the exclusion area, and if it can eventually achieve a DRF of 50, the whole body dose will also control the size of the low population zone and thus the population center distance. It is important to note that these conclusions are independent of the reactor size, the containment leak rate, the site size, and the site meteorology and are only dependent on the assumed fractions of iodine and noble gases released into the containment atmosphere.

3. PERFORMANCE OF IODINE REMOVAL SYSTEMS

It can be shown mathematically that, for iodine removal systems which operate for the complete duration of the accident, an instantaneous puff release results in the highest doses; therefore, all further analyses will be based on a puff release of fission products into a well mixed containment atmosphere.

The iodine removal systems used as emergency safeguards in most of the large PWR's, in essence, exhaust back into the containment atmosphere and are thus of the recirculating (or internal) type. It is important that such systems are not confused with iodine removal systems which exhaust to the environs and are thus of the once-through type. The reason is that, not only is there a basic difference in the operation and performance of
once-through and recirculating type systems, but there is also another basic difference resulting from the ability of certain forms of iodine to penetrate certain types of iodine removal systems.

If a once-through iodine removal system is used to process radioiodine containing a small fraction of a penetrating form, the amount of iodine remaining in the containment atmosphere can be expressed by equation (3), and the amount leaked to the environs can be expressed by equation (4).

\[ I = e^{-\lambda_L t} \]  

\[ \bar{I} = [f + (1-f)(1-e)][1-e^{-\lambda_L t}] \]  

For recirculating type systems, the respective equations are:

\[ I = f e^{-\lambda_L t} + (1-f)e^{-(\lambda_L + \epsilon\lambda_R)t} \]  

\[ \bar{I} = f[1-e^{-\lambda_L t}] + \frac{(1-f)\lambda_L}{(\lambda_L + \epsilon\lambda_R)} [1-e^{-L + \epsilon\lambda_R t}] \]  

Since \( \lambda_L \) is usually small, equation (6) simplifies to:

\[ \bar{I} = f \lambda_L t + \frac{(1-f)\lambda_L}{\epsilon\lambda_R} [1-e^{-\epsilon\lambda_R t}] \]  

Figures 4 and 5 graphically illustrate the basic differences between the two types of system. It can be seen that once-through systems are not
Fig. 5. The effect of system efficiency and penetrating forms on the performance of recirculating type iodine removal systems.

Time dependent but are greatly degraded by losses in efficiency. Although recirculating systems do have an initial time dependence, losses in the system's efficiency have only a minor effect on the overall performance. Thus it is quite clear that definite distinctions must be made between the types of systems and between the system's efficiency and the fraction present in a penetrating form.

Most of the large power reactors presently in the design and construction stages will use iodine removal systems to reduce their site real estate from about 5 square miles (required by TID-14844) to about 0.8 square miles, sometimes considerably less. Usually these systems will be of the recirculating type; therefore, it is desirable to know the system performance or the iodine removal rate constant ($\lambda_R$) required of this type of system to achieve a desired DRF. Figure 6 shows the DRF for the two-hour thyroid dose as a function of the systems iodine removal rate constant ($\lambda_R$) and the fraction of iodine present in a penetrating form ($f$).

3.1. Containment Spray Systems

The rate at which elemental iodine can be removed from the containment atmosphere by a reactive chemical spray can be calculated using Griffiths' method [4] or using Parsly's computerized method [5]. Both calculations are based on the experimental work of Taylor [6], which showed that the rate at which elemental iodine is transferred into reactive solutions is controlled by the gas film resistance, and on the experimental work of Ranz and Marshall [7] [8], which developed a correlation for calculating the mass transfer coefficient between a gas phase and liquid drops when the rate of transfer is controlled by the gas film resistance. Since the gas
The effect of the iodine removal constant and penetrating forms on the two-hour iodine dose reduction factor.

Phase resistance is the rate controlling resistance, the overall mass transfer coefficient ($K_G$) is essentially equal to the gas film resistance ($k_G$), and thus the Ranz and Marshall correlation, equation (8), can be used to evaluate $k_G$:

$$K_G = \frac{D \rho H_T}{M_m d} \left[ 2 + 0.6 \frac{d \nu}{\mu} \right]^{1/2} \left( \frac{\mu}{D_p} \right)^{1/3}$$  \hspace{1cm} (8)$$

Equation (8) may be rewritten in terms of the iodine deposition velocity, $V_G$, by converting from iodine partial pressure units to iodine concentration units.

$$V_G = \frac{RT \frac{D M_T}{M_m d}}{p} \left[ 2 + 0.6 \frac{d \nu}{\mu} \right]^{1/2} \left( \frac{\mu}{D_p} \right)^{1/3}$$  \hspace{1cm} (9)$$

Since the maximum possible iodine concentration in the large containment volume is less than $10^{-7}$ gm/cc (100 mg/m$^3$), the partial pressure of air in the gas film, $p$, can be taken as the total pressure, and the mean molecular weight, $M_m$, can be taken as the molecular weight of the gas phase, $M_A$. Thus if the gas equation is used, equation (9) may be simplified to equation (10) by substituting $M_A/RT$ for $\rho/p$.

$$V_G = \frac{D}{d} \left[ 2 + 0.6 \frac{d \nu}{\mu} \right]^{1/2} \left( \frac{\mu}{D_p} \right)^{1/3}$$  \hspace{1cm} (10)$$
The surface area of drops available for iodine absorption can be calculated from equation (11) which is based on the assumption that all the drops are spherical and have the same diameter.

\[ S = \frac{\pi d^2 F_0}{6} = \frac{6F_0}{d^3} \quad (11) \]

If the containment atmosphere is assumed to be well-mixed and if all the drops are assumed to contain an excess of chemical reagent to react with the iodine and convert it to a nonvolatile form, the rate of removal of elemental iodine from the containment atmosphere following a puff release of the radiiodine can be expressed by equation (12).

\[
\frac{dI}{dt} = -\epsilon \left( -\frac{V_S}{V} \right) I = -\epsilon \lambda_R I \quad (12)
\]

where

\[
\lambda_R = \frac{V_S}{V_c} = \frac{6FHD}{V_c V d^2} \left[ 2 + 0.6 \left( \frac{dv}{d_0} \right)^{1/2} \left( \frac{d_0}{d} \right)^{1/3} \right] \quad (13)
\]

For typical power reactors the values of \( \lambda_R \) range from 10 to 100 per hour, thus by referring to Figures 3 and 6, it can be seen that spray systems can provide DRF considerably larger than the value of 13 which is required to minimize the exclusion area by having the whole body dose control the siting.

Since hydrogen iodide absorption is also controlled by a gas film resistance, equations (8) through (13) should apply equally well to hydrogen iodide, and since HI has a higher diffusion coefficient than I\(_2\), the end result of a calculation should show that HI is removed faster than I\(_2\).

3.2. Charcoal Filter Systems

The rate at which a charcoal filter system can remove the radiiodine from the containment atmosphere following a puff release can be expressed by the equation (14), which is based on the assumption that the reactor building atmosphere is well mixed.

\[
\frac{dI}{dt} = -\epsilon \lambda_R t \quad (14)
\]

where

\[
\lambda_R = \frac{Q}{V_c} \quad (15)
\]

For typical, large power reactors using rather large charcoal filter units, the value for \( \lambda_R \) is usually between 2 and 6 per hour. Again by referring to Figures 3 and 6, it can be seen that only an unusually large charcoal filter system can process the containment atmosphere at a high enough rate to achieve DRF's approaching 13.

4. CONCLUSIONS

Based on the reactor siting criteria in the United States, the use of iodine removal systems greatly reduces the required site and low population zone sizes and shortens the population center distance.
Until a practical means becomes available for removing the noble gases from the containment atmosphere, the best iodine removal systems must only provide an ultimate iodine dose reduction factor of 50 in order to minimize the low population zone size and the population center distance. Even after Xe and Kr, removal is practical, the site size will still be minimized by iodine removal systems which provide a DRF of 13 in two hours because the removal of the noble gases will inherently be a much slower process than the removal of iodine.

Both containment spray systems and charcoal filter systems follow the same equations except for the evaluation of the iodine removal rate constant, \( \lambda_r \).

Changes in containment spray system and charcoal filter system efficiency merely slow the iodine removal rate proportionally, but these changes can be compensated by proportional increases in the system flow rate since these systems are of the recirculating type.

The presence of iodine forms which can penetrate the removal system limit the maximum DRF attainable, approximately proportional to \( 1/f \).

Containment spray systems have a very fast response time due to the large \( \lambda_r \), and thus they can reduce the two-hour thyroid dose very effectively.

Charcoal filter systems are inherently much slower than containment spray systems; therefore, although charcoal filter systems are effective at reducing the low population zone size and the population center distance, they are much less effective at reducing the required site size.

REFERENCES

NOMENCLATURE

B breathing rate, m³/sec (for 2 hour exposures B = 0.000347 m³/sec and for longer exposures B = 0.000232 m³/sec)

D咽 thyroid dose due to iodine exposure, rem

D咽 whole body dose based on β-γ radiation from passing cloud or plume, rem

D咽 specific dose to the thyroid from inhaled iodine, rem/curie

DRF iodine dose reduction factor; the iodine dose without an iodine removal system divided by the iodine dose with a removal system

d drop diameter, cm

E total radiation energy [9], Mev/dis

F spray flow rate, ft³/hr

FR fraction of isotope in fuel which is available for leakage from the containment at t = 0

f fraction of the airborne iodine in the penetrating form

H drop fall height, cm

I fraction of iodine in the containment atmosphere and available for leakage at any time, t

I咽 fraction of airborne iodine which escapes from the containment over the time period, t

KG overall mass transfer coefficient, gms/cm²·sec-atm

KG gas-film mass transfer coefficient, gms/cm²·sec-atm

MI molecular weight of iodine, gms/gm-mol

MA average molecular weight of gas phase in the containment, gms/gm-mol

MM mean molecular weight of the iodine-gas phase mixture in the gas film boundary layer, gms/gm-mol

P reactor power, MWt

p containment pressure, or partial pressure of non-diffusing components in the gas film, atm

Q charcoal filter flow rate, ft³/hr

q specific activity of isotope in fuel, curies/MWt

R universal gas constant = 82.057 atm·cm³/°K·gm-mol

S surface area of drops suspended in gas phase, cm²

T absolute temperature, °K

t time, hrs

VG overall deposition velocity of iodine, cm/sec

VC free volume in the containment, ft³

v relative velocity between the drop and the gas phase, or approximately the terminal velocity of the drop, cm/sec

ε efficiency of the iodine removal system

ρ density of gas phase in the containment, gms/cm³

μ viscosity of gas phase in the containment, gm/cm·sec
DISCUSSION

G. BURLEY: A containment leakage of 0.1%/day is not necessarily conservative. If there is a non-removable fraction of iodine, the iodine reduction factors required to determine whether the thyroid or whole-body dose is controlling may differ somewhat from the numbers quoted. The ultimate iodine reduction factor obtainable is determined by the non-removable (volatile) fraction.

D.A. NITTI: The value used for the containment leak-rate will affect the exclusion area and low population zone sizes of a specific site, but will not affect the decision whether iodine (thyroid) or whole-body dose controls the siting, as shown in Fig. 3 of the paper. The iodine-dose reduction factor required to determine whether thyroid or whole-body dose is the controlling factor is dependent only on the fractions of iodine and noble gases in the core which are released to the containment atmosphere. The effect of non-removable or penetrating forms of iodine is to limit the maximum attainable dose reduction factor.

G. BURLEY: I have a further comment. The values given here for spray removal constants are either calculated or based on small-scale experiments. No full-scale tests have been reported to date.

D.A. NITTI: I agree that the values of the spray removal constants are based on calculations and on experiments smaller than full-scale tests, but the experiments were certainly not small-scale, since they were performed in vessels with free volumes of about 1300 and 25,000 ft³, with realistic flow rates and iodine concentrations. The smaller experiments were done in steam-air atmospheres and the larger have so far been done only in air, but testing will be done in a steam-air atmosphere.

G.F. MERZ: The comparison of the spray and filter systems was based on performance during a maximum credible accident, a basis which we all seem to use — though we should perhaps also consider lesser, but more probable, accidents. Do you plan to establish a limit, in terms of accident magnitude, beneath which you would not want to operate the sprays? If the economic penalty for spray operation is high, do you believe that the reactor operator will be reluctant to use it during ill-defined accidents or to test the system properly?

D.A. NITTI: Spray systems are intended only for loss-of-coolant accidents, where pressure reduction and iodine removal are both required. For loss-of-coolant accidents, the system will be actuated automatically. The spray system will be designed so that it can be tested without spraying water into the containment.
For smaller accidents, iodine removal systems are not required to meet the siting criteria, but small charcoal filters in the containment ventilation system would facilitate re-entry to the containment and would also reduce iodine leakage.

M.I. GOLDMAN: Most PWR reactor containment buildings are provided with systems for purging the building air prior to personnel entry. These purge systems contain high-efficiency particulate and charcoal filters. Thus, for "small" releases this system could be used for decontamination. Similarly, in many installations, such filter systems are provided in auxiliary areas outside the containment where such small releases are likely, or possible.

J.L. KOVACH: What is a "rather large" and an "unusually large" charcoal filter system?

D.A. NITTI: By "rather large" I mean filter systems with removal constants of 2 to 6 per hour. By "unusually large" I mean filter systems with removal constants between 6 and 10, which are required for the whole-body dose to control the reactor siting.

J.L. KOVACH: If the spray system is to be used only for a maximum credible accident and auxiliary building or purge filters are to take care of minor accidents, what happens in between? Is there a grey area?

D.A. NITTI: An academic exercise to explore many hypothetical and specific accident sequences may identify what might be termed a "grey area". However, it is unlikely that accidents smaller than the MCA fission-product releases would result in a siting problem.

O.L. CORDES: The ratio of iodine dose to the whole-body dose will depend on the model used to calculate these doses. What model did you use to calculate the whole-body dose?

D.A. NITTI: The method used to calculate the whole-body dose was the method used in WASH-740 (Ref.3) which assumes immersion in a semi-infinite cloud. I believe the semi-infinite results from the ground reflection of the cloud. This method yields a conservative value for the whole-body dose (higher doses). In evaluating the iodine dose reduction factor required for the whole-body dose to control the reactor siting, care must be taken not to be too conservative in evaluating the whole-body dose, since the higher the whole-body dose, the lower will be the required iodine dose reduction factor (DRF). At first, I included 1% of the mixed fission products in the radioactive source within the cloud, but the required DRF values were considerably below the values of 13 and 50 indicated in Fig.3. Although the required DRF values are dependent on the calculational model, I believe that the values in the paper are realistic and consistent with the present evaluating methods.

N.R. HORTON: Why was TID-14844 chosen as a reference for developing source terms? The use of this guide results in source terms which are at least factors of 500 greater than realistic calculations would indicate. Moreover, since redundant core spray systems and auxiliary power systems are provided, it will be virtually impossible to achieve the accident hypothesized in TID-14844.

D.A. NITTI: I agree that fission-product releases of the magnitude stated in TID-14844 are extremely unlikely, if not impossible, in the current generation of power reactors. However, although the siting criteria (10 CFR 100) do state that "Any applicant who believes that factors other than those set forth in the guide should be considered by..."
the Commission will be expected to demonstrate the applicability and significance of such factors", it is expedient, to avoid licensing difficulties, to rely on the conservative values in the guide, since that is the intent and function of the guide.

Furthermore, although the magnitude of the release does affect the distance factors (exclusion area, low population zone, and population centre distance) for a specific site, the magnitude of the release does not affect the DRF required for the whole-body dose to control the reactor siting. Only the ratio of the iodine and noble gases released to the containment atmosphere is important when determining the required performance of iodine removal systems.
REACTOR CONTAINMENT SPRAY TECHNOLOGY PROGRAM*

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Abstract

REACTOR CONTAINMENT SPRAY TECHNOLOGY PROGRAM. The design basis accident in water-moderated power reactors is a loss-of-coolant accident in which water sprays are generally employed to control the containment pressure transient by condensing the released steam-air mixture. Additives to the spray have been proposed as a way to increase their usefulness by enhancing the removal of various forms of radionuclides from the containment atmosphere. A program to investigate the gas-liquid systems involved is co-ordinated by ORNL for the US Atomic Energy Commission. A basic part of the program is the search for various chemical additives that will increase the spray affinity for molecular iodine and methyl iodide. A method for evaluating additives was developed that measures equilibrium distribution coefficients for iodine between air and aqueous solutions. Additives selected are used in single drop wind tunnel experiments where the circulating gas contains iodine or CH₃I. Mass transfer coefficients and transient distribution coefficients have been determined as a function of relative humidity, temperature, drop size, and solution pH and concentration. Tests have shown that surfactants and organic amines increase the solution ability to getter CH₃I. Results from single drop tests help in planning spray experiments in the Nuclear Safety Pilot Plant, a large (~38 m³) facility, where accident conditions are closely simulated. Iodine and CH₃I removal rates have been determined for a number of solutions, including 1 wt% Na₂S₂O₃ + 3000 ppm B + 0.153 M NaOH and 3000 ppm B + 0.153 M NaOH. The additive has very little effect in removal of I₂ with half-lives of less than 1 min typical for any aqueous solution. These same solutions remove CH₃I with a half-life of one hour. Analytical models for the removal processes have been developed.

INTRODUCTION

The number of nuclear power plants ordered by utilities in the United States has increased significantly in the past two years and the outlook for continued growth is very favorable. The capacity of these plants ranges from 500 to greater than 1000 MWe. Such power levels coupled with the available sites has made plant siting more difficult.

A significant number of the plants to be built are of the pressurized water reactor (PWR) type and have containment building spray systems for pressure reduction in the event of a loss-of-coolant accident. These spray systems are an accepted engineered safeguard. A logical step in the evolution of the plant safeguards to facilitate siting was to utilize the fission product removal accompanying spray operation and to enhance this process through chemical additives if possible.

* Research sponsored by the US Atomic Energy Commission under contract with the Union Carbide Corporation.
The need for evaluation of the effectiveness of reactor containment sprays is evident. The Oak Ridge National Laboratory coordinates all spray system research for the U. S. Atomic Energy Commission.

PROBLEMS OF CONTAINMENT SPRAY SYSTEMS

The spray system in a PWR is designed to use refueling water storage as a supply until exhausted, at which time the solution is recirculated from sumps in the containment building. The sump solution is also recirculated through the core for shutdown cooling. For a typical PWR design basis accident the spray must be evaluated for iodine, organic iodide, and particulate removal effectiveness. Accident conditions will subject the spray solution to short-term temperatures in core of 320°F, and long-term values of 200°F. The radiation exposure will result in accumulated doses of $10^6$ rad in eight days. The solution must not be corrosive to the point that it violates containment or hinders safety systems operation and it should not remove significant quantities of protective coatings within the containment structure. With these problem areas as guidelines a program was formulated to investigate containment spray systems.

PROGRAM RESEARCH

A significant portion of the program is devoted to the identification of useful solutions, additives and conducting tests directed to development of analytical models for spray removal of the contaminants of interest. In the months prior to establishing the problem two solutions were chosen by industry as likely candidates: sodium thiosulfate and sodium hydroxide, both in a borated refueling water medium. Significant effort has been devoted to evaluating these solutions. However, we did feel it necessary to evaluate other additives should one or both of these two choices prove unusable.

Solution Search

The solution search is conducted under subcontract to Furman University. This part of the program acts as a feeder for other experimental facilities and gives information on the basic reaction mechanisms and temperature sensitivity. A method was developed to measure equilibrium iodine capacities, $K_d^*$, of various test solutions (2), where

$$K_d^* = \frac{\text{Total dissolved } I_2 \text{ as moles } I_2 \text{ equivalent}}{\text{Moles } I_2 \text{ (gas)}}$$

A number of additives for $I_2$ have been tested and iodine capacities as a function of concentration determined; these are listed in Table I.

As indicated before, initial work concentrated on the solutions under consideration by industry, the variation of $K_d^*$ with temperature and concentration for some of these solutions is given in Table II.

The data generated in this portion of the program allows selection of the most promising solutions so that optimum use can be made of the large facilities.

Single Drop-Wind Tunnel

While spray experiments in large experimental facilities are an important aspect of the problem, it is very difficult to resolve the various effects such as drop size, humidity, contaminant concentration, rate of
### Table I. Survey of Potential Additives to Sprays or Pools for I$_2$ Removal [5,6]

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration</th>
<th>$K'_d$ at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td></td>
<td>92</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>$2.31 \times 10^{-3}$ M</td>
<td>250</td>
</tr>
<tr>
<td>NaOH</td>
<td>$2.52 \times 10^{-3}$ M</td>
<td>250</td>
</tr>
<tr>
<td>KOH</td>
<td>$2.39 \times 10^{-3}$ M</td>
<td>202</td>
</tr>
<tr>
<td>Piperidine</td>
<td>~$2.5 \times 10^{-3}$ M</td>
<td>369</td>
</tr>
<tr>
<td>Morpholine</td>
<td>~$2.5 \times 10^{-3}$ M</td>
<td>277</td>
</tr>
<tr>
<td>NH$_4$H$_2$SO$_4$</td>
<td>$2.32 \times 10^{-3}$ M</td>
<td>618</td>
</tr>
<tr>
<td>H$_2$O-CH$_2$-CH$_2$-OH</td>
<td>10 vol. %</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>15 vol. %</td>
<td>426</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>~$2.5 \times 10^{-3}$ M</td>
<td>728</td>
</tr>
<tr>
<td>NaN$_2$(sodium nitrate)</td>
<td>$9.56 \times 10^{-2}$ M</td>
<td>103</td>
</tr>
<tr>
<td>CH$_3$CO$_2$H (acetic acid)</td>
<td>$2.56 \times 10^{-3}$ M</td>
<td>109</td>
</tr>
<tr>
<td>NaClO$_2$ (sodium chlorate)</td>
<td>$9.8 \times 10^{-2}$ M</td>
<td>112</td>
</tr>
<tr>
<td>H$_2$SO$_4$' (sulfuric acid)</td>
<td>$2.252 \times 10^{-3}$ M</td>
<td>117</td>
</tr>
<tr>
<td>Na$_3$C$_2$H$_7$O$_7$ (sodium citrate)</td>
<td>$2.41 \times 10^{-3}$ M</td>
<td>122</td>
</tr>
<tr>
<td>NH$_4$OH (ammonium hydroxide)</td>
<td>$1.775 \times 10^{-3}$ M</td>
<td>131</td>
</tr>
<tr>
<td>LiOH (lithium hydroxide)</td>
<td>$2.755 \times 10^{-3}$ M</td>
<td>513</td>
</tr>
<tr>
<td>Na$_2$B$_4$O$_7$$\cdot$10H$_2$O (sodium tetraborate or borax)</td>
<td>$0.1$ M</td>
<td>874</td>
</tr>
<tr>
<td>Creatinine</td>
<td>$2.52 \times 10^{-3}$ M</td>
<td>114</td>
</tr>
<tr>
<td>Glycine</td>
<td>$2.37 \times 10^{-3}$ M</td>
<td>123</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$2.5 \times 10^{-3}$ M</td>
<td>197(a)</td>
</tr>
<tr>
<td>AgNO$_3$(silver nitrate)</td>
<td>$2.255 \times 10^{-3}$ M</td>
<td>242(a)</td>
</tr>
<tr>
<td>4-aminopyridine</td>
<td>$2.5 \times 10^{-3}$ M</td>
<td>391(a)</td>
</tr>
<tr>
<td>Quinoline</td>
<td>$2.5 \times 10^{-3}$ M</td>
<td>450(a)</td>
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<tr>
<td>Piperazine</td>
<td>$2.5 \times 10^{-3}$ M</td>
<td>517(a)</td>
</tr>
<tr>
<td>1,4-Diazabicyclo (222) Octane</td>
<td>$2.76 \times 10^{-3}$ M</td>
<td>702(a)</td>
</tr>
<tr>
<td>1,3,5-Trihydroxybenzene</td>
<td>$2.32 \times 10^{-3}$ M</td>
<td>817(a)</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>$2.5 \times 10^{-3}$ M</td>
<td>1100(a)</td>
</tr>
<tr>
<td>Urea</td>
<td>$2.501 \times 10^{-3}$ M</td>
<td>115</td>
</tr>
<tr>
<td>CH$_3$N$_2$·HNO$_3$ (guanidine nitrate)</td>
<td>$2.32 \times 10^{-3}$ M</td>
<td>119</td>
</tr>
<tr>
<td>KCNS (potassium thiocyanate)</td>
<td>$2.16 \times 10^{-3}$ M</td>
<td>368</td>
</tr>
<tr>
<td>Semicarbazide-HCl</td>
<td>$2.29 \times 10^{-3}$ M</td>
<td>690</td>
</tr>
<tr>
<td>Thiourea</td>
<td>$2.48 \times 10^{-3}$ M</td>
<td>767</td>
</tr>
<tr>
<td>Thiosemicarbazide</td>
<td>$2.34 \times 10^{-3}$ M</td>
<td>1015</td>
</tr>
<tr>
<td>Carboxydradize</td>
<td>$2.40 \times 10^{-3}$ M</td>
<td>1512</td>
</tr>
<tr>
<td>Glycerine</td>
<td>30% by volume</td>
<td>173</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>30% by volume</td>
<td>205</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>20% by volume</td>
<td>215</td>
</tr>
<tr>
<td>Dioxane</td>
<td>20% by volume</td>
<td>235</td>
</tr>
<tr>
<td>Dimethylformide</td>
<td>20% by volume</td>
<td>278</td>
</tr>
<tr>
<td>Triethylene glycol</td>
<td>20% by volume</td>
<td>342</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>10% by volume</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>45% by volume</td>
<td>426</td>
</tr>
</tbody>
</table>

a. (s) - Results in solid product.
Table II. \( K'_{d} \) Variation with Temperature and Concentration \([3,5]\)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration</th>
<th>25°C</th>
<th>45°C</th>
<th>66.2°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O )</td>
<td></td>
<td>92</td>
<td>87</td>
<td>72</td>
</tr>
<tr>
<td>( H_2BO_3 ) in ( H_2O )</td>
<td>3000 ppm B</td>
<td>85</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3) in ( H_2O )</td>
<td>0.921 x 10(^{-3})M</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.31 x 10(^{-3})M</td>
<td>250</td>
<td>288</td>
<td>345</td>
</tr>
<tr>
<td></td>
<td>4.62 x 10(^{-3})M</td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3) + ( H_2BO_3 )</td>
<td>2.31 x 10(^{-3})M</td>
<td>237</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH in ( H_2O )</td>
<td>1.012 x 10(^{-3})M</td>
<td>155</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.52 x 10(^{-3})M</td>
<td>250</td>
<td>219</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>5.05 x 10(^{-3})M</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH + ( H_2BO_3 )</td>
<td>2.52 x 10(^{-3})M</td>
<td>83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3) - NaOH</td>
<td>2.42 x 10(^{-3})M</td>
<td>261</td>
<td>221</td>
<td></td>
</tr>
</tbody>
</table>

(Total: 50:50 mixture)

---

**Fig. 1.** Effect of both additive type and concentration on mass transport (at -26°C and drop radius = 0.21 cm).
contaminant uptake, additive concentration, solution pH, temperature, etc. in these experiments. Therefore, studies are being conducted with a single drop of spray solution suspended in a wind tunnel where the gas contains a regulated amount of contaminant. Here the effects mentioned can be studied individually under controlled conditions. As in the solution search, a major portion of the initial work was devoted to evaluation of the solutions proposed by industry.

A large number of separate experiments has been completed in the wind tunnel studies and Table III lists some of the solutions and contaminants examined. There are 8-9 spray solution activation analyses and 5-7 wind tunnel gas analyses required for each experiment.

The results of these experiments allow comparison of proposed spray additives so that selection of the most effective ones can be made. The effect of additive concentration on the mass transfer coefficient for ammonium sulfide, acid borated thiosulfate and hydrazine is given in Fig. 1.
FIG. 2. Effect of pH and temperature on the mass transport of CH₃I.

FIG. 3. The effect of relative humidity on the rate of uptake of CH₃I by a drop of 1% solution of Na₂S₂O₃ at pH 7.4.
The variation of pH and the effect of tunnel gas relative humidity on the mass transfer coefficient were determined for the sodium thiosulfate system, Figs. 2 and 3.

In that the use of plain base as an additive is also of significant industrial interest, this was evaluated for pH effect, Fig. 4.

These studies have pointed out the benefits to be gained from going to a basic media for the spray solution.

Nuclear Safety Pilot Plant

This 38 m³ stainless steel containment facility offers the capability for conducting spray experiments with an environment similar to that
Table IV. Summary of Results Obtained in Elemental Iodine Absorption Experiments at the NSPP

<table>
<thead>
<tr>
<th>Run No.</th>
<th>21</th>
<th>22</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>30</th>
<th>31</th>
<th>32</th>
<th>33</th>
<th>37</th>
<th>38</th>
<th>42</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of spray nozzles</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Nozzle identification</td>
<td>J-140D&lt;sup&gt;a&lt;/sup&gt;,J-140D,1713&lt;sup&gt;b&lt;/sup&gt;,1713</td>
<td>1713</td>
<td>1713</td>
<td>1713</td>
<td>1713</td>
<td>1713</td>
<td>1713</td>
<td>703&lt;sup&gt;b&lt;/sup&gt;</td>
<td>703</td>
<td>703</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Solution Composition**

| | 13.7 g/l boric acid | 3.4 g/l sodium hydroxide | 8 g/l sodium thiosulfate |
|-----------------|--------------------------|--------------------------|
| 21              | x                        | x                        | x                        |
| 22              | x                        | x                        | x                        |
| 26              | x                        | x                        | x                        |
| 27              | x                        | x                        | x                        |
| 28              | x                        | x                        | x                        |
| 30              | x                        | x                        | x                        |
| 31              | x                        | x                        | x                        |
| 32              | x                        | x                        | x                        |
| 33              | x                        | x                        | x                        |

<table>
<thead>
<tr>
<th>37</th>
<th>38</th>
<th>31</th>
<th>48</th>
<th>48</th>
<th>24</th>
<th>38</th>
<th>41</th>
<th>21</th>
<th>20</th>
<th>11</th>
<th>12</th>
<th>14/80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation removal half-life, sec</td>
<td>37</td>
<td>38</td>
<td>31</td>
<td>48</td>
<td>48</td>
<td>24</td>
<td>38</td>
<td>41</td>
<td>21</td>
<td>20</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>Calculated removal half-life, sec</td>
<td>3</td>
<td>3</td>
<td>98</td>
<td>107</td>
<td>102</td>
<td>36</td>
<td>37</td>
<td>98</td>
<td>94</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Spray Engineering Company catalog number; <sup>b</sup> Spraying Systems Company catalog number.
existing in a reactor containment following a loss-of-coolant accident [5].

Experiments involving elemental iodine and a number of solutions of interest have been completed, Table IV.

The change in nozzles over the period of experiments progressed from the misting nozzles already installed at the time spray experiments were started (J-1401) to a ramp bottom (hollow cone) nozzle typical of an industrial system (1713), to a full cone nozzle (703) for full coverage and ease of modeling. The half-life for removal of I₂ is less than one min in practically all cases, while the predicted half-life is slightly longer in most cases.

A number of experiments with CH₃I have been completed, Table V. These experiments indicate that CH₃I is not removed efficiently by spray solutions currently designed for I₂ removal. It should be noted that we observed thermal decomposition of CH₃I in Runs 39, 40, and 41. The experimental facility was arranged so that the CH₃I passed through a hot (No. 39 and No. 40 - 170°C, No. 41 - 130°C) stainless steel tee before entering the containment vessel. This tee was heated externally with a steam jacket so that the contacted surface was dry.

**Laboratory Scale Experiments**

A small (11.1 liter) recirculating loop laboratory facility has the capability for determining the removal of CH₃I by sprays [5, 6]. Experiments performed in this facility using 0.1 M Na₂S₂O₃ spray solution indicate a removal half-life in good agreement with single drop and NSPP work.

**Containment Systems Experiment (CSE)**

Work in the facilities at ORNL is complemented by existing facilities at other AEC-supported installations. The largest facility currently available for conducting spray experiments is located at Battelle Northwest Laboratory, Richland, Washington.

This facility [7] is a factor of 23 larger in gross volume than the NSPP. This proof test facility will contribute to analytical modeling and when combined with NSPP results the two should be capable of answering practically all of the removal process questions.

A summary of the first two runs at CSE is presented in Tables VI and VII. The results agree quite well with NSPP data and analytical models.

**Hydrazine Studies**

Schwendiman et al. at BNWL have been studying the removal of CH₃I by hydrazine sprays. This work includes chemical studies of the CH₃I-hydrazine system and the spray removal effectiveness [8]. The investigation indicated that the reaction rate constant for hydrazine at 22°C is approximately the same as sodium thiosulfate, \(3 \times 10^{-2}\) liters mole⁻¹sec⁻¹. Removal half-lives of about 10 min can be obtained if a 140 micron MMD spray of 35-37% hydrazine is used, while 40-45 min was determined for 5% solution. In both cases the initial temperature was 80°C.

**Radiation and Thermal Stability**

This work has been directed to answering the numerous questions about solutions placed in both high temperature and radiation fields [5]. Some of the significant points considered are pH change, loss of iodine
Table V. Summary of Methyl Iodide Experiments in the NSPP

<table>
<thead>
<tr>
<th>Run No.</th>
<th>MCV Temperature, °C</th>
<th>MCV Pr, psig</th>
<th>Spray Solution</th>
<th>Nozzle type</th>
<th>Flow, gpm</th>
<th>Spray Period</th>
<th>Overall D. F.</th>
<th>Half-Life</th>
<th>Gamma Data</th>
<th>Solutions</th>
<th>Gas Samples, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>30</td>
<td>11</td>
<td>x</td>
<td>17/3</td>
<td>.15</td>
<td>2 hr</td>
<td>3</td>
<td>150 min</td>
<td>Long</td>
<td>103</td>
<td>65</td>
</tr>
<tr>
<td>35</td>
<td>130</td>
<td>45</td>
<td>x</td>
<td>17/3</td>
<td>.15</td>
<td>2 hr</td>
<td>3.6</td>
<td>150 min</td>
<td>Long</td>
<td>94</td>
<td>69</td>
</tr>
<tr>
<td>36</td>
<td>130</td>
<td>45</td>
<td>x</td>
<td>17/3</td>
<td>12</td>
<td>2 hr</td>
<td>3.6</td>
<td>25 min</td>
<td>27</td>
<td>52</td>
<td>40</td>
</tr>
<tr>
<td>39</td>
<td>130</td>
<td>45</td>
<td>x</td>
<td>17/3</td>
<td>11</td>
<td>2 hr</td>
<td>11.1</td>
<td>25 min</td>
<td>30</td>
<td>52</td>
<td>36</td>
</tr>
<tr>
<td>40</td>
<td>130</td>
<td>45</td>
<td>x</td>
<td>17/3</td>
<td>11</td>
<td>2 hr</td>
<td>146</td>
<td>42</td>
<td>42</td>
<td>52</td>
<td>36</td>
</tr>
<tr>
<td>41</td>
<td>30</td>
<td>10</td>
<td>x</td>
<td>7G3</td>
<td>11</td>
<td>3 hr</td>
<td>8</td>
<td>87</td>
<td>87</td>
<td>52</td>
<td>36</td>
</tr>
<tr>
<td>43</td>
<td>30</td>
<td>10</td>
<td>x</td>
<td>7G3</td>
<td>11</td>
<td>3 hr</td>
<td>1.03</td>
<td>188</td>
<td>188</td>
<td>52</td>
<td>36</td>
</tr>
<tr>
<td>44</td>
<td>130</td>
<td>45</td>
<td>x</td>
<td>7G3</td>
<td>11</td>
<td>3 hr</td>
<td>10.4</td>
<td>16</td>
<td>Infinity</td>
<td>52</td>
<td>36</td>
</tr>
</tbody>
</table>

a. Thermal decomposition of CH$_3$I suspected; b. Solution also contained $10^{-5}$M surfactant, cetyl trimethylammonium bromide.
Table VI. Summary of Physical Conditions - Runs A-3 and A-4 in CSE

<table>
<thead>
<tr>
<th>Date of Test</th>
<th>Run A-3</th>
<th>Run A-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>Main CSE Vessel Plus Open Drywell</td>
<td>Same as A-3</td>
</tr>
<tr>
<td></td>
<td>Wet Wells Sealed Off</td>
<td></td>
</tr>
<tr>
<td>Spray Period</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Spraying pressure, psig</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Flow rate, gpm</td>
<td>12.8</td>
<td>12.8</td>
</tr>
<tr>
<td>Spray flux, gpm/ft²</td>
<td>0.026</td>
<td>0.026</td>
</tr>
<tr>
<td>Drop sizea MMD, microns</td>
<td>1210</td>
<td>1210</td>
</tr>
<tr>
<td>Geo. Std. Dev., σg</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td>Fall, nozzle to deck, ft.</td>
<td>33.8</td>
<td>33.8</td>
</tr>
<tr>
<td>Nozzle to DW bottom, ft.</td>
<td>50.5</td>
<td>50.5</td>
</tr>
<tr>
<td>Calc: % upper volume sprayed</td>
<td>45.3</td>
<td>45.3</td>
</tr>
<tr>
<td>Spray solution (3000 ppm H₃BO₃ + NaOH), pH</td>
<td>9.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Wall-impingement, gpm</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Air circulation, cfm</td>
<td>2400</td>
<td>2400</td>
</tr>
<tr>
<td>Nozzle (quantity) and typea</td>
<td>(3) 3/4-703</td>
<td>(3) 3/4-703</td>
</tr>
</tbody>
</table>

| Time from 0, min | 40.0 | 140.0 | 1473.0 | 40.5 | 140.0 | 1205.0 |
| Duration, min | 10.0 | 30.0 | 60.0 | 10.0 | 30.0 | 45.0 |
| Flow, gpm | 12.8 | 12.8 | 12.5 | 48.8 | 49.3 | 41.6 |
| Pressure, psi | 40.0 | 40.0 | 40.0 | 40.0 | 40.0 | 29.0 |
| Est. Drop size MMD, microns | 1210 | 1210 | 1210 | 1210 | 1210 | 1360 |
| Solution, pH | 9.5b | 9.5b | 6.8c | 9.5b | 9.5b | 9.6d |

a. Spraying Systems Co., Bellwood, Ill.; b. 3000 ppm H₃BO₃ + 0.037 H NaOH; c. Demineralized water, not recirculated; d. Recirculated from CV sump.
Table VII. Aerosol Concentration Half-lives Due to Operation of Sprays - Runs A-3 and A-4 (minutes)

<table>
<thead>
<tr>
<th>Containment Conditions</th>
<th>Elemental Iodine</th>
<th>Particulate Iodine</th>
<th>CH$_3$I</th>
<th>Cesium</th>
<th>Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Spray, Run A-3</td>
<td>5.4</td>
<td>11.3</td>
<td>73</td>
<td>16</td>
<td>34</td>
</tr>
<tr>
<td>1st Spray, Run A-4</td>
<td>1.64</td>
<td>2.6</td>
<td>53</td>
<td>3.5</td>
<td>7</td>
</tr>
<tr>
<td>2nd Spray, Run A-3</td>
<td>6.2</td>
<td>13</td>
<td>170</td>
<td>16.7</td>
<td>32</td>
</tr>
<tr>
<td>2nd Spray, Run A-4</td>
<td>10.4</td>
<td>8.7</td>
<td>240</td>
<td>10.3</td>
<td>21</td>
</tr>
</tbody>
</table>
equivalence, solids generation, and H₂ generation under irradiation. Solutions are irradiated under a number of gas-to-liquid ratios, solution pH and concentrations, temperature and cover gases, with and without reacted iodines.

Initial work in this part of the program was oriented to those solutions proposed for use by the nuclear industry; they include: (1) 1 wt % Na₂S₂O₅, 3000 ppm B, and 0.153 M NaOH in H₂O; (2) 3000 ppm B and 0.153 M NaOH in H₂O; (3) distilled H₂O; (4) 3000 ppm B in H₂O; and (5) 1 wt % Na₂S₂O₅ and 3000 ppm B in H₂O.

Table VIII. Radiolytic H₂ Production as a Function of Total Dose
Gas-to-liquid ratio, all samples: 25

<table>
<thead>
<tr>
<th>Dose (r)</th>
<th>Radiolytic H₂ Produced (cc/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>π 10⁷</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.05</td>
</tr>
<tr>
<td>1.87</td>
<td>0.14</td>
</tr>
<tr>
<td>2.81</td>
<td>0.27</td>
</tr>
<tr>
<td>4.74</td>
<td>0.36</td>
</tr>
<tr>
<td>9.46</td>
<td>0.69</td>
</tr>
</tbody>
</table>

The first work completed on these solutions indicated that solution No. 5, borated thiosulfate (pH approximately 5), was probably not acceptable because of the large quantity of solid sulfur generated (1.65 mg/ml of solution at 1 x 10⁸ R). Loss of iodine capacity and change in pH were also found to be excessive for solution No. 5.

The amount of radiolytic gas, H₂ in particular, generated is of particular interest. Studies on solutions 1, 2, 4 indicate little difference in H₂ generation under the conditions studied, Table VIII.

The effect on H₂ generation of gas/liquid ratio and dose rate were examined also, Tables IX and X.

Since the H₂ generation appears to be a problem the use of a solution additive to reduce the production rate of H₂ was investigated. The result of adding nitrate to the spray solution is given in Table XI. A definite decrease in H₂ production is noted.

A study was conducted to determine whether radiolytic H₂ evolved by the spray solutions reaches a gas-liquid equilibrium state in the dose range expected, in no case is an equilibrium situation reached at 2 x 10⁸ R, as shown in Fig. 5.

An investigation of the thermal stability of the solutions is being conducted because of the expected temperatures following an accident. A
Table IX. Effect of Gas-to-Liquid Ratio on Radiolytic $H_2$ Production in Test Solution 1

Total radiation dose, all samples: $4 \times 10^7$ r

Test conditions: all sample capsules sealed with gas-to-liquid ratio shown

Cover gas - Air

<table>
<thead>
<tr>
<th>Gas-to-liquid Ratio</th>
<th>$H_2$ Evolved (cc/ml)</th>
<th>$G(H_2)^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.16</td>
<td>0.2</td>
</tr>
<tr>
<td>25</td>
<td>0.26</td>
<td>0.3</td>
</tr>
<tr>
<td>8</td>
<td>0.41</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>0.57</td>
<td>0.6</td>
</tr>
<tr>
<td>0.8</td>
<td>0.92</td>
<td>1.0</td>
</tr>
</tbody>
</table>

a. Molecules changed per 100 ev of energy.

Table X. Radiolytic $H_2$ Production of Solution 1 as a Function of Dose Rate

Total dose, all samples: $1 \times 10^7$ r

Gas-to-liquid ratio: 25

Cover gas - Air

<table>
<thead>
<tr>
<th>Dose Rate (r/min)</th>
<th>Radiolytic $H_2$ Produced (cc/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^3$</td>
<td>0.05</td>
</tr>
<tr>
<td>$4.8 \times 10^3$</td>
<td>0.05</td>
</tr>
<tr>
<td>$7.0 \times 10^3$</td>
<td>0.06</td>
</tr>
<tr>
<td>$1.6 \times 10^4$</td>
<td>0.06</td>
</tr>
<tr>
<td>$1.0 \times 10^5$</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Table XI. Effect of NO$_3^-$ on Radiolytic H$_2$ Production in Solution 1

- Radiation dose, all samples: $1 \times 10^7$ r
- Gas-to-liquid ratio: ~10
- Cover gas - Air

<table>
<thead>
<tr>
<th>NO$_3^-$ Added (wt %)</th>
<th>Radiolytic H$_2$ Produced (cc/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.09</td>
</tr>
<tr>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>0.25</td>
<td>0.07</td>
</tr>
<tr>
<td>0.50</td>
<td>0.06</td>
</tr>
<tr>
<td>0.75</td>
<td>0.06</td>
</tr>
<tr>
<td>1.00</td>
<td>0.05</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig. 5.** Radiolytic gas pressure plotted against dose.
A comparison between the two thiosulfate systems (basic and acid) is given in Fig. 6.

Corrosion

Planning of the necessary test program is in progress. A list of corrosion samples was compiled from examination of a number of plant descriptions and discussions with industrial representatives.

Reactor Containment Coatings

A program is established that will result in a standard for coatings as related to accident conditions. This involves collection of the necessary accident condition information and review of this by appropriate program and industry personnel. After agreement on the conditions the information will be turned over to a professional society-sponsored committee to write the standard. Concurrent with this an experimental program on paint evaluation is being conducted by Idaho Nuclear Corporation. This part of the program will establish requirements for coatings in spray system protected plants.

CONCLUSIONS

At the present state of the investigation the following tentative conclusions can be made:

1. Properly designed spray systems can be used as an effective safeguard for I₂ removal.

2. Hydrogen generation by spray solutions must be given consideration.

3. Solution additives will be proven to be effective for CH₃I removal.
ACKNOWLEDGEMENT

The author is indebted to the following group leaders responsible for the investigations in the Spray Program: Dr. C. S. Patterson of Furman University, Dr. B. A. Soldano, Dr. L. F. Parsley, Jr., and Dr. H. E. Zittel of ORNL; Dr. L. C. Schwendiman and Dr. G. J. Rogers of BNWL; and Dr. H. L. Rohde of Idaho Nuclear Corporation.

REFERENCES


AIRBORNE WASTES FROM INCINERATION

(Session VII, Part 1)
Chairman: M. W. FIRST
DEPOUSSIERAGE DES GAZ DE COMBUSTION DANS UN INCINERATEUR DE RESIDUS RADIOACTIFS

Y. SUTRA-FOURCADE, B. CAIRE ET F. GALLISSIAN
CEA, CENTRE DE PRODUCTION DE PLUTONIUM DE MARCOULE, FRANCE

Abstract — Résumé

REMOVAL OF DUST FROM COMBUSTION GASES IN AN INCINERATOR FOR RADIOACTIVE WASTES.

Incineration is a method of eliminating radioactive wastes which gives very large volume reduction factors. The purification of combustion gases from incineration, however, raises numerous problems which the authors consider in this paper: high gas temperatures, acidity due to combustion of plastic materials, the presence of lampblack, and so on. The characteristics of the aerosols formed and the behaviour of the radioisotopes contaminating the wastes are studied, the incinerator of the Marcoule Centre being taken as a specific example.

DEPOUSSIERAGE DES GAZ DE COMBUSTION DANS UN INCINERATEUR DE RESIDUS RADIOACTIFS.

L’incinération est un procédé d’élimination des résidus radioactifs qui permet d’obtenir des facteurs de réduction en volume très importants. L’épuration des gaz de combustion pose cependant de nombreux problèmes que les auteurs passent en revue: haute température des gaz, acidité due à la combustion de matières plastiques, présence de noir de carbone. Les caractéristiques des aérosols formés et le comportement des radioéléments contaminant les résidus sont étudiés en prenant comme exemple l’incinérateur radioactif du Centre de Marcoule.

INTRODUCTION


L’un des plus importants problèmes à résoudre lors de l’étude d’un incinérateur est le choix du dispositif d’épuration des gaz issus de la combustion des résidus radioactifs. Nous nous proposons, dans ce qui suit, d’étudier ce problème grâce à l’expérience acquise sur le Centre de production de plutonium de Marcoule [5-7].
CHOIX DU DISPOSITIF D'ÉPURATION

Les critères permettant de fixer un choix sont nombreux et importants:

**Température des gaz:** elle est, à la sortie de la chambre de post-combustion, de l'ordre de 1000°C. Suivant que la filtration se fera « à chaud » ou « à froid », il faudra prévoir ou non un refroidissement préalable. A noter que, dans l'état actuel de la technique, la filtration à chaud ne semble pas avoir été très utilisée.

**Risques de corrosion:** ces risques sont intimement liés à la nature des résidus à incinérer ; ainsi, dans le cas de la combustion de matières plastiques, ils s'avèrent très importants et imposent un choix judicieux des matériaux de construction. Ils peuvent en partie être limités par dessiccation totale de l'air introduit dans la chambre de combustion.

**Combustion et post-combustion:** la présence et surtout la quantité de noir de carbone susceptible de se déposer dans le circuit d'épuration des gaz sont fonction de la qualité de la combustion et, à cet égard, l'utilisation d'une chambre de post-combustion s'avère indispensable.

Le réglage de l'admission d'air est également important ; si elle est insuffisante, la combustion ne peut se faire complètement par manque de comburant, et si elle est trop importante, la température du foyer baisse.

**Nature des matériaux de construction:** il est bien évident que certains des problèmes précédents pourraient être aisément résolus s'il était possible de disposer de matériaux résistant à une haute température, présentant une passivité élevée vis-à-vis des agents chimiques même à chaud, et surtout d'un prix de revient compétitif.

**Prix des matériaux:** le prix de revient d'une installation étant un facteur primordial, il est bon de faire un bilan chiffré et de tenir compte de la durée de vie probable de chacune des matières employées en fonction de son prix. Il pourra ainsi s'avérer plus rentable d'utiliser des matériaux courants assez bon marché, quitte à remplacer plus souvent certains organes du circuit. A Marcoule, il n'a pas été estimé rentable de généraliser l'emploi de l'acier inoxydable dans les circuits d'évacuation des gaz de l'incinérateur de déchets radioactifs.

**Nature des résidus à incinérer:** un grand soin doit être apporté à l'élaboration des sacs de déchets afin d'éviter que la combustion de matières riches en carbone ne provoque une émission importante de noir de carbone susceptible de favoriser le colmatage des préfiltres.

**Filtration après refroidissement préalable**

Le choix des matériaux utilisables pour le dépoussiérage et la filtration est assez limité, et leur prix excessif s'ils doivent supporter des températures élevées.

Plusieurs solutions de base peuvent être retenues pour le refroidissement préalable :

- **Dilution des gaz issus de la chambre de post-combustion par de l'air extérieur:** cette méthode simple et séduisante présente l'inconvénient d'augmenter considérablement la capacité des appareils d'épuration ainsi que la surface des éléments filtrants.

- **Pulvérisation d'eau froide à contre-courant dans une tour de ruissellement:** l'échange thermique est excellent car le gaz est en contact direct avec l'eau. L'acidité libre des fumées est partiellement absorbée...
et les particules de poussière les plus grosses sont éliminées. Toutefois, cette méthode conduit à une production d'effluents radioactifs non négligeable et entraîne une corrosion importante dans l'appareil de refroidissement ou le matériau doit travailler en milieu humide et à haute température.

- Circulation des gaz dans un échangeur à faisceaux tubulaires étanches, refroidis à l'extérieur par un fluide qui peut être l'air ou l'eau. L'utilisation de l'eau présente plusieurs inconvénients: risques d'entartrage, de corrosion et, en cas de fuite, de vaporisation brutale risquant d' entraîner de graves dommages à l'installation. L'utilisation de l'air est donc préférable malgré la nécessité d'avoir une surface d'échange plus importante. Le refroidissement des gaz par deux étages successifs d'échangeurs haute et basse température semble le système le plus favorable. Il est toutefois nécessaire de prévoir un réchauffage préalable de l'air de refroidissement qui, trop frais, risque de provoquer des condensations d'eau à l'intérieur des faisceaux tubulaires.

Les gaz ayant donc été refroidis à 150°C environ, il faut procéder au dépoussiérage et à la filtration.

La encore, plusieurs voies semblent offertes:

* Voie humide: Elle permet une bonne épuration chimique; toutefois, les rendements d'épuration pour les poussières sont en général moins élevés que par voie sèche. En outre, les matériaux de construction doivent pouvoir résister à la corrosion en milieu humide à des températures de l'ordre de 130°C. De plus, malgré un recyclage indispensable, le volume d'effluents radioactifs produit n'est pas négligeable. Enfin, la nécessité de disposer d'une épuration très poussée conduit à utiliser malgré tout des éléments à filtres secs, donc de piéger préalablement les vésicules liquides entraînées à la sortie des séparateurs humides et de réchauffer les gaz au-dessus de leur point de rosée pour éviter toute condensation dans les éléments filtrants.

* Voie sèche: Cette méthode permet de limiter la corrosion dans les étages de filtration. Toutefois, il est indispensable d'éviter toute condensation dans les différentes parties du circuit de filtration en appliquant un calorifugeage très soigné.

Pour la préfiltration, des préséparateurs du type cyclone ne posent pas de gros problèmes d'exploitation, mais ne donnent qu'un dépoussiérage grossier. L'utilisation de filtres à manches ou d'électrofiltres permet une préfiltration assez poussée. Les premiers, réalisés en fibre de verre siliconée, résistant à des températures allant jusqu'à 260°C, ont une perte de charge relativement importante (35 à 40 mmCE), mais possèdent une bonne résistance à la corrosion et un pouvoir d'arrêt satisfaisant... L'essentiel pour leur bon fonctionnement est de disposer d'un décolmatage automatique associant le secouage mécanique au décolmatage pneumatique.

Les électrofiltres ont un rendement de filtration élevé et une perte de charge minime, mais ils sont volumineux, chers et sensibles à la corrosion.

Le dernier étage de filtration pourra comporter des préfiltres destinés à protéger des filtres dits absolu et à en prolonger la durée de vie. Ces éléments filtrants doivent pouvoir travailler à des températures atteignant 150°C et, par mesure de sécurité, il est bon de prévoir leur résistance jusqu'à 500°C. Dans cet ordre d'idée, les éléments constitués de média en fibre de verre sont satisfaisants.
Filtration sans refroidissement préalable

Des études intéressantes ont déjà été entreprises dans ce domaine et ont abouti à des résultats encourageants. En particulier, un filtre adapté aux besoins de l'industrie nucléaire [8] utilise l'amiante comme média filtrant. L'amiante défibrée est pulvérisée sur la surface intérieure de bougies en toile métallique. Des essais satisfaisants ont été poursuivis jusqu'à des températures de 700°C environ. Des projets d'incinérateurs dotés de ce type de filtration sont actuellement en cours d'étude ou de réalisation. Le circuit d'épuration comporte un certain nombre de bougies filtrantes, un dispositif destiné à éliminer les poussières accumulées sur le média filtrant et le média filtrant lui-même lorsque la perte de charge devient prohibitive. Un système de pulvérisation permet ensuite de reconstituer la couche d'amiante défibrée sur la toile métallique de la bougie.

Par ailleurs, il n'est pas impensable de supposer que, les progrès de la technique aidant, certains matériaux nouveaux puissent être découverts qui permettraient de fabriquer des média filtrants résistant à la fois à des températures élevées (800 à 1000°C) et à une corrosion très sévère. Dans ce cas, l'élimination du noir de carbone issu de la combustion s'effectuerait sur le média filtrant (par combustion).

Risques de corrosion

Ces risques sont intimement liés à la nature des résidus à incinérer. Dans l'incinérateur de Marcoule, la corrosion s'est révélée inquiétante pendant les premiers essais en inactif, mais cette difficulté a été surmontée par l'évacuation des condensats acides de l'échangeur et le calorifugeage de l'installation. La corrosion ne pose pas de problèmes particuliers dans l'incinérateur proprement dit, l'échangeur haute température et le cyclone. En revanche, elle pose des problèmes dans l'échangeur basse température et existe à un degré moindre dans le caisson des filtres à manches.

Une autre cause de diminution de la corrosion a été le remplacement du vinyle, dont la combustion provoquait la formation de quantités importantes d'acide chlorhydrique, par du polyéthylène, qui a une composition chimique plus favorable. Cela a eu toutefois pour conséquence une réduction sensible de la capacité de traitement de l'incinérateur; le polyéthylène a, en effet, un pouvoir calorifique très supérieur à celui du vinyle (8500 à 9000 kcal/kg au lieu de 6000 à 6500 kcal/kg) et il a fallu espacer davantage les charges pour maintenir la température du four dans les limites admissibles (700 à 1100°C) et réduire la formation de noir de carbone susceptible d'entraîner des risques d'incendie et de colmatage rapide de l'échangeur et des filtres.

Enfin, dans le cas d'incinération d'huiles fluorées susceptibles d'enraîner la formation d'acide fluorhydrique, un procédé breveté [9] de neutralisation des éléments en suspension et en solution est utilisé. Ce procédé consiste en l'addition d'octoate de calcium, la quantité ajoutée étant en rapport avec la teneur en fluor et l'indice d'acidité libre. Le principe de la neutralisation réside dans la décomposition au niveau des brûleurs de l'octoate de calcium et la formation instantanée de fluorure de calcium avec l'acide fluorhydrique. L'inconvénient principal du procédé provient du dépôt de ce fluorure de calcium dans les suies.
Combustion et post-combustion

Si les déchets à introduire dans l’incinérateur sont combustibles, le démarrage et l’entretien de la combustion doivent néanmoins être facilités par des brûleurs. Ceux-ci peuvent être alimentés en propane, gaz de ville ou mazout. Les deux premiers ont l’inconvénient de libérer en brûlant une quantité d’eau assez importante qui favorisera les condensations dans le circuit de fumée en augmentant la température du point de rosée. Le mazout émet en revanche de l’anhydride sulfurique provenant de l’oxydation du soufre toujours présent à l’état d’impureté.

Différents modes de combustion peuvent être envisagés. Dans le mode normal, l’air primaire préchauffé ou non arrive par le bas dans le cendrier et sort par le haut du foyer avec les fumées; la teneur en imbrûlés dans les cendres est minimale mais les risques d’entraînement de poussières dans les fumées sont certains. Dans le mode de combustion inversé, l’air primaire de combustion généralement préchauffé arrive par le sommet du foyer et s’échappe avec les fumées à la base du cendrier; les risques d’entraînement des poussières dans les fumées sont assez réduits mais la teneur en imbrûlés est plus importante.

Le type de chargement influe aussi sur l’entraînement des particules. La couche épaisse évite un entraînement important de poussières puisque le lit de résidus forme filtre; en revanche, la teneur en imbrûlés risque d’être importante, la combustion est ralentie, et certains produits de distillation peuvent éventuellement être entraînés, augmentant ainsi le danger d’incendie. La couche mince donne une combustion plus complète mais les risques d’entraînement d’imbrûlés sont plus grands.

Enfin, un dispositif de post-combustion convenablement étudié et utilisé permet de diminuer la concentration en imbrûlés dans les fumées et par là même soulage le travail du dispositif d’épuration et limite les risques d’incendie dus à l’accumulation de noir de carbone sur les préfiltres.

Nature des matériaux disponibles

Lors de la conception de l’installation, l’utilisation d’aciers spéciaux très onéreux avait été écartée, toutefois, ceci n’implique pas que la recherche systématique de nouveaux matériaux ait été négligée.

Ainsi, en ce qui concerne l’ensemble refroidisseur de fumées, différents types de tubes ont été essayés. Des tubes de verre sur support d’acier ont tenu pendant un laps de temps correspondant à l’incinération de 30 tonnes de résidus. Des tubes en acier inoxydable au cuivre ou en acier inoxydable au titane n’ont tenu que pendant un laps de temps correspondant à l’incinération de 50 à 60 tonnes de déchets. En revanche, des tubes en acier au molybdène et des tubes en titane résistent encore après l’incinération de 220 tonnes de résidus.

Pour le caisson de filtres à manches, deux types de manches en fibre de verre ont été essayés: normales et graphitées. Ces dernières sont actuellement en service mais, bien qu’elles résistent à des températures supérieures, leur durée de vie (cinq mois environ) semble inférieure à celle des manches normales.

Pour le caisson de filtration dite absolue, différents types de préfiltres ont été testés. Le choix actuel préfiltre/pare-flamme et filtres absolus en fibre de verre a été guidé par des raisons de facilité d’approvisionnement et de montage.
Il est à noter également que sur les ventilateurs actuels la turbine est en Uranus BG (les revêtements plastiques sont à proscrire car la force centrifuge tend à les décoller) et la volute est en acier avec revêtement de matière plastique.

Enfin, le caisson de la tour de neutralisation réalisé en acier ébonité n'a pas, jusqu'à présent, posé de problèmes. Des pièces à revêtement d'hypalon ont dû être remplacées, mais il faut souligner qu'elles avaient eu à souffrir d'un début d'incendie dans le dispositif d'épuration.

Un essai est actuellement en cours avec des éléments de raccordement en polyester stratifié.

**Prix des matériaux disponibles**

Etant donné le prix élevé des aciers spéciaux, des essais ont été effectués avec des matériaux plastiques tels que le lucoflex et le polyester stratifié, moins sensible à la corrosion. Les parties non soumises aux vibrations seront donc à l'avenir équipées en éléments plastiques; gaines de sortie de l'échangeur basse température, gaines de raccordement entre les divers éléments du dispositif d'épuration.

**Nature des résidus à incinérer**

Les résidus radioactifs solides collectés dans un centre atomique industriel représentent un assortiment très diversifié. Cependant, ces déchets combustibles ne correspondent qu'à un lot limité de matières premières, cellulosiques ou plastiques. Ils sont caractérisés par leur pouvoir calorifique utile, leur état physique et leur nature chimique. Cette diversité rend indispensable un triage préalable destiné, d'une part, à éviter l'introduction de combustibles dangereux, de fines poussières ou de solvants, et, d'autre part, à éliminer les matières non combustibles (métal par exemple) et permettre un équilibre judicieux du régime de la combustion par l'élaboration de lots de déchets hétérogènes. Cette pratique évite les dégagements importants de noir de carbone dus à l'incinération de lots importants de matières riches en carbone (caoutchouc ou polyéthylène). Ces dégagements, étant susceptibles de provoquer un colmatage rapide des préfiltres, augmentent les risques d'incendie.

Les déchets radioactifs liquides appartiennent en général à la catégorie des huiles minérales de graissage. Il convient avant toute chose de les filtrer afin d'éliminer les particules susceptibles d'obturérer les buses des brûleurs. D'autres liquides radioactifs peuvent également être incinérés: solvants lourds ou résidus de distillation.

**DESCRIPTION D'UNE INSTALLATION**

L'installation (fig. 1 et 2) édifiée sur le Centre de production de plutonium de Marcoule par le Service de protection contre les radiations et d'assainissement radioactif [10] comporte:

- Une table de triage séparée permettant un équilibrage judicieux des lots de déchets à incinérer;
- Le sas de chargement de l'incinérateur;
FIG. 1. Schéma de l'installation d'incinération de résidus radioactifs.

1. Chargeur automatique
2. Sas étanche à double porte
3. Ventilateur dépression
4. Porte coulissante
5. Porte basculante
6. Monte-charge poubelle
7. Boîte à gants ringard cendrier
8. Brûleurs
9. Cheminée d'expansion
10. Evacuation air chaud
11. Aspiration air frais
12. Caisson intermédiaire
13. Échangeur haute température
14. Échangeur basse température
15. Ventilateur
16. Conduit évacuation cendres
17. Cyclone de dépoussiérage
18. Obturateurs rotatifs
19. Filtre à manche
20. Préfiltres
21. Filtres absolus
22. Cuve de rétention des boues
23. Caisson de refroidissement
24. Tour de neutralisation
25. Filtre à impact
26. Filtres pare-étincelles
27. Souffleur suies
28. Ventilateur de décolmatage
29. Siphon.

- L'incinérateur proprement dit avec une chambre de combustion, une chambre de post-combustion et une chambre de détente et de fin de combustion; les brûleurs sont alimentés au propane, le mode de combustion est du type normal et le chargement s'effectue en couche mince;

- Un ensemble refroidisseur de fumée composé d'un échangeur haute température (1000-400°C) et d'un échangeur basse température (400-150°C) raccordés par un caisson de liaison refroidi extérieurement; le refroidissement des échangeurs s'effectue par air frais prélevé à l'extérieur; deux types de tubes sont actuellement en service: tubes en acier spécial inoxydable au molybdène et tubes en acier au titane;
FIG. 2. Vue partielle de l'installation: sas de chargement et foyer.

- Un pré-séparateur cyclonique en acier doux avec trémie et obturateur rotatif permettant un dépoussiérage grossier des fumées; son efficacité est de 90% pour des particules de 10 μm;

- Un caisson de panneaux pare-étincelle anti-flamme en acier inoxydable; la surface de refroidissement présentée aux étincelles et aux flammes en cas d'incendie est constituée par un épais matelas de treillis en acier inoxydable;

- Un caisson de filtres à manches à décolmatage automatique; ce caisson cylindrique étanche en acier doux contient 32 manches en fibre de verre avec imprégnation de graphite; ce type de manche résiste à une température de 350°C, mais en réalité ne reçoit que des gaz à une température maximale de 170°C; la surface filtrante totale est de 122 m²; le décolmatage des manches s'effectue par suctions suivies de gonflages grâce à un système de registres manœuvrés par vérins pneumatiques et à un programmateur; l'efficacité des filtres à manches est de 98% pour des particules d'un diamètre moyen égal ou supérieur à 1 μm et de 90% environ pour des particules de 0,3 μm;

Un caisson de préfiltres et de filtres absolus prévu pour un débit d'air de 4000 m³/h à une température de 120°C; ce caisson en acier inoxydable comporté des panneaux combinés de préfiltres pare-étincelles constitués d'un matelas de laine de verre maintenu entre deux couches de treillis métallique, et des filtres du type dit absolu en papier de verre plié supporté par des intercalaires en aluminium; l'efficacité des filtres absolus, déterminée par un essai au bleu de méthylène, est de 99,95%;
- Un groupe de deux ventilateurs d'extraction en parallèle de 5000 m$^3$/h dont un est utilisé en secours (fig. 3); leur turbine est en Uranus BG et leur volute en acier recouvert de plastique; en cas de coupure ou de panne métallique sur l'un des ventilateurs, la reprise du ventilateur défaillant est assurée automatiquement par la mise en service, soit du groupe électrogène de secours asservi au manque de tension sur le réseau, soit du ventilateur de secours, grâce à un signal transmis par le pressiomètre du ventilateur en panne;

- Un groupe de refroidissement et de neutralisation des gaz composé d'un caisson de refroidissement suivi d'une tour de neutralisation des gaz avant rejet à la cheminée; le caisson de refroidissement est en acier doux avec revêtement interieur en hypalon; la température des gaz à l'entrée est de 120°C et à la sortie de 60°C; la tour de ruissellement et son bassin de pied sont en acier ébonité; le remplissage est assuré par une charge de lave concassée; la solution sodée destinée au refroidissement et à la neutralisation est recyclée afin d'éviter l'évacuation d'un volume d'effluents important; enfin, un caisson de filtres à impact placé entre le sommet de la tour et la cheminée de rejet empêche les entraînements vésiculaires dans les gaz épurés.

BILAN RADIOACTIF

L'étude de l'installation a été effectuée pour une capacité de traitement de 100 kg/h avec des déchets dont la composition moyenne en volume était:
SUTRA-FOURCADE et al.

Polychlorure de vinyle : 40%
Coton : 25%
Papier carton : 10%
Caoutchouc : 10%
Bois : 5%
Polyéthylène : 5%
Bitume : 5%

Toutefois, les déchets réels approvisionnés à partir de la table de triage après la mise en service de l'installation correspondaient à la composition :

Coton chiffons : 56%
Polyéthylène : 13%
Bois : 16%
Papier carton : 10%
Caoutchouc : 5%

Cette composition a par la suite évolué. Elle est actuellement :

Polyéthylène : 80%
Bois : 5%
Papier : 8%
Divers : 7%

Par ailleurs, l'incinérateur, en plus de déchets solides, brûle égallement des huiles contaminées. Au total, la capacité de traitement est :

Déchets solides + huiles : 60 à 70 kg/h de déchets solides
20 à 25 litres/h d'huile
Huile seulement : 50 litres/h

L'incinérateur fonctionne 20 à 22 heures par jour dont 11 à 13 heures en brûlant uniquement de l'huile et le reste du temps en brûlant de l'huile et des déchets solides. La quantité de résidus incinérés depuis la mise en service en 1963 s'élève à 430 tonnes, dont 250 tonnes d'huile et 180 tonnes de déchets solides. Ces derniers correspondent à un volume de 1500 m³ environ. Le facteur de réduction en poids est de 4/100 et celui en volume est très approximativement de 1,2/100.

Répartition granulométrique des poussières

Des prélèvements de poussières sur des filtres membranes ont été réalisés à l'entrée du cyclone et à l'entrée du caisson des filtres absolus. Ces prélèvements ont été examinés au microscope, le plus petit diamètre mesurable étant 0,5 μm. Les résultats obtenus sont indiqués dans le tableau I.

Efficacité des différents étages de filtration

Le pouvoir d'arrêt des différents étages de filtration a été contrôlé à la fois par des mesures de radioactivité et des mesures massiques. Les résultats obtenus pour des régimes normaux de combustion sont donnés dans le tableau II.
TABLEAU I. REPARTITION GRANULOMETRIQUE DES POUSSIÈRES

<table>
<thead>
<tr>
<th>Diamètre ( \phi ) des poussières (( \mu m ))</th>
<th>Nombre de poussières de diamètre supérieur à ( \phi )(%)</th>
<th>Entée du cyclone</th>
<th>Entée des filtres absolus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1964</td>
<td>1967</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1964</td>
<td>1967</td>
</tr>
<tr>
<td>0,5</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>45</td>
<td>36</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>11,5</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>5,9</td>
<td>2,2</td>
<td>3,7</td>
</tr>
<tr>
<td>4</td>
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<tr>
<td>10</td>
<td>0,7</td>
<td>0,07</td>
<td>0,06</td>
</tr>
<tr>
<td>20</td>
<td>0,26</td>
<td>0,006</td>
<td>0,005</td>
</tr>
</tbody>
</table>

TABLEAU II. EFFICACITÉ DES DIFFÉRENTS ETAGES DE FILTRATION

<table>
<thead>
<tr>
<th>Etage de filtration</th>
<th>Pouvoir d'arrêt (%)</th>
<th>Mesures de radioactivité</th>
<th>Mesures massiques</th>
<th>Test au toron fumant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone</td>
<td></td>
<td>( \alpha )</td>
<td>( \beta \gamma )</td>
<td>10</td>
</tr>
<tr>
<td>Filtre à manche</td>
<td>( 98,8 \pm 99,5 )</td>
<td>97 à 98,5</td>
<td>non</td>
<td>mesureable</td>
</tr>
<tr>
<td>Filtre absolu et tour de neutralisation</td>
<td>90</td>
<td>98 à 99</td>
<td>0,3 - 0,4 ( \mu m )</td>
<td></td>
</tr>
</tbody>
</table>

Ces résultats mettent en évidence l'importance considérable des filtres à manches pour la protection du caisson de filtres absolus. Il est possible d'en déduire que la combustion d'une moyenne de 500 kg/j de résidus entraîne la production de 40 kg/mois de suies. Les valeurs du pouvoir d'arrêt massique et du pouvoir d'arrêt déduit des mesures de radioactivité \( \beta \gamma \) correspondent à une composition réelle de déchets se répartissant ainsi: polyéthylène 60%, coton 12%, bois 10%, papier carton 8%, PVC 5%, caoutchouc 5%. Le pouvoir d'arrêt déduit des mesures de radioactivité \( \alpha \) a été vérifié sur des résidus spéciaux ne correspondant pas à la composition ci-dessus (majorité de PVC); c'est ce qui explique la différence constatée sur l'efficacité du cyclone.

Répartition de la radioactivité dans le circuit

L'exploitation des mesures faites sur les prélèvements effectués pendant une période correspondant à l'incinération de 354 tonnes de résidus
### TABLEAU III. REPARTITION DE LA RADIOACTIVITE DANS LE CIRCUIT

<table>
<thead>
<tr>
<th>Nature</th>
<th>Quantité totale</th>
<th>Radioactivité des émetteurs $\beta$</th>
<th>Radioactivité des émetteurs $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Activité totale (mCi)</td>
<td>%</td>
</tr>
<tr>
<td>Cendres à 15% d'eau</td>
<td>8247 kg</td>
<td>2996</td>
<td>94,3</td>
</tr>
<tr>
<td>Boues</td>
<td>79,5 m³</td>
<td>170</td>
<td></td>
</tr>
<tr>
<td>Effluents de la tour de neutralisation</td>
<td>24,0 m³</td>
<td>12</td>
<td>5,7</td>
</tr>
<tr>
<td>Rejet de cheminée</td>
<td>$3,8 \times 10^3$ m³</td>
<td>$1,1 \times 10^{-1}$</td>
<td>négligeable</td>
</tr>
</tbody>
</table>

(184 tonnes de résidus solides et 170 tonnes d'huile) est présentée dans le tableau III.

Ces résultats doivent être considérés comme des valeurs approchées eu égard aux difficultés rencontrées pour prélever dans des volumes importants ou non homogènes des échantillons parfaitement représentatifs.

La valeur moyenne de la radioactivité $\beta$ des résidus incinérés depuis 1965 est faible, 9 mCi/t, et reste de l'ordre de grandeur de celle observée en 1964 au début du fonctionnement de l'incinérateur, soit 13,7 mCi/t, ou en 1965, soit 15 mCi/t [5,7].

La diminution apparente enregistrée résulte de la proportion croissante de la quantité d'huile incinérée.

La production moyenne de cendres est de 23,4 kg/t. Cette valeur est en diminution par rapport aux résultats obtenus en 1965 (31 kg/t) du fait de l'accroissement des quantités d'huiles incinérées. Le volume des boues résultant de l'entraînement des suies par les eaux de rinçage représente en moyenne 225 litres/t, soit environ 2,5 kg de suies sèches.

La valeur de la radioactivité globale des cendres représente près de 95% de la valeur de la radioactivité totale $\beta \gamma$ des déchets brûlés et plus de 99% de leur radioactivité $\alpha$. Un essai effectué avec des résidus uniquement contaminés en $\alpha$ a fait apparaître une proportion de radioactivité dans les cendres de plus de 99,9%.

Par ailleurs, il apparaît que moins de 0,01% de la valeur de la radioactivité totale $\beta \gamma$ échappe au dispositif d'épuration et se trouve rejetée par la cheminée dans l'atmosphère. L'ensemble du dispositif d'épuration des gaz possède donc un pouvoir d'arrêt global supérieur à 99,99%. Ainsi, à la sortie de la cheminée, les gaz ont une radioactivité atmosphérique mesurée dans nos régions en 1963 à la suite des retombées consécutives aux essais nucléaires ($4 \times 10^{-12}$ Ci/m³ $\beta \gamma$).

La répartition en pourcentage de la radioactivité des éléments émetteurs $\alpha$ et $\beta \gamma$ dans les différents étages du circuit d'épuration est donnée dans les tableaux IV et V.
Ces tableaux montrent que la radioactivité des suies est due pour une grande part au soufre-35, radioélément créé par l'activation dans les réacteurs du bisulfure de molybdène contenu dans les produits de graissage (réaction $^{34}$S(n, $\gamma$) $^{35}$S). Le soufre est transformé, au cours de la combustion, en gaz sulfureux dont une partie est piégée par les suies qui ont un caractère basique. Le reste, toujours sous forme de gaz sulfureux, passe à travers les filtres absolus et se trouve piégé dans la tour de neutralisation sous forme d'un mélange de sulfite de sodium et de sulfate de sodium. Le $^{35}$S est pratiquement le seul élément qui échappe aux filtres absolus.

Les variations dans les proportions relatives des différents radioéléments dans les cendres d'une part et dans les suies d'autre part rendent compte des volatilités respectives de ces éléments. Ainsi, le cérium...
et le zirconium ne présentent qu'une faible volatilité; par contre, le césium et le ruthénium se trouvent en proportion plus grande dans les suies.

Le rapport des deux isotopes du strontium $^{89}\text{Sr}/^{90}\text{Sr}$ reste sensiblement constant aux différents stades de la combustion, ce qui est logique et permet a posteriori une vérification des mesures radiochimiques.

En considérant les chiffres de la troisième colonne du tableau IV, il ne faut pas perdre de vue que les valeurs de la radioactivité mesurées dans les effluents de la tour de neutralisation sont très faibles. Ainsi, le plutonium est intégralement retenu dans les cendres et les suies; quant à l'uranium, il atteint la tour de neutralisation, mais n'existe toutefois qu'à l'état de traces dans les effluents. Sa présence peut être attribuée au fait que la combustion simultanée de composés fluorés a provoqué la formation d'hexafluorure d'uranium, composé gazeux, qui a pu ainsi traverser les filtres absolus. Il est naturellement décomposé dans la tour de neutralisation.

Au cours de l'étude de l'incinérateur, il était apparu nécessaire de prendre des précautions spéciales pour l'arrêt de l'iode-131 et du ruthénium-103 et 106, susceptibles de se volatiliser dans le foyer. La tour de neutralisation avait donc été réalisée non seulement dans le but de neutraliser les gaz tels que l'acide chlorhydrique, mais aussi pour piéger ces radionucléides. Jusqu'à présent, les résidus incinérés ont toujours été contaminés par des produits de fission beaucoup trop vieux pour que des quantités significatives d'iode-131 puissent être mises en évidence dans le circuit d'épuration. En ce qui concerne le ruthénium, la plus grande partie demeure dans les cendres, seule une proportion de 10% est emportée dans les suies.

CONCLUSION

Le système d'épuration des gaz à quatre étages: cyclone, filtre pare-étincelles, filtres à manche, préfiltres/filtres absolus, conduit à un pouvoir d'arrêt global supérieur à 99,99%.

Du point de vue technique, le problème essentiel réside dans la corrosion. Les solutions techniques de filtration utilisables à l'époque de la conception et de la construction de l'installation nécessitaient le refroidissement des gaz.

Il est certain que la voie choisie n'est pas sans inconvénients. La réduction de l'étage basse température de l'échangeur (entre 250 et 150°C par exemple) permettrait de diminuer les frais d'entretien car les interventions seraient limitées à des éléments de plus petites dimensions. Les autres solutions (dilution par l'air, refroidissement par pulvérisation d'eau à contre-courant) ne font que déplacer les problèmes de la corrosion et de la filtration. La dilution supprime l'échangeur mais augmente le volume d'air à traiter tandis que le refroidissement par pulvérisation augmente la corrosion (milieu humide à haute température), entraîne la formation de boues créant un risque de colmatage et conduit à la production d'effluents radioactifs qui devront être traités.

Il semblerait donc préférable de s'orienter vers des solutions permettant la filtration des gaz à haute température. Des filtres résistant à des températures élevées permettraient alors l'élimination ou la combustion en
continu du noir de carbone qui s'y déposerait. Des solutions de ce type ne sont encore qu'au stade de l'expérimentation. Il faut toutefois noter qu'elles ne permettent pas de résoudre le problème de l'élimination des produits gazeux (iode, soufre, mercure, etc.) qui ne peuvent être arrêtés que dans une tour de lavage.

REFERENCES


DISCUSSION

M.W. FIRST (Chairman): If the only purpose of the neutralization tower is to remove acid gases before discharge to the atmosphere, might it not be possible to substitute a solid chemisorbant, effective for acid gases, with equal or better results, in order to have an all-dry system?

Y. SUTRA-FOURCADE: The neutralization tower was built not only to neutralize the acidity of the gases, but also to trap iodine-131 and ruthenium-103 and -106. The absorbent would therefore have to perform the same functions.

G.E. BENEDICT: What were the gas and liquid flow rates in the neutralization tower?

Y. SUTRA-FOURCADE: The air flow was 4000 m³/h. Liquid flowed in a closed circuit. I do not remember the exact flow-rate, but it would be about 4 m³/h.
FABRIC FILTRATION OF FLUE GASES FROM AN ACTIVE INCINERATOR: STUDIES ON DESIGN OPTIMIZATION AND OPERATIONAL ANALYSIS

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BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

Abstract

FABRIC FILTRATION OF FLUE GASES FROM AN ACTIVE INCINERATOR: STUDIES ON DESIGN OPTIMIZATION AND OPERATIONAL ANALYSIS. The paper describes the use of bag filters in the dry gas cleaning system of an incinerator as a safe and economical method for treatment of the flue gas from an incinerator burning low-level radioactive solid combustibles. Various types of fabrics were evaluated to find the filtration characteristics during the entire cycle of operation. Data on pilot plant studies carried out to optimize a suitable design of fabric filter for flue gas cleaning is included. Cost comparison of different fabrics based on the life of the fabric and the cost of fabric filtration per unit of solid wastes treated has been given. The physical, chemical and radiochemical nature of the aerosols encountered in various parts of the incinerator system are described.

1. INTRODUCTION

Incineration is a widely accepted method for the volume and weight reduction of radioactive solid combustible wastes. The main problem associated with incineration is the cleaning of flue gases containing complex airborne pyrolitic products of combustion besides radioactivity. However, it was found that the problem of gas cleaning can be simplified to some extent by adopting better means of combustion, taking special care to reduce the volatile condensible matter arising from the burning pile and escaping to the colder regions of the system. If improved systems for combustion of the waste are suitably combined with modern techniques of fabric filtration, it is expected that the cleaning of flue gases from active incinerators will be a simpler and cheaper treatment process. Studies were undertaken on this aspect to gather operational data which will be directly applicable for the design of fabric filtration units for similar plants.

Studies on locally available fabrics have been carried out to assess their suitability for cleaning flue gases from an active incinerator. Studies on special types of fire and chemical resistant fabrics recently put onto the world market are yet to be completed. Data on operational analysis of a bag filter employing various types of fabrics for cleaning flue gases from the incinerator burning low-level radioactive solid combustible wastes are the subject of this report.
2. DESIGN FEATURES OF THE INCINERATOR PLANT

2.1. General

A 100-lb/h incinerator plant is being operated for regular treatment of low-level solid combustible waste arising from various active plants and laboratories of the Establishment. The above plant comprises a multi-chamber refractory-lined steel-cased incinerator furnace and a dry gas cleaning system which includes a cyclone, fabric filters and a high efficiency filter. Figure 1 represents the flow diagram of the incinerator plant.

2.2. Furnace and accessories

The incinerator consists of primary and secondary combustion chambers separated by two bridge walls with a downpass. The walls and the arch of the furnace are made of extra-heavy refractory lining of 18 inches thickness, thus having a high heat storage capacity. Figure 2 gives the details of the incinerator furnace.

The combustion air, about 150% in excess of the estimated theoretical requirements, is distributed as under fire, over fire and secondary air. Two low-pressure adjustable oil burners are provided in the primary chamber and the downpass for auxiliary heating.

2.3. Gas Cleaning Equipment

2.3.1. Cyclone

A standard cyclone collector made of type 316 stainless steel is provided as a first stage in the flue gas clean-up system. The velocity at the inlet of the unit is 3000 ft/min.
2.3.2. Fabric filter

Figure 3 shows the details of the cleanable type of fabric filter used for obtaining the data presented in this paper. Since it was mainly intended to study the characteristics of filter fabric, a simple design of bag housing was employed. The fabric filter contains one large filter bag of 4 ft 2 in. in diameter and 18 ft in length providing about 200 ft² of filtration area. Cleaning is effected by mechanical shaking along the vertical axis of the bag. Sampling of flue gas at the upstream and downstream side of the fabric filter has been carried out using CWS-6 filter paper. Two identical fabric filters are used to make the operation continuous.

2.3.3. High-efficiency filters

High-efficiency filters of standard construction are provided as the final stage of cleaning.

3. TYPE OF WASTE

The wastes consist of contaminated paper mops, rags, rubber, plastics etc., as commonly collected from reactors and research laboratories. The maximum radiation level of the wastes charged to the incinerator was 20 mR/h.
4. PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE AEROSOL IN THE FLUE GASES

Details of the physical, chemical and radiochemical nature of the dust collected in the fabric filter are given in Table I. The analysis is representative of the nature of dust collected during the entire period of study while burning the type of wastes described above.

5. OPERATIONAL DATA OF VARIOUS FABRICS

5.1. General

To arrive at a suitable design of fabric filter for cleaning the incinerator flue gases, studies were undertaken for the characterization of various filter fabrics which include cotton, terylene, wool, dacron and glass. Important parameters like filtration efficiency, cake discharge characteristics and plugging characteristics were studied. Physical characteristics of interest for these fabrics are given in Table II.
As a result of these investigations, it was possible to establish the following.

(1) Feasibility of using the specific type of filter fabric for the required service
(2) Area of the filter fabric required for a given capacity of the incinerator plant
(3) Optimum pressure drop across the fabric filter
(4) Frequency of bag cleaning
(5) Cost of fabric filtration based on the useful life of the filter bag.

5.2. Plugging and cake discharge characteristics

The pressure drop across a clean filter bag is very low and is of the order of a fraction of 1 m.w.g. During the first few hours of operation of the plant the pressure drop across the filter bag rises because of dust collection. During cleaning cycles the pressure drop across the filter bag drops. However, this is always higher than the pressure drop of a clean fabric. This is due to the reduction in porosity of the fabric because of permanent deposition of dust particles in the interfibre space and sticking of the dust to the surface of the fabric. The pressure drop difference between the lower normal value during operation and that of a clean filter bag is a measure of plugging and cake discharge characteristics of the fabric.

5.3. Filtration efficiency

Filtration efficiency of the fabrics was evaluated both on weight basis and activity basis. The results are given in Tables III to VI.

**TABLE I. PHYSICAL AND RADIOCHEMICAL CHARACTERISTICS OF DUST COLLECTED IN THE FABRIC FILTER**

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Black powder apparently free of oily matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.5</td>
</tr>
<tr>
<td>Combustibles</td>
<td>68%</td>
</tr>
<tr>
<td>Ash content</td>
<td>32%</td>
</tr>
<tr>
<td>Activity analysis (Treatment with boiling conc. HNO₃)</td>
<td></td>
</tr>
<tr>
<td>Gross activity</td>
<td>$2.34 \times 10^{-5}$ µCi/mg</td>
</tr>
<tr>
<td>Caesium-137</td>
<td>$2.14 \times 10^{-6}$ µCi/mg</td>
</tr>
<tr>
<td>Strontium-90</td>
<td>$5.16 \times 10^{-7}$ µCi/mg</td>
</tr>
<tr>
<td>Phosphorus-32</td>
<td>$4.29 \times 10^{-7}$ µCi/mg</td>
</tr>
<tr>
<td>Serial No.</td>
<td>Fabric</td>
</tr>
<tr>
<td>------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1</td>
<td>Cotton Flannel</td>
</tr>
<tr>
<td>2</td>
<td>Terylene Felt</td>
</tr>
<tr>
<td>3</td>
<td>Wool Fabric</td>
</tr>
<tr>
<td>4</td>
<td>Dacron Fabric</td>
</tr>
<tr>
<td>5</td>
<td>Glass Fabric</td>
</tr>
</tbody>
</table>
TABLE III. FILTRATION EFFICIENCY OF COTTON FLANNEL FILTER BAG
(Weight basis)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Operation (h)</th>
<th>% efficiency on weight basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>95.85</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>97.29</td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>99.19</td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>99.31</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>78.23</td>
</tr>
</tbody>
</table>

5.4. Minimum area requirements of filter fabric

From practical considerations, the fabric filter was operated at a pressure drop not exceeding 5 in. w.g., as may be the general practice in such systems. For installations operating within this pressure differential, minimum filtration area required can be readily estimated for the operation of a particular fabric for a similar service using the experimental data presented in Table VII.

5.5. Frequency of bag cleaning

Frequency of bag cleaning was decided on the basis of the rate of rise of pressure drop in each cycle and the maximum pressure drop allowed across the fabric filter.

5.6. Cost comparison of different fabrics

A cost comparison of various fabrics based on the performance is given in Table VIII. For this purpose, only the cost of the fabric is included as the power requirements for the operation of the fabric filter are negligible.

6. DISCUSSION

6.1. Temperature considerations

The hot flue gases from the furnace have to be suitably cooled so that filtration can be carried out below the maximum temperature the fabric can withstand. The method of providing an extra length of duct for heat dissipation has proved very economical. This again can be combined with dilution of the hot flue gas with atmospheric air to achieve good
TABLE IV. FILTRATION EFFICIENCY OF TERYLENE FELT FILTER BAG  
(Weight and activity basis)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Operation (h)</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Weight basis</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>92.4</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>87.5</td>
</tr>
<tr>
<td>3</td>
<td>22</td>
<td>86.0</td>
</tr>
<tr>
<td>4</td>
<td>31</td>
<td>96.2</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>96.0</td>
</tr>
<tr>
<td>6</td>
<td>77</td>
<td>79.5</td>
</tr>
<tr>
<td>7</td>
<td>93</td>
<td>74.1</td>
</tr>
<tr>
<td>8</td>
<td>103</td>
<td>99.0</td>
</tr>
<tr>
<td>9</td>
<td>121</td>
<td>83.2</td>
</tr>
<tr>
<td>10</td>
<td>141</td>
<td>88.9</td>
</tr>
<tr>
<td>11</td>
<td>156</td>
<td>77.8</td>
</tr>
<tr>
<td>12</td>
<td>171</td>
<td>75.1</td>
</tr>
<tr>
<td>13</td>
<td>187</td>
<td>41.5</td>
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<td>14</td>
<td>201</td>
<td>40.6</td>
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<td>15</td>
<td>212</td>
<td>63.9</td>
</tr>
<tr>
<td>16</td>
<td>222</td>
<td>81.2</td>
</tr>
<tr>
<td>17</td>
<td>234</td>
<td>70.0</td>
</tr>
<tr>
<td>18</td>
<td>240</td>
<td>24.0</td>
</tr>
</tbody>
</table>
## TABLE V. FILTRATION EFFICIENCY OF WOOL FABRIC FILTER BAG
(Weight and activity basis)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Operation (h)</th>
<th>% Efficiency</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Weight basis</td>
<td>Alpha activity basis</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>97.4</td>
<td>66.9</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>95.4</td>
<td>88.6</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>61.4</td>
<td>98.8</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>79.9</td>
<td>72.8</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>98.8</td>
<td>98.9</td>
</tr>
<tr>
<td>6</td>
<td>44</td>
<td>83.7</td>
<td>92.9</td>
</tr>
<tr>
<td>7</td>
<td>49</td>
<td>76.5</td>
<td>98.3</td>
</tr>
<tr>
<td>8</td>
<td>57</td>
<td>88.0</td>
<td>88.9</td>
</tr>
<tr>
<td>9</td>
<td>68</td>
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<td>10</td>
<td>76</td>
<td>93.4</td>
<td>93.9</td>
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<td>11</td>
<td>81</td>
<td>71.6</td>
<td>97.5</td>
</tr>
<tr>
<td>12</td>
<td>87</td>
<td>98.2</td>
<td>96.2</td>
</tr>
<tr>
<td>13</td>
<td>90</td>
<td>85.5</td>
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<td>15</td>
<td>106</td>
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<td>16</td>
<td>115</td>
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<td>120</td>
<td>88.8</td>
<td>81.8</td>
</tr>
<tr>
<td>18</td>
<td>128</td>
<td>79.1</td>
<td>87.9</td>
</tr>
<tr>
<td>19</td>
<td>139</td>
<td>92.9</td>
<td>75.2</td>
</tr>
<tr>
<td>20</td>
<td>141</td>
<td>50.8</td>
<td>60.4</td>
</tr>
</tbody>
</table>
TABLE VI. FILTRATION EFFICIENCY OF GLASS FABRIC FILTER BAG (Weight and activity basis)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Operation (h)</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Weight basis</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>20.7</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>26.7</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>97.1</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>98.0</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>79.0</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>88.1</td>
</tr>
<tr>
<td>7</td>
<td>113</td>
<td>89.4</td>
</tr>
<tr>
<td>8</td>
<td>118</td>
<td>80.3</td>
</tr>
<tr>
<td>9</td>
<td>120</td>
<td>15.8</td>
</tr>
<tr>
<td>10</td>
<td>124</td>
<td>94.1</td>
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<tr>
<td>11</td>
<td>126</td>
<td>57.0</td>
</tr>
<tr>
<td>12</td>
<td>130</td>
<td>90.9</td>
</tr>
<tr>
<td>13</td>
<td>145</td>
<td>70.6</td>
</tr>
<tr>
<td>14</td>
<td>159</td>
<td>32.2</td>
</tr>
</tbody>
</table>
TABLE VII. CHARACTERISTICS OF FILTER FABRICS FOR CLEANING FLUE GASES FROM THE INCINERATOR

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Minimum area of the filter fabric ft² per 100 lb/h incinerator capacity (ft²)</th>
<th>Pressure drop across the fabric filter (in w.g.)</th>
<th>Frequency of bag cleaning</th>
<th>Frequency of bag replacement (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton flannel</td>
<td>200</td>
<td>2.5</td>
<td>1 h</td>
<td>36</td>
</tr>
<tr>
<td>Terylene felt</td>
<td>200</td>
<td>3.0</td>
<td>8 h</td>
<td>240</td>
</tr>
<tr>
<td>Wool fabric</td>
<td>200</td>
<td>2.0</td>
<td>8 h</td>
<td>160</td>
</tr>
<tr>
<td>Dacron fabric</td>
<td>200</td>
<td>5.0</td>
<td>15 min</td>
<td>42</td>
</tr>
<tr>
<td>Glass fabric</td>
<td>200</td>
<td>5.0</td>
<td>15 min</td>
<td>200</td>
</tr>
</tbody>
</table>

TABLE VIII. COST COMPARISON OF FILTER FABRICS

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Fabric</th>
<th>Total life time of the bag (h)</th>
<th>Total quantity of waste treated (ft³)</th>
<th>Cost of the filter bag (Rupees)</th>
<th>Cost of fabric per ft³ of waste treated (Rupees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cotton flannel</td>
<td>36</td>
<td>300</td>
<td>160 000</td>
<td>0.53</td>
</tr>
<tr>
<td>2</td>
<td>Terylene felt</td>
<td>240</td>
<td>1730</td>
<td>2 000 000</td>
<td>1.15</td>
</tr>
<tr>
<td>3</td>
<td>Wool fabric</td>
<td>160</td>
<td>1236</td>
<td>1 000 000</td>
<td>0.80</td>
</tr>
<tr>
<td>4</td>
<td>Dacron fabric</td>
<td>40</td>
<td>353</td>
<td>600 000</td>
<td>1.70</td>
</tr>
<tr>
<td>5</td>
<td>Glass fabric</td>
<td>200</td>
<td>1766</td>
<td>1 000 000</td>
<td>0.56</td>
</tr>
</tbody>
</table>

control over the filtration temperature. In such a case it appears feasible to employ cheaper material like wool fabrics and felts, as they have been found to meet most of the requirements of an active incinerator system, though such materials are usually not favourably considered because of their temperature limitations.
6.2. Plugging and cake discharge characteristics

It has been observed that plugging and cake discharge characteristics of fabrics differ very much. In the case of glass filter fabric, as shown in Fig.4, the pressure drop of a bag in use normally comes down after cleaning to more or less equal to that of a clean bag. This represents low plugging and good cake discharge characteristics. However, in the case of flannel filter fabric as shown in Fig.5, the pressure drop of a bag in use is higher after cleaning than that of a clean bag. Recently certain manufacturers have claimed to have improved the cake discharge characteristics of fabrics by various treatments like silicon coating of glass fabric, etc. It will be interesting to carry out evaluation of such materials in incinerator flue gas cleaning systems.
Fig. 5 (cont.)
Fig. 6 (cont.)
Fig. 7 (cont.)
6.3. Filtration efficiency

It is observed that there is a wide variation in the efficiency of a filter bag during operation. This is because the efficiency of a bag just after a cleaning cycle is low. However, the overall efficiencies of all the filter bags are high and have been found to meet the requirements.

6.4. Frequency of cleaning

In this respect the characteristics of the fabrics differ very much. Also, for the same fabric, the frequency is not the same for the entire
operation as seen from Figs 4 to 8. However, it is observed that in case of terylene felt and wool fabrics frequency of cleaning is much less compared to that of glass and dacron fabrics. One of the reasons for this is attributed to the higher dust hold-up capacity of these fabrics, which are known to have larger interfibre spaces.

6.5. Frequency of bag replacement

Because of the varied type of chemical contamination in the flue gases and also because of the temperature and mechanical stresses which the bag material is subjected to during the operations, the bag fails after a certain period, needing replacement. The service life of the bag varies depending on its resistance to chemical corrosion and mechanical and temperature stresses etc. As indicated in Table VIII, the service life of a cotton flannel filter bag is 36 hours, whereas a wool filter bag serves as much as 240 hours.

BIBLIOGRAPHY


DISCUSSION

G.E. BENEDICT: What is the temperature of your bag filter?
K.T. THOMAS. The temperature of the flue gases at the entrance to the bag filter is about 250°F.

J. PRADEL: In view of Mr. Sutra-Fourcade's results, it might be possible to omit the cyclone from a well-adjusted incinerator. Do your results support this idea?

K.T. THOMAS: No. We feel that the cyclone serves a very useful purpose in removing relatively coarser dust with very good efficiency. The cyclone permits better overall dust collection than the fabric filter. An additional advantage is that the cyclone helps to cool the incoming gases.

J.F. FISH: Have you ever tried applying a filter aid to the surface of the fabric collector and have you experienced any problems in restoring the original pressure drops of fabric collectors by simple mechanical shaking?

K.T. THOMAS: No, we have not tried any filter aids. The fabric filter will not have the same efficiency and the pressure drop will not be the same after each shaking or cleaning of the bag. After some use, when the pressure drop increases or the fabric loses its efficiency, the filter is replaced. The report indicates the lives of different fabrics.

J.J. COHEN: Have you done any studies on the radioactivity content of the fly ash material collected in the cyclones?
K.T. THOMAS: We do not carry out such studies on a routine basis, although we may have made analyses on particular occasions for specific needs.

W.G. BELTER: As equipment costs are quite high in your country and the volume of your laboratory solid wastes is rather low, have you considered replacing the incineration of these wastes by some less expensive disposal method, such as land burial?

K.T. THOMAS: For the particular location of Trombay, near Bombay City, we have to reduce the wastes as much as possible, before using land for their disposal. Hence incineration is very useful at Trombay. The incinerator we have is not very costly and the operating costs are very reasonable, so we feel justified in using it for volume reduction.

For other locations of nuclear establishments outside Bombay, we have not yet taken a decision regarding incinerators.

Y. SUTRA-FOURCADE: Would it not be useful to improve the combustion rate so as to decrease the amount of unburnt matter and carbon black, by maintaining a post-combustion device in permanent operation?

K.T. THOMAS: In view of its design, our furnace is quite efficient. The wall and arch of the furnace are made of 18-inch thick refractory brick lining. Thus the furnace has a very high heat-storage capacity. Even though carbon black is present at the pre-filter stage, the concentration is such that it does not lead to any hazardous condition. The unburnt matter does not contain oily matter.

R.E. HOLMES: Do the wastes fed to your incinerator include animal wastes and plastic materials (particularly PVC)?

K.T. THOMAS: The incinerator is not used to burn animal wastes. As regards plastic materials, particularly PVC, we do not segregate the wastes, so there will be some plastic materials in the feed to the incinerator. Of this, only PVC can give serious trouble, but in our case the PVC content is too low to cause any trouble.
STUDIES OF INCINERATOR AIR CLEANING SYSTEMS

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Atomic Energy Research Institute,
Seoul, Korea

Abstract

STUDIES OF INCINERATOR AIR CLEANING SYSTEMS. The purpose of this paper is to report on the experimental results obtained with a small institutional radioactive waste incinerator and a gas cleaning system designed and constructed at the Korean Atomic Energy Research Institute. The system consists of an incinerator with overfire and tangential air supply, a dilution valve, a two-stage cyclone collector, a heat-exchanger, a filter of domestic technical-grade glass fibre and an electrostatic precipitator for final collection of the particles within the flue gas.

The particle collection efficiency of the gas cleaning units was measured and the distribution of the particle size at each unit was investigated. Sawdust charges with different concentrations of radioactive tracers, $^{198}$Au, $^{51}$Cr and $^{35}$S, were burned and the radioactive concentrations at the downstream end of the system were measured. As a result of the experiment, the following units may be recommended as a standard incineration system for small laboratories or in countries where filters or electrostatic precipitators are difficult to obtain or expensive. (1) incinerator with tangential firing, (2) dilution valve, (3) two-stage cyclone collector, (4) roughening filter of technical-grade glass fibre.

1. INTRODUCTION

As utilization of radioisotopes gradually increased at the Atomic Energy Research Institute, Seoul, the treatment and safe disposal of the waste to the surroundings became one of the major problems to be studied. Therefore in 1964 a waste disposal plant was constructed on the site and a three-stage liquid waste treatment facility, in which low-level waste ($10^{-5} - 10^{-6}$ $\mu$Ci/ml) is absorbed by local clay, was designed and constructed in the plant. To solve the problems of the storage of compressed radioactive solid waste, a small-scale incinerator and an air-cleaning system were designed and constructed in 1965 [1]. A research project was initiated in 1966 to study the efficiency of this incineration system under a research contract with the International Atomic Energy Agency. The purpose of the present paper is to report on a part of the work carried out under the research contract.

Intensive studies on small-scale radioactive incinerators have been carried out at the Harvard Air Cleaning Laboratory [2, 3] which showed that the generation of tar and combustible gases such as carbon monoxide may be minimized by supplying primary air from above the materials to be burned instead of underfire air supply. It was also shown that a tangential air supply is more effective than a radial one. In 1963 Bloore [4] designed a small incinerator based on the experiments of the Harvard Air Cleaning Laboratory. The design of the present incinerator was based on this experience.

The general arrangement of the incineration system is shown in Fig. 1. The 15 kg/h incinerator has overfire primary and secondary air supplies which enter the combustion chamber tangentially. The oil burner is also
mounted tangentially and its nozzle is tilted 25° downward. Waste materials are introduced into the combustion chamber in lots of 11 litres through a sliding door in the side.

The combustion gas is cooled by dilution air introduced at the incinerator outlet. The air-cleaning system consists of a two-stage cyclone collector, a heat exchanger to protect the following unit from damage, a homemade glass-fibre filter for pre-filtering and an electrostatic precipitator to furnish the maximum collection efficiency. The d.c. voltages applied to the ionizing part and the collecting plates are 18 and 9 kV respectively. An exhaust blower is located at the end of the system.

![Schematic diagram of the original incinerator system.](image)

2. THE PERFORMANCE OF THE INCINERATOR

Although effective gas-cleaning depends on the dust collector used, complete combustion of the waste in the incinerator and the characteristics of the combustion may have some influence on the overall efficiency of the gas cleaning system. Therefore some brief comments on the results of the evaluation of the performance of the incinerator will be made here. Detailed results will be reported separately.

A water model of the incinerator was constructed of transparent Lucite and the tracks of plastic particles injected into the model were photographed and analysed to obtain the velocity distribution. As well as the model of the existing incinerator, two modified models were also investigated. Altogether about 800 still pictures were obtained for the final analysis. Retention time of the fluid within the water model was measured using $^{24}$Na as tracer. To determine the actual combustion efficiency of the incinerator, combustion gas analysis experiments were conducted. The condition of combustion within the incinerator was varied by changing the method of air supply, number of waste boxes within the furnace and the time interval between waste charges to the incinerator. The following are the major conclusions drawn from these experiments:
(1) The burner height should be lowered so as to concentrate the high velocity fluid close to the waste charge
(2) The angle of tilt of the burner nozzle should be decreased to avoid penetration of the flames under the bottom grill
(3) Better combustion efficiency may be obtained by injecting fuel and the primary combustion air at the same point; additional primary air at the primary combustion chamber does not appear to be necessary
(4) To obtain maximum combustion efficiency, combustion should be carried out with maximum charge of the waste box so that a combustion annulus may be formed between the box and the furnace wall.

The recommended basic geometry of the incinerator is shown in Fig. 2.

![Fig. 2. Geometry of the incinerator.](image)

3. EXPERIMENTAL APPARATUS AND PROCEDURE

3.1. Particle size distribution

To investigate the inherent characteristics of the incinerator and the gas-cleaning system, measurements of the dust particle size distribution on the downstream side of each apparatus were made. Sample particles were collected with gummed paper placed against the stream. Downstream of the incinerator, however, dust particles were collected with a probe filled with glass fibre because of the excessive heat from the stream. The combustion gas was sucked through the probe with a vacuum pump.

Care was taken to obtain minimum coagulation of the particles. The close-up photographs of the particles were taken with high-definition film and projected onto a screen to measure the long and short axes in order to obtain mean diameters of the particles.
3.2. Dust collection efficiency

For the present purpose, a glass dust tube [5, 6] filled with chemical-grade glass fibre was used to measure the dust collection efficiency. Figure 3 shows a cross-sectional view of the glass dust tube used for the experiment. The glass fibre was filled loosely at the upstream side of the tube and densely (0.3 g/cm$^3$) at the downstream side to prevent clogging and increase in the pressure drop. The diameter of the glass fibre was 20 μm. The dust sampling ports were located sufficiently downstream from the bends to obtain better distribution of the dust particles within the dust. The arrangement of the equipment for the dust sampling is shown in Fig. 4. Conditions of isokinetic sampling were maintained throughout dust sampling to minimize the experimental errors involved. Simultaneous measurement of the dust load upstream and downstream of each dust-collection unit were made with two sets of equipment.

The collection efficiency $\eta$ of the dust collector was calculated from the following:

$$\eta = \frac{C_1 - C_0}{C_1} \times 100\%$$

where $C_1$ and $C_0$ are the dust concentrations in g/m$^3$ (s.t.p.) at the inlets and outlets of the collectors, respectively.
3.3. Radioactive tracer test

To determine the decontamination capability of the air cleaning system, a series of radioactive tracer tests or hot tests was carried out using $^{51}\text{Cr}$, colloid $^{198}\text{Au}$ and $^{35}\text{S}$ as tracer elements. The final form of these tracer elements was as shown in Table I.

The activities per ml of these solutions were measured and then dispersed into 1 to 2 kg of sawdust for combustion within the incinerator. The gas activity was measured at the downstream side of the electrostatic precipitator before it was discharged to the atmosphere. A stack sampler similar to that described by Starkey [7] was used for the present purpose. Two different procedures involved in the present hot test were:

(1) Several boxes of sawdust with identical total activity were prepared and these were charged into the incinerator at constant intervals and several batch samplings at the stack were made.

(2) A single box of sawdust with a known total activity was burned and the activity within the flue gas measured. The total activity of the charge was then varied to observe the change in the flue-gas activity.

<table>
<thead>
<tr>
<th>TABLE I. FINAL FORM OF RADIOACTIVE TRACERS USED</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{51}\text{Cr}$</td>
</tr>
<tr>
<td>Colloid $^{198}\text{Au}$</td>
</tr>
<tr>
<td>$^{35}\text{S}$</td>
</tr>
</tbody>
</table>

4. RESULTS AND DISCUSSION

4.1. Particle size distribution

The collection efficiency of the dust collector is predominantly a function of the particle size and the velocity of the particle in the gas stream. To examine the distribution of the particle sizes within the combustion gases, dust particles were collected at the inlet and outlet of each dust collector simultaneously. A kind of frequency distribution method was applied to express the particle size distribution for the present purpose. Although this method is normally considered as less accurate, it gives a clearer picture of the distribution characteristics. The particle size from the incinerator is such that sizes over 30 $\mu$m were considered here.

It was noticed from the measurement that the distribution of the particle at the outlet of the incinerator is to some extent influenced by the condition of combustion within the incinerator. This is clearly seen from Fig. 5, where two extreme conditions within the incinerator were compared. It is interesting to notice that when the combustion is incomplete, there seems to be more chance of producing larger particles. With the present method of presentation, the maximum percentage frequency was always between 50 and 100 $\mu$m when the incinerator is under optimum combustion conditions.
Figure 6 shows the change of the particle size distribution as the flue gas passes through various dust collectors. The results shown in Fig. 6 were obtained by simultaneous sampling. Growth of the particles when these pass through the cyclone collector can also be seen from Fig. 6. This may be due to the residual rotational gas flow from the incinerator, turbulent and steep velocity gradient within the cyclone collector and the cooling effect within the collector. In fact, a temperature drop of about 300 degC was observed at the cyclone collector. Another significant change was noticed at the downstream side of the filter. Industrial glass fibre
(0.09 g/cm²) without any pre-treatment was used as filtering media and the filter was very lightly loaded when the measurements were made. Probably the structure of the filter may have acted so as to squeeze the particles into the 100 to 200-μm range. The growth of the particles at the filter may have a significant negative effect on the collection efficiency of the electrostatic precipitator.

Although no results are presented here, no significant change in the distribution was observed both upstream and downstream of the electrostatic precipitator. This was as anticipated because the effective particle size for better collection is below the range of the present measurements.

The pressure drop and the face or inlet velocity at each collector are shown in Table II; the diameter of the flue duct was 12.5 cm.

**TABLE II. PRESSURE DROP AT DUST COLLECTORS**

<table>
<thead>
<tr>
<th>Collector</th>
<th>( \Delta p ) (mm H₂O)</th>
<th>Velocity (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-stage cyclone</td>
<td>200</td>
<td>7</td>
</tr>
<tr>
<td>Filter</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>E.S.P.</td>
<td>7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**TABLE III. MEASURED DUST COLLECTION EFFICIENCY AND THE DUST CONCENTRATION OF THE SYSTEM**

<table>
<thead>
<tr>
<th>Dust concentration</th>
<th>Incinerator</th>
<th>Cyclone</th>
<th>Filter</th>
<th>E.S.P. To stack</th>
</tr>
</thead>
<tbody>
<tr>
<td>dilution valve closed (g/m³, s.t.p.)</td>
<td>5.23</td>
<td>5.75×10⁻¹</td>
<td>9.79×10⁻²</td>
<td>1.27×10⁻²</td>
</tr>
<tr>
<td>dilution valve open (g/m³, s.t.p.)</td>
<td>5.67×10⁻¹</td>
<td>6.23×10⁻²</td>
<td>1.65×10⁻²</td>
<td>1.39×10⁻³</td>
</tr>
<tr>
<td>Collection efficiency (%)</td>
<td>89</td>
<td>83</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Overall efficiency (%)</td>
<td></td>
<td></td>
<td>99.5</td>
<td></td>
</tr>
</tbody>
</table>

4.2. Dust collection efficiency

Table III shows the dust concentration throughout the system and the collection efficiency of each dust collector. The results presented in Table III are for the best conditions obtainable. The dust concentrations were measured for two cases, firstly when the air dilution valve at the outlet of the incinerator was closed and secondly when it was open. In both cases the final concentration of the dust within the flue gas was below \( 2 \times 10⁻² \) g/m³, which is normally considered as an upper limit of very low dust concentration. It is interesting to note from Table III that the dust concentration at the outlet of the E.S.P. when the air dilution valve
was closed is almost equivalent to the concentration at the outlet of the filter when the valve was open. As far as the dust concentration is concerned, the dilution valve appears to be as effective as the electrostatic precipitator and this suggests the possibility of simplification of the system by eliminating the electrostatic precipitator from the present system.

4.2.1. Two-stage cyclone collector

An interesting phenomenon observed during the dust collection experiment was that the second stage of the two-stage cyclone collector acts not only as a dust collector but also as a moisture collector. A large temperature drop (about 300 degC) of the flue gas at the cyclone collector may be the cause of large amounts of condensation within the collector. The average moisture content in the flue gas from the incinerator was 18% by volume when sawdust was used for the experiments. It appears that the coagulation of the particles may be accelerated by the condensation within the second stage and this may improve the collection efficiency at the cyclone collector. It is, therefore, concluded from the review of the experimental results that the choice of a two-stage instead of a one-stage cyclone collector for the incinerator gas-cleaning system appears to be reasonable in spite of larger power consumption at the exhaust blower.

The cyclone collector may also act as a heat exchanger. Some vaporized radioactive elements may return to the original phase when the flue gas is cooled sufficiently within the cyclone collector, which increases the possibility of collection before discharge to the environment. The existing heat exchanger in the present system does not appear to be necessary.

4.2.2. Filter

Absolute filters are often used as final filters in gas or air cleaning systems in many nuclear establishments. However, absolute filters are not manufactured locally and the price of imported ones is prohibitive. Therefore, in the present system filters were used only for pre-filtering purposes and the role of final dust collection was given to the electrostatic precipitator designed and constructed by one of the authors.

It was also thought that the small institution type incinerator should have a gas-cleaning system with cheaper and easily obtainable materials. Therefore, cheap and locally made chemical- and technical-grade glass fibre without any pre-treatment was used as filtering media. This glass fibre was packed so as to make the weight per unit area 0.09 g/cm² with a thickness of 1.5 cm.

Figure 7 shows the experimental results obtained with glass-fibre filters. It can be clearly seen that the pressure drop of the filter increases sharply with the increase in sawdust burned and this trend continues up to the point where 60 to 70 kg of sawdust was burned. Beyond this point, the pressure drop does not change appreciably. This is quite the opposite of the results obtained by Adley [9] using natural settled dust. Adley showed that the rate of increase of the pressure drop increases with the increase in the loading on the filter. This may be because the size of the natural settled dust is only of the order of one micron.
FIG. 7. Collection efficiency and pressure drop at the glass-fibre filter.

FIG. 8. Collection efficiency of the electrostatic precipitator.

It is also seen from Fig. 7 that the dust collection efficiency of the filter is quite dependent on the loading of the filter. As Pradel [8] indicates, it is generally admitted that filter efficiency increases with clogging. Probably, in this case, tarry or oily aerosols may be responsible for lowering the filtering efficiency with clogging. Although the dust collection efficiency is fairly low as compared to commercial filters, as shown in Fig. 7, the lower cost of the filter may justify the use of the domestic one as a pre-filter. The price of the filter used in the present experiment is less than one tenth of that of imported ones.
4.2.3. Electrostatic precipitator

The precipitator consists of a high-voltage rectifier, an ionizing unit (0.5-mm diam. tungsten wire and 25-mm diam. steel pipe) and a collector cell made of stainless steel sheets.

The dust collection efficiency of the precipitator as a function of dust loading is shown in Fig. 8. The trend that the efficiency decreases with the increase in dust loading is similar to that of the filter. Here two possible reasons why the precipitator gives considerably lower collection efficiency may be considered. As mentioned previously in connection with the particle size distribution, the proportion of larger-size particles increases when the flue gas is filtered with the filter. This will naturally decrease the dust collection efficiency of the precipitator. Another possibility is that for measuring the dust collection efficiency glass dust tubes with glass fibres were used and therefore some submicron particles may not have been intercepted and there may be some error in the value of the efficiency.

![Figure 9: Collection efficiency of the electrostatic precipitator.](image-url)

The degree of dependence of the collection efficiency on the cleanliness of the collector plates, voltage of the ionizer and collector and the degree of compensation with beta emitters was studied. The results are shown in Fig. 9. It is obvious from Fig. 9 that the radioactive source definitely increases the efficiency, sometimes by 50%. However, it was found with the present equipment and experimental conditions that the efficiency is not so dependent on voltage above about 10 kV. This may be due to the fact that as the voltage applied increases, the collector and the ionizer current increase and, as a result, a voltage drop occurs across the series resistors. This may well decrease the actual voltage on the ionizer and the collector. From the above discussion it may be concluded that increasing the voltage is by no means a positive solution to improving the efficiency of the precipitator. Rather, the utilization of a beta-emitting source appears to be a better method of increasing the efficiency.
4.3. Radioactive tracer test

Figure 10 shows the effluent gas activity at the outlet of the electrostatic precipitator when sawdust with colloid $^{198}\text{Au}$ was continuously burned in the incinerator. The original activity was 30 to 71 $\mu\text{Ci/ml}$ colloid. In this case it can be seen from Fig. 10 that the effluent gas activity is far below the MPC level. Even though care was taken to disperse the colloid thoroughly within the sawdust, an uneven concentration distribution may be one source of the fluctuation of the effluent gas activities. It was noted during the actual combustion test that the condition of combustion fluctuates with time and this may be another reason why the activity in Fig. 10 varies somewhat periodically with time.

The change of the effluent gas activity with the increase of total activity of $^{51}\text{Cr}$ within the sawdust was measured and the result is presented in Fig. 11. Although the results indicate the increase in the effluent gas activity with the increase in initial concentration to some extent, very severe data scatter was noticed when the amount of the radioactive solution was increased to 30-40 ml. This suggests that when the amount of the solution within the charge is increased, the gas activity may rather decrease. One possible explanation is that the increase in $^{51}\text{Cr}$ concentration means the increase in the water content in the sawdust charge. Then, condensation may occur within the second stage of the cyclone collector and this may result in an appreciable increase in the collection efficiency at this stage.

Figure 12 shows the experimental results with $^{35}\text{S}$ and the general tendency may be observed from the figure.

From the above discussion it was concluded that the decontamination capability of the present incinerator and gas-cleaning system is quite sufficient for laboratories with small research reactors. Even if the electrostatic precipitator is eliminated from the system, this conclusion may remain valid.
5. GENERAL CONCLUSIONS

The introduction of fresh air from the dilution valve at the incinerator outlet appears to be a very good way of reducing the temperature and the dust concentration of the flue gas.

A two-stage cyclone collector appears to be an essential unit of the incineration system as a dust collector, moisture collector and heat exchanger.

The following units may be recommended as a standard incineration system for small laboratories or in countries where filters or electrostatic precipitators are difficult to obtain or very expensive:

1. Incinerator with tangential firing
2. Dilution valve
3. Two-stage cyclone collector
4. Roughening filter with technical-grade glass fibre.
ACKNOWLEDGEMENTS

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REFERENCES


DISCUSSION

E.W. BLOORE: I have several comments and questions. First, I would like to point out that we did not design our incinerator alone, but worked in collaboration with the USAEC and the US Army. R. Dennis and W. Kyntsis, both formerly of the Harvard Air Cleaning Laboratory, were primarily responsible. Second, I would like to state that it is our philosophy to use air dilution to avoid the use of scrubbers and heat exchangers and we therefore do not use a heat exchanger, as you do. Moreover, we feel that the electrostatic precipitator (ESP) can handle the bulk of the material from the incinerator, so we lead directly into the ESP from the cyclone and back the ESP with a filter to collect blow-down from it and any dislodged material generated during shake-down.

In your conclusions on the performance of the incinerator, you stated that the height of the burner should be lowered. I can only state that we have had no difficulty with our gas-fired burners at the height we use them. There might be some difference because you are using oil burners. I agree that you should decrease the angle of tilt of the burner nozzle. We obtained best results with horizontal inlets and this is what we are using. I cannot agree with your proposal to use only one inlet in the combustion chamber, to feed both fuel and air. I feel that multiple inlets are required to maintain uniform cyclone flow.

In your final conclusions, you state that the cyclone is essential and that the ESP is not required. We have found the opposite. Because of the low efficiency of the cyclone and the high efficiency of the ESP, we have considered eliminating the cyclone and passing directly into the ESP. If we have hesitated, it is simply because we have no data on particle size as a function of combustion time and, as Mr. Thomas has pointed out, there might be large particulate release during the initial stages of ignition.
Regarding your radioactivity data, I would like to state that in studying $^{89}\text{Sr}$ we ran up to 200 $\mu$Ci/kg of activity and at this upper level the stack effluent was at $4 \times 10^{-12} \mu$Ci/cm$^3$. We feel that we can handle even higher levels of activity.

I have two questions. What was your operating temperature, and do you propose to add a filter after the ESP to prevent the discharge of blow-off and shake-down residues?

K. LEE: Thank you for your valuable comments. In our case, we have used an oil burner and the velocity of the flame is very small compared with that of a gas burner, so that the flame barely touches the top of the waste load. We consider it reasonable to lower the position of the burner and the water model experiment supports this. As to the multiple air inlets at the combustion chamber, we found from the water model experiment that air injection with the fuel at one point is sufficient to give uniform cyclonic flow.

The temperature within our incinerator was about 1000°C, and I suggest that you check the second stage of your cyclone collector; you may find some condensates in your ash collector. As to your final question, I do not want to place a filter after the ESP, because our filter also releases residues.

E.W. BLOORE: I am surprised to hear that you are using such high temperatures, because using approximately the same temperature, i.e. 1600-2000°F, we have not been aware of any condensation in our facility, even when incinerating carcasses.
FILTER FOR THE PURIFICATION OF HIGH-TEMPERATURE INCINERATOR GASES. The authors describe a recoverable filter for hot incinerator gases. This consists of metal foil cylinders on which asbestos fibres have been deposited by pneumatic spray to constitute the filtering medium. The special feature of its operation lies in the fact that partially burnt materials from the incinerator, especially lamp black, complete their combustion on the filter, as they are produced. This greatly reduces choking of the filters, which are expected to operate for several hundreds of hours between cleanings. This filter has been tested on a reduced-scale model followed by a long period of industrial use in a pilot plant with a capacity of 20 kg/h. The authors describe the plant and present the results obtained.

1 - INTRODUCTION

L'épuration des gaz d'incinérateur est généralement effectuée après refroidissement. Il y a deux raisons principales à cette manière de procéder : les difficultés de réalisation d'un filtre à haute température et le risque de destruction de ce filtre par combustion des imbrûlés. Or, la filtration à basse température présente des inconvénients : nécessité de refroidir, corrosion plus rapide qu'à chaud et colmatage du filtre par les imbrûlés tel qu'on doive prévoir un décolmatage très fréquent, voire continu.

L'idée d'un filtre régénérable, constitué par un dépôt de fibres d'amiante sur une grille métallique, avait été lancée en 1957 par POELMAN [1], mais l'inflammation spontanée des imbrûlés, après leur accumulation sur le filtre, provoquait la destruction de la grille.

Cette idée a été reprise et exploitée [2] [3] avec des modifications relatives à la formation de la couche filtrante et aux conditions de fonctionnement. C'est ainsi qu'on a choisi une température de filtration et une composition du mélange gazeux tels que les imbrûlés, au fur et à mesure de leur production, achèvent leur combustion sur le filtre sans l'endommager. Le colmatage est ainsi très réduit, même lorsqu'on incinère des matières or-
ganiques produisant beaucoup de noir de carbone. En outre, comme le médium filtrant est régénérable, on rassemble les déchets incombustibles sous un faible volume.

2 - DESCRIPTION

L’élément filtrant de base est une bougie de diamètre 35 mm et de longueur 600 mm en métal déployé à mailles fines. Un filtre est constitué de plusieurs de ces bougies assemblées verticalement sur une platine par une extrémité ouverte, l’autre étant fermée (figure 1). Les bougies sont garnies intérieurement d’un dépôt de fibres d’amiante qui constitue le médium filtrant. L’entrée du filtre est au-dessus de la platine, la sortie est au-dessous.

3 - FONCTIONNEMENT

3.1 - Garnissage

L’opération au cours de laquelle on forme le dépôt de fibres d’amiante est appelée opération de garnissage. Pour ce faire, on prépare un mélange d’amiante soigneusement défilbré contenant 50 % de fibres cuites à 800°C.
L'amianté est mis en suspension dans l'air au moyen d'un appareil de flocage, de fabrication courante, et cet aérosol de fibres d'amianté est envoyé à l'entrée du filtre, en fonctionnement au débit de 10 m$^3$/h par bougie, ce qui correspond à une vitesse de 4 cm/s à travers le métal déployé.

L'opération dure 30 minutes, la masse d'amianté déposée est de 4 grammes par bougie soit 6 mg/cm$^2$. Le garnissage est ensuite consolidé par la cuisson qui intervient normalement lors de la première utilisation du filtre à chaud. La présence de l'amianté précuit réduit les effets du retrait.

3.2 - Filtration

Le débit de filtration normal à 800°C est de 15 m$^3$/h par bougie, ce qui correspond à une vitesse de 6 cm/s à travers le médium filtrant. La perte de charge est de 10 à 15 mm d'eau. L'efficacité de filtration mesurée au photomètre Sinclair, avec un aérosol de chlorure de potassium produit par un mélange fumigène, est égale à 100 (99 %). À titre indicatif, cette méthode donne, pour un filtre de ce type, des résultats assez voisins de ceux de la méthode au DOP monodispersé de 0,3 μ.

3.3 - Régénération

Lorsque le filtre est colmaté, on le régénère par un dégarnissage suivi d'un regarnissage. L'opération de dégarnissage consiste à retirer le dépôt de fibres d'amianté et les poussières stockées. On utilise une canne flexible reliée à un aspirateur à travers un cyclone et un filtre absolu. Le diamètre extérieur de la canne est un peu inférieur au diamètre intérieur des bougies. La canne est introduite dans les bougies pour aspirer le dépôt.

L'opération peut être conduite manuellement, bougie par bougie, à travers une hotte à gants qui vient se placer au-dessus du filtre. On peut aussi prévoir un dispositif automatique avec une rampe de cannes qui dégarnit une rangée de bougies à la fois [4]. Le débit d'aspiration nécessaire est de 30 m$^3$/h par bougie.

4 - RESULTATS EXPERIMENTAUX

Ce filtre a été expérimenté sur une maquette de 9 bougies et sur un prototype de 150 bougies associé à un incinérateur industriel.

Le dispositif d'essai de la maquette est représenté figure 2. Il est composé d'un poêle et d'une chambre de post-combustion, figurant un incinérateur. Le filtre est placé dans un caisson à calorifuge chauffant. La circulation des gaz est assurée par des éjecteurs d'air.

En réalité, le filtre n'est traversé que par une fraction des gaz de combustion, de l'ordre de 10 %, le reste étant évacué directement par une cheminée. Cette disposition permettait de limiter l'importance de la maquette, tout en assurant une plus grande souplesse de fonctionnement.

Les objectifs de ce montage étaient, entre autres, de vérifier l'efficacité de la chambre de post-combustion et d'étudier le comportement du noir de carbone.

Le noir de carbone était produit par la combustion, sur un lit de coke, de matériaux plastiques, principalement des résines méthacryliques (plexiglas). Les points de mesure de température sont repérés par des chiffres de 1 à 7 sur la figure 2. La mesure importante, pour suivre le comportement du noir de carbone, est celle du point 3 qui indique la température au niveau des filtres.

La figure 3 représente un enregistrement des différentes températures réalisé au cours d'une expérience mettant en évidence la combusion du noir de carbone sur le filtre. La courbe en trait continu représente l'évolution de la température au niveau du filtre (point 3). Alors que le circuit est en régime établi avec une température au filtre de 625°C, on introduit de la
matière plastique dans l'incinérateur. Aussitôt la température du filtre s'élève. Cette élévation a deux causes distinctes. La première est la combustion de la matière plastique dans le foyer, dont la chaleur est révélée par le thermocouple n°2 situé à l'entrée du filtre. Mais il y a une deuxième cause qui intervient au niveau même du filtre puisque la pente A de la courbe 3 est nettement supérieure à la pente B de la courbe 2. Il s'agit de la combustion du noir de carbone dont le caractère intermittent et brutal est traduit par les variations de température. Au cours de ces expériences, on a également observé des variations importantes de la perte de charge du filtre puisqu'elles ont atteint 400 mm d'eau.

Pour éviter l'inflammation brusque des dépôts de noir de carbone sur le filtre, on a augmenté la température de celui-ci, et on a obtenu une combustion régulière vers 800°C. Au cours d'une expérience d'une heure, on a chargé la matière plastique, d'abord au taux de 6 kg/h, puis au taux de 12 kg/h(1). La perte de charge du filtre est restée égale à 12 mm d'eau et sa température n'a varié que de 770 à 785°C, sans oscillation (fig.4).

(1) On rappelle que la maquette ne filtre qu'une fraction réduite des gaz de combustion.
FIG. 3. Diagramme des températures montrant la combustion du noir de carbone (montage sans chambre de post-combustion).

FIG. 4. Fonctionnement de la maquette en régime stable.
La figure 5 représente le circuit d’exploitation du prototype de 150 bougies. Le filtre est placé au plus près de l’incinérateur pour que la température nécessaire à son bon fonctionnement soit atteinte sans apport de chaleur autre que celui des gaz. La circulation est assurée par un ventilateur placé au pied d’une cheminée. Une entrée d’air extérieure permet, par dilution, de limiter à 150°C la température au niveau du ventilateur.

Cette installation a fonctionné en exploitation réelle avec un même garnissage pendant 7 jours consécutifs, à raison de 9 heures par jour. En 60 heures, on a incinéré une tonne de déchets divers : chiffons, matières plastiques, cadavres d’animaux, au taux de 15 à 20 kg/h. La perte de charge, qui était au début de 10 mm d’eau, a atteint 14 mm en cours d’exploitation. Sa valeur, à la fin de la campagne, en l’absence d’incinération, était de 11 mm d’eau. Le débit des gaz traversant le filtre était de 2 300 m³/h à 750°C (660 m³/h à 20°C).

La durée totale de fonctionnement du filtre est actuellement supérieure à 200 heures avec, toutefois, plusieurs essais de régénération. On prévoit une campagne continue de 200 heures avec prélèvements pour le contrôle de l’efficacité en noir de carbone et en radioactivité.

5 - CONCLUSION

Le filtre décrit constitue une solution satisfaisante pour l’épuration des gaz d’incinérateurs radioactifs. Les résultats obtenus en exploitation industrielle permettent d’estimer que les régénérations seront espacées de plusieurs centaines d’heures. Dans le cas où son efficacité est jugée insuffisante, compte tenu de la nocivité des déchets traités, il est facile de lui associer un filtre absolu. Des projets d’installation complète ont déjà été établis et proposés. L’un d’eux est en cours de réalisation.

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OPERATIONAL EXPERIENCE
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CONCEPTION ET REALISATION DES SYSTEMES D'EPURATION DE L' AIR DANS LES INSTALLATIONS NUCLEAIRES FRANCAISES

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Abstract — Résumé

DESIGN AND CONSTRUCTION OF AIR PURIFICATION SYSTEMS IN FRENCH NUCLEAR INSTALLATIONS.
The fission products present in nuclear installations create a potential hazard of environmental contamination against which precautions must be taken. This is, specifically, the purpose of purification equipment. The first problem is to define the containment and its leakage rate. The efficiency of purification on the off-gas system must be adapted to the hazard and the choice will be guided by the characteristics of the site, in particular the weather conditions and the doses regarded as acceptable for the surrounding population. Purification systems will accordingly vary depending on the type of installation in which they are to be used (reactors, factories, laboratories). This paper describes the different possibilities and shows that systems which are both effective and adaptable can be built. It considers durability of equipment properties and also the additional hazards entailed in handling purification equipment and the accidents which could result from its use. The financial aspects of the different solutions are also discussed.

CONCEPTION ET REALISATION DES SYSTEMES D'EPURATION DE L' AIR DANS LES INSTALLATIONS NUCLEAIRES FRANCAISES. Les produits de fission présents dans les installations nucléaires créent un risque potentiel de contamination de l'environnement contre lequel il faut se prémunir; c'est en particulier le rôle des dispositifs d'épuration. Il s'agit tout d'abord de définir le confinement et son taux de fuite. Sur le dispositif de rejet prévu, l'efficacité de l'épuration doit être adaptée au risque. Les critères du choix sont imposés par les caractéristiques du site, en particulier par les conditions météorologiques et par les doses que l'on peut admettre pour la population environnante. Dans ces conditions, les systèmes d'épuration seront différents suivant les types d'installations (piles, usines, laboratoires). On décrit les différents cas possibles en montrant que des systèmes souples et efficaces peuvent être réalisés. La permanence des propriétés des dispositifs est examinée, ainsi que les risques supplémentaires entraînés par la manutention et les accidents d'utilisation des dispositifs d'épuration; l'aspect économique des solutions spécifiques est également abordé.

1. PRINCIPES DE L'EPURATION DE L' AIR

1.1. Généralités

L'existence de produits de fission ou d'activation dans les usines, les laboratoires ou les piles crée des risques de contamination importants pour l'environnement (les problèmes posés par la protection du personnel travaillant dans ces installations ne seront pas examinés dans ce qui suit).

Les dispositifs d'épuration de l'air constituent un des moyens de contenir cette contamination. Ils doivent être suffisamment souples pour pouvoir s'adapter aux conditions de fonctionnement habituelles et accidentelles.
1.2. Evaluation du danger auquel une installation nucléaire expose la population

On peut estimer la dose délivrée à la population (ou l'activité du dépôt au sol) dans la mesure où l'on peut déterminer:
- la fréquence et l'importance des rejets,
- le confinement d'une partie de l'activité dans l'enceinte primaire,
- le dépôt d'une partie de l'activité sur les parois,
- la rétention d'une partie de l'activité sur des filtres ou pièges,
- la dilution dans l'atmosphère.

1.3. Fréquence et importance des rejets

Les rejets d'activité peuvent être:
- continus ou périodiques, de débit moyen connu (p.ex.: épuration des fluides d'un réacteur, travaux en cellule chaude),
- occasionnels, à la suite d'accidents mineurs (p.ex.: manutention d'un élément combustible, explosion d'une boîte à gants),
- exceptionnels, à la suite d'un accident important (p.ex.: fusion totale ou partielle du cœur d'un réacteur, incendie des filtres d'un laboratoire).

Dans chaque cas, on doit évaluer l'identité et l'activité des matières rejetées et la répartition de cette activité dans les diverses enveloppes de confinement.

1.4. Confinement de l'activité

Il est obtenu par une succession d'enceintes comprenant au moins:
- une enveloppe primaire (cuve du réacteur avec sa protection biologique, boîte à gants, cellule chaude),
- une enveloppe secondaire (bâtiment contenant l'enceinte primaire) et, si possible, au moins une enveloppe intermédiaire: local contenant l'enceinte primaire, séparé des parois extérieures du bâtiment par des locaux dans lesquels l'activité est faible ou nulle.

Des fuites d'activité peuvent se produire à travers l'enceinte primaire en cas d'accident. L'enceinte secondaire empêche la contamination de se répandre hors du bâtiment, grâce à une dépression qui permet la sortie d'air éventuellement contaminé après passage à travers le système d'épuration et de rejet.

Le choix du confinement procuré par l'enceinte secondaire se réduit en pratique à l'alternative: enceinte étanche ou enceinte à fuite contrôlée.

Dans le premier cas la sécurité ne repose pas essentiellement sur les dispositifs de filtration mais plutôt sur l'étanchéité de l'enceinte, qui est souvent variable dans le temps. Le prix de revient est élevé et des contrôles fréquents sont nécessaires.

L'enceinte à fuite contrôlée permet une construction moins coûteuse. Le confinement est réalisé par la mise en dépression du bâtiment grâce à la ventilation. L'air extrait est filtré avant rejet dans une cheminée. L'efficacité d'un tel dispositif repose sur:
- le pouvoir d'arrêt des dispositifs de filtration,
- la dilution obtenue en diffusant la contamination dans l'atmosphère.
- la diminution du débit extrait en cas d'accident,
- la limitation des rejets.

Les conditions météorologiques du site règlent les rejets admissibles. La «double enceinte» est un autre type d'enveloppe secondaire, compliquée et coûteuse: on n'envisage son emploi en France que si la surpression en cas d'accident est faible et si l'on exige une excellente étanchéité.

Le confinement de l'activité permet d'attendre, après un accident important, la décroissance radioactive des produits à vie courte. On l'obtient, soit par l'enceinte secondaire, soit par une chambre de rétention insérée dans le circuit d'extraction.

1.5. Choix de la dépression dans l'enceinte extérieure

La dépression nécessaire peut être très différente selon l'installation considérée.

S'il s'agit d'un réacteur de puissance, l'activité libérée dans un accident important est si grande que l'on doit s'efforcer d'éviter toute fuite à l'extérieur, même si le vent met en dépression certaines façades. Sur un site exposé à des vents violents, la dépression dans le bâtiment peut être réglée à 50 mm CE.

Dans le cas où les installations de ventilation seraient en panne à la suite de l'accident, il est utile de pouvoir fermer l'entrée d'air sans obstruer la sortie vers la cheminée. La dépression dans le bâtiment pourrait être maintenue malgré le débit d'infiltration, grâce à la dépression créée par le vent au sommet de la cheminée.

S'il s'agit d'une usine ou d'un laboratoire, l'activité totale est beaucoup plus faible que dans un réacteur de puissance, l'accident conceivable n'en libère qu'une faible fraction, la proportion de gaz rares est plus faible. L'établissement d'une enveloppe intermédiaire, grâce à des locaux froids entourant les locaux chauds, réduit encore le niveau d'activité qui peut venir en contact avec les parois extérieures. Dans ces conditions, une dépression d'environ 3 à 5 mm CE par rapport à la pression statique extérieure assure une protection suffisante contre les risques de fuites dans des régions de vents moyens modérés (la France continentale par exemple). Dans une région de vents violents, il faudrait, soit augmenter la dépression dans les locaux, soit réaliser des façades convenablement étanches et réduire ou supprimer les ouvertures sur les façades soumises à de fortes dépressions extérieures.

On peut également, si les locaux actifs sont complètement séparés des parois extérieures par des locaux froids, mettre ces derniers en surpression par rapport à l'extérieur. Toutefois, il faut être sûr que les locaux en surpression resteront certainement froids en toutes circonstances y compris les fausses manœuvres (passage obligatoire par des vestiaires ou, pour le matériel, par des sas).

On doit noter enfin que l'influence du vent sur les fuites de contamination peut être éliminée si la prise d'air et la cheminée du rejet de la ventilation sont étudiées (moyennant une mesure en soufflerie, au besoin) pour se trouver soumises toutes deux à une dépression voisine de la moitié de la pression dynamique du vent.
1.6. Risques de surpression dans l'enceinte extérieure

Le problème de l'étanchéité des enveloppes ne peut être considéré seul: on doit étudier la fuite de l'enveloppe sous l'effet d'une surpression donnée. Le choix est limité à l'enceinte résistant à une pression de quelques bars, avec un débit de fuite d'environ 1% par jour, et au bâtiment traditionnel résistant à 0,04 bar par exemple, dont on peut limiter le débit de fuite à moins de 100% par jour.

L'enceinte étanche d'un réacteur de faible puissance peut résister à la surpression de quelques bars résultant de l'accident explosif le plus pessimiste.

Si il s'agit d'un réacteur important pour la production d'électricité, aucune enceinte étanche de dimensions et de prix raisonnables ne peut résister à l'accident calculé à partir d'hypothèses systématiquement pessimistes.

Il est alors indispensable d'évaluer avec précision les conséquences d'un accident en se limitant aux risques réellement susceptibles de survenir et même de les affecter d'un facteur de probabilité qui doit tenir compte de l'importance de la population exposée à ces risques. Compte tenu du petit nombre de réacteurs en service et de l'incertitude sur l'évolution de la densité de population dans les dizaines d'années de vie d'un réacteur, il paraît prudent de garder de grandes marges de sécurité, et, tout particulièrement, de rechercher avant tout la limitation des risques par la conception des organes principaux du réacteur. Le rôle de l'enceinte primaire est ici particulièrement important.

1.7. Dépôts d'activité sur les parois

Une fraction de l'activité libérée peut rester sur les parois internes, soit par adsorption, soit par dépôt à partir d'un aérosol, soit par condensation ou sublimation. Des nombreuses études consacrées à ce sujet il ressort que l'activité libérée dans l'air d'un local peut être réduite, d'un facteur compris entre 1 et 10, par ces dépôts. Comme il faudra ensuite décontaminer les parois, de tels dépôts sont donc légèrement avantageux dans le cas d'un accident important de réacteur, et certainement désavantageux dans tous les autres cas.

1.8. Dispositifs de filtration de l'air

1.8.1. Types de filtres

Rappelons que de nombreux types de préfiltres (cyclones, filtres à manches, venturi laveurs, séparateurs d'eau, laveurs à circulation de solutions chimiques, etc.) sont utilisables pour éliminer de grosses particules, réduire des concentrations élevées, neutraliser des agressifs chimiques, etc. Lorsque leur emploi est imposé par de telles nécessités, ils contribuent en partie à la lutte contre la radioactivité de l'air.

Les gaz rares sont, soit rejetés à l'atmosphère après stockage de décroissance, soit prélevés dans l'enceinte primaire et épurés par adsorption.

Les aérosols sont retenus dans des filtres à poussières à haute efficacité, en papier de fibre de verre ou d'amiante.
L'iode est retenu dans des pièges à adsorption sur du charbon actif. Il est bien entendu que l'efficacité des filtres ne peut être définie que pour des poussières d'une granulométrie donnée, et pour une méthode de contrôle donnée. Les désignations «filtre absolu», «filtre à haute efficacité», n'ont pas été normalisées.

On notera que les filtres décrits ci-après ont une efficacité d'au moins 99,95% à la méthode DOP.

Les constructeurs indiquent habituellement un débit de référence, et ils donnent la perte de charge correspondante. En réalité, le débit peut varier très largement (entre 20% et 300% du débit de référence) sans compromettre l'efficacité. Toutefois, la perte de charge due au colmatage variant comme le carré du débit, il en résulte des différences importantes, soit dans la perte de charge finale, soit dans la durée d'utilisation du filtre.

1.8.2. Filtres à haute efficacité

Les filtres français se présentent sous forme de dièdre (Etablissements Schneider Pœlman) de forme parallélépipédique, de 60 cm de longueur, 6,5 cm de hauteur et 20 cm de profondeur.

Les éléments comprennent deux nappes de papier d'amianté plissé, collées à angle aigu sur une monture au moyen d'un ciment réfractaire. Au débit de 100 m³/h, la vitesse moyenne de passage à travers l'amianté est de 0,55 cm/s.

Dans les installations importantes, ils sont groupés en paniers de 10 éléments superposés, puis par assemblages de paniers, en cages de 40 ou 80 dièdres.

Des cellules filtrantes existent aussi sur le marché français (filiale Sofiltrà de la Société St-Gobain Techniques Nouvelles). De conception identique à celle des précédents, ces filtres n'en diffèrent que par la nature du papier: papier de fibre de verre analogue au papier américain, et par l'assemblage de plusieurs dièdres en blocs ou «cellules» de 35 m² qui leur assure un débit de 1500 m³/h. Ils sont groupés en caisson à sas étanche de trois ou quatre cellules.

1.8.3. Pièges à iodes

Deux modèles différents sont disponibles:

La cartouche (Etablissements Schneider Pœlman), cylindre de 40 cm de hauteur et de 25 cm de diamètre garni de charbon de noix de coco actif réparti en couche annulaire de 5 cm d'épaisseur maintenue comprimée par un ressort. Au débit de 270 m³/h, la vitesse moyenne de passage est de 30 cm/s et la perte de charge de 35 mm CE. Ces cartouches sont montées en parallèle pour constituer des pièges de débit plus important.

La cellule adsorbante (Sofiltrà - St-Gobain Techniques Nouvelles), de mêmes dimensions que la cellule filtrante. Le charbon actif est réparti dans une structure multidimédre de 5 cm d'épaisseur. Le débit est de 1000 m³/h pour une vitesse de passage de 0,30 m/s. Un caisson commun peut grouper en parallèle plusieurs cellules-pièges, précédées éventuellement par des cellules filtres.
L'efficacité des charbons actifs, imprégnés ou non, vis-à-vis de l'iode moléculaire ou organique, en présence d'air plus ou moins humide, a fait l'objet de nombreuses études [1, 2]. Les charbons utilisés en France ont été étudiés également [3] et ont montré des propriétés analogues.

Le vieillissement des pièges à iode, ou leur empoisonnement par des solvants ou des vapeurs d'huile, peut être surveillé en plaçant un piège-témoin, de faible débit, en parallèle avec le piège principal, et en surveillant l'efficacité de ce dernier lorsque le piège témoin s'est montré défaillant.

1.9. Dilution dans l'atmosphère

Ce facteur a été étudié sur neuf sites français, au cours d'une centaine d'expériences [4] qui ont permis l'établissement d'abaques donnant le rapport (concentration au sol / débit à la cheminée) en fonction de la distance à la cheminée, pour deux conditions de temps: «normales» et «mauvaises».

La concentration au sol ne dépend pas de la vitesse du vent, car si la dilution est améliorée par vent fort, la meilleure stabilité du panache en direction compense cet effet.

Si les rejets sont émis au voisinage du sol, on admet que le débit est dilué dans un volume numériquement égal au produit de la vitesse du vent par la surface de l'obstacle opposé au vent par le bâtiment.

1.10. Dose admissible

En dernier ressort, ce sont les doses susceptibles d'être reçues par la population qui servent de critère à la sûreté de l'installation.

Lors des opérations de fonctionnement normal, les doses dépendent de la fréquence des rejets et de l'addition possible d'autres rejets provenant des diverses installations pouvant exister sur le même site. Pour ce dernier motif, en particulier, le niveau souhaitable ne doit être qu'une fraction de la concentration maximale admise pour les populations.

La dose admissible pour la population en cas d'accident grave n'est pas définie par un règlement. Pour apprécier les conséquences de tels accidents, on peut cependant s'inspirer des prescriptions relatives aux personnes professionnellement exposées en cas d'irradiation ou de contamination non concertées [5].

1.11. Dangers propres aux dispositifs d'épuration

Lorsqu'on définit les installations nécessaires à l'épuration de l'air, on ne doit pas oublier que, si elles diminuent certains risques, elles peuvent en créer de nouveaux. On peut citer par exemple, dans un réacteur:

- le rayonnement des produits de fission déposés sur les parois intérieures de l'enceinte,
- la contamination locale provenant des produits de fission déposés dans les fissures d'une enceinte étanche en béton,
- les effluents liquides résultant d'une pulvérisation d'eau dans une enceinte contaminée, dans un laboratoire aussi bien que dans un réacteur,
- la désorption de produits actifs (iode, tritium, etc.) fixés sur les filtres,
- l'inflammation de matières pyrophoriques collectées par un préfiltre, suivie d'un incendie des filtres principaux,
- la contamination des abords d'un bâtiment par un accident de manutention, lors d'une évacuation de filtres contaminés,
- la désagrégation d'un filtre par attaque chimique, suivie d'une éjection de débris radioactifs.

Tous ces risques peuvent être vaincus par des moyens appropriés et, d'ailleurs, la plupart ne font qu'augmenter un risque pré-existant: les effluents liquides, par exemple, sont dangereux dans tout bâtiment chaud susceptible de décontamination par voie humide; l'adjonction d'un système de pulvérisation peut en augmenter considérablement le volume, mais la nécessité d'un confinement, d'une évacuation, de prélèvements pour dosages, d'une filtration des évents, d'un stockage en dépression, etc. est la même dans tous les cas.

Les dangers cités ci-dessus, résultant de l'existence des filtres, doivent être examinés avec une attention particulière: ils peuvent constituer le risque principal d'un laboratoire. L'incendie des filtres n'est pas extrêmement rare (quoique difficile à reproduire expérimentalement). On doit s'attacher à en réduire la probabilité par des dispositifs simples.

### 2. DESCRIPTION D'UN ENSEMBLE-TYPE D'ÉPURATION DE L'AIR

#### 2.1. Enceintes de confinement

L'enceinte primaire répond à des spécifications qui sortent du cadre de ce mémoire. Son atmosphère est souvent mise en dépression, par un circuit particulier avec filtres à proximité de l'extraction puis passage sur les filtres généraux avant rejet. Quand un débit d'air est nécessaire pour évacuer de la chaleur, un filtre à l'entrée de l'enceinte assure le confinement en cas d'arrêt de la ventilation.

Dans le cas particulier de l'enceinte primaire en surpression (pour éviter la pollution d'un gaz inerte par des infiltrations d'air), une aspiration dans une chambre intermédiaire entre deux joints d'étanchéité permet d'évacuer les fuites.

L'enceinte secondaire à fuites contrôlées, c'est-à-dire le bâtiment lui-même, n'exige que du son dans les scellements des huisseries, vitrages et traversées de fourreaux, s'il s'agit d'un bâtiment en béton et briques avec enduit en ciment peint intérieurement, comme c'est le cas pour la plupart des installations françaises. Une construction métallique de même étanchéité est en général plus coûteuse. On sait qu'une enceinte étanche métallique l'est encore plus, et que la vérification de son étanchéité est difficile si l'on exige une fuite de 1% par jour environ.

#### 2.2. Bouches et gaines d'extraction

Compte tenu des avantages et inconvénients des dépôts d'activité sur les parois, les bouches d'extraction devraient être disposées:
- si possible, à proximité immédiate des zones exposées à de faibles dégagements périodiques ou accidentels (joints, raccords, bouchons, etc.),
- de préférence en partie basse des locaux contaminables pour des aérosols de poussières denses, en partie haute pour les dégagements de tritium ou de gaz chauds,
- et, en ce qui concerne l'extraction dans l'enceinte d'un réacteur après (et seulement après) un accident important, en une zone distincte de celle qui a reçu la première éjection de produits actifs.

Les gaines d'extraction doivent, autant que possible, être maintenues en dépression, principalement pour éviter de transmettre la contamination à des locaux peu actifs. Pour la même raison, elles seront de construction étanche: assemblages par soudures continues, brides boulonnées avec joints interposés.

Elles doivent être conçues pour éviter la transmission aux filtres d'un incendie en amont (non par des volets coupe-feu qui ne sont utiles que pour confiner l'incendie dans un filtre, mais par des obstacles au déplacement d'objets enflammés: grillages, sections de gaines à vitesse d'air réduite, interposition de culs-de-sac sur le trajet, etc.).

Rappelons qu'une partie des gaines peut être aménagée en enceinte de confinement pour la décroissance radioactive de gaz rares, et aussi en chambre de refroidissement (avec une grande surface de parois d'inertie thermique convenable) pour éviter d'amener aux pièges à iode des gaz trop chauds en cas d'accident de réacteur.

2.3. Filtres et pièges

2.3.1. Groupement en circuits distincts

Au lieu de diriger l'ensemble du débit extrait vers un seul groupe de filtration, il est avantageux de filtrer dans des groupes distincts l'air habituellement contaminé, celui qui ne l'est qu'exceptionnellement et celui qui peut contenir de l'iode. Cette séparation, qui est facile dans un laboratoire, a moins d'intérêt dans un réacteur, où l'ensemble des locaux peut être exposé au même accident important.

Les mêmes considérations s'appliquent aux chambres de rétention destinées à laisser décroître l'activité des gaz rares.

2.3.2. Installation et remplacements

Les filtres qui retiennent une activité alpha sont généralement disposés dans un local du bâtiment, afin d'utiliser les vestiaires et les locaux de décontamination existants en cas de contamination après manipulation. On les change sous vinyle. Le local est ventilé.

Les filtres et pièges qui retiennent une activité gamma sont entourés de murs de protection biologique et sont manipulés à distance, par exemple en soulevant la dalle de couverture sous laquelle est accroché le filtre. Il est parfois avantageux d'enterrer l'ensemble du filtre et des collecteurs d'air au voisinage du bâtiment. Les risques de vieillissement des pièges à iode imposent la possibilité de remplacement, comme pour les filtres à poussières.
2.3.3. Vérification du vieillissement

La durée de vie des filtres est limitée, soit par excès d'activité, soit, plus généralement, par excès de colmatage. On peut vérifier périodiquement l'activité au contact avec un compteur mobile. La perte de charge est mesurée par un manomètre installé à demeure: il est utile de mesurer la somme des pertes du filtre et d'un registre compensateur de colmatage. Ce registre, presque fermé quand le filtre est neuf, est ouvert progressivement pour lire une perte constante.

La durée de vie des pièges à iode est limitée, soit par excès d'activité, soit par manque d'efficacité. L'activité se mesure avec un compteur mobile, comme pour les filtres. L'efficacité peut se mesurer à partir d'une émission en amont, avec comptage d'activité en aval, mais on a des mesures plus commodes si l'on dispose de pièges-témoins en parallèle des pièges principaux, avec la même épaisseur de charbon et la même vitesse de passage d'air.

Lorsque le débit d'air n'est pas trop grand, il peut être avantageux de parer aux dangers du vieillissement des pièges à iode en les doublant par un groupe identique (y compris son piège-témoin) en parallèle. Le prix et l'encombrement sont trop élevés si l'on doit filtrer de grands débits d'air: on préfère alors retirer du circuit d'extration le piège qui n'est mis en service qu'à la suite d'un accident libérant de l'iode. Si, en même temps, le débit extrait est diminué, cette solution est très économique.

2.3.4. Risques dus aux filtres

Un filtre incendié peut libérer une activité importante. On peut limiter le risque par les moyens exposés au paragraphe 2.2; on peut aussi subdiviser un groupe filtrant en plusieurs éléments, chacun d'eux étant équipé d'un détecteur de fumée et d'un registre étanche en aval.

On peut pallier la défaillance d'un piège à iode en faisant barboter dans un liquide le gaz pollué [6-8]. C'est le cas, de par leur construction, dans les réacteurs dont le cœur est immergé dans l'eau ou le sodium.

2.4. Ventilateurs d'extration

Ils maintiennent en dépression l'ensemble des circuits d'extration et d'épuration, et doivent être intercalés en aval des filtres, de préférence à proximité de la cheminée de rejet.

On évite les risques de panne en doublant le ventilateur en service par un autre de secours. Si le débit extrait est important, il est avantageux de le répartir sur deux ventilateurs (au moins) tournant simultanément en parallèle.

En principe, un groupe unique d'extration, asservi à un groupe unique de soufflage, permet de compter sur un échelonnement correct des dépressions dans les locaux, sans risque de surpression ni de fuites à l'extérieur en cas de panne d'un des ventilateurs (panne commandant l'arrêt d'un ventilateur de l'autre groupe, par le jeu de l'asservissement).

Cependant, en dérogation à ce principe, de nombreuses installations comportent plusieurs ventilateurs d'extration desservant des circuits partiels, souvent pour des raisons d'économie d'exploitation. La sécurité
est alors maintenue par des asservissements plus complexes, ou par
une surveillance permanente du fonctionnement. On adopte souvent ces
circuits partiels pour l'extraction de cellules chaudes et pour l'extraction
des infiltrations après un accident dans un bâtiment de réacteur.
Dans ce dernier cas en effet, il est utile de réduire autant que possible
le débit de rejet, mais la mise en circuit de filtres (avec ou sans pièges
à iodé) augmente la perte de charge : les ventilateurs de marche normale
ne conviennent pas à ce régime exceptionnel.

2.5. Cheminée

La cheminée unique pour tous les rejets d'un bâtiment est de règle,
ce qui est d'ailleurs favorable à l'installation d'un groupe unique d'extraction.
Les prochaines années verront peut-être construire des cheminées
communes à plusieurs bâtiments.
La hauteur du rejet est fonction des dimensions du bâtiment pour les
laboratoires ou usines. Pour les réacteurs, c'est le maximum de concentration
au sol ou le rayonnement du panache qui impose une hauteur
de 50 à 100 m.

2.6. Prix des installations d'épuration

La moitié du prix varie à peu près comme le débit (registres, filtres
et pièges) et l'autre moitié, comme la racine carrée du débit (gaines et
cheminées) ; le prix de l'enceinte de confinement n'est pas compté dans
cette estimation.
Le prix des filtres est fonction, entre autres, de la vitesse de passage
de l'air à travers le papier : une grande vitesse diminue les frais d'installation
mais augmente beaucoup les frais de remplacement après colmatage.
L'optimisation devrait être faite dès l'avant-projet du bâtiment,
car le volume du local nécessaire peut être important. Le prix
des pièges dépend aussi de la vitesse de passage de l'air, qui est imposée
par l'efficacité exigée (fonction du temps de séjour dans le charbon).

3. EXEMPLES DE SYSTEMES D'EPURATION INSTALLES EN FRANCE

Les figures 1 à 4 montrent les systèmes d'épuration d'air de quatre bâtiments.

3.1. Réacteur EL4 à Brennilis (fig.1)

Puissance: 250 MW(th), 70 MW(e),
Modérateur: eau lourde,
Refroidissement: CO₂ circulant en tubes de force.

On remarquera les particularités suivantes:
Une chambre de refroidissement, garnie de plaques en fonte, limite
la température des gaz avant leur arrivée sur les pièges en charbon,
en cas de rupture du circuit de CO₂.
Un ventilateur est en service, l'autre en secours.
Un jeu de vannes permet, en cas de rupture d'un collecteur de CO₂, d'isoler l'enceinte, dont la surpression peut atteindre 5000 mm CE. La surpression est résorbée en évacuant 25 000 m³/h avec possibilité de mettre les filtres hors circuit.

Les pièges à iode sont traversés en permanence par le débit d'air extrait. Un contrôle périodique de l'efficacité permettra de décider de leur remplacement.

Les filtres (Schneider Pœlman) sont répartis en sept cages de 80 dièdres. Les pièges à iode (Schneider Pœlman) comportent 420 cartouches.

3.2. Réacteur OSIRIS à Saclay (fig.2)

Piscine à eau légère de 50 MW(th).

L'extraction du débit total de 62 300 m³/h se fait par un seul groupe de trois ventilateurs, asservi à un groupe de trois ventilateurs de soufflage (non représenté).
Les pièges à iodé sont traversés en permanence par le débit d'air extrait. Leur remplacement pourra se faire selon les résultats des contrôles périodiques de l'efficacité.

Les ensembles "filtres + pièges" Schneider Poeelman sont répartis en quatre circuits:
- hall et sous-sol, débit 47 900 m$^3$/h - cinq cages de 80 dièdres et cinq cages de 40 cartouches.
- ateliers chauds, débit 4 700 m$^3$/h - une cage de 50 dièdres sans piège à iodé,
- deux cellules chaudes, débit 2 * 1300 = 2 600 m$^3$/h portes fermées ou 7 300 m$^3$/h avec une des deux portes ouverte - un préfiltre de 36 dièdres par cellule, et pour l'ensemble une cage de 40 dièdres et une cage de 52 cartouches,
3.3. Réacteur RAPSODIE à Cadarache (fig.3)

Surrégénérateur refroidi au sodium, de 24 MW (th).

L'enceinte étanche en acier peut résister à une surpression de 2,5 bars (résultant de la consommation de tout l'oxygène contenu dans l'enceinte au cours d'un feu de sodium brûlant en nappe et du dégagement de chaleur associé).

L'extraction d'air se fait
- en marche normale: dans le «grenier» de la pile (local au-dessus de la cuve primaire, contenant les mécanismes de barres de commande et de sécurité),
- en cas d'accident: dans les locaux du sous-sol, afin de retarder le début du rejet des gaz actifs.

La vanne à fermeture rapide télécommandée (une petite vanne en parallèle permet l'échappement d'un débit réduit) arrête la ventilation en cas d'accident.

Un des deux groupes «filtres + pièges» est en service, l'autre en secours, avec vanne en parallèle permettant l'extraction sans passer par les filtres.

Un ventilateur est en service, l'autre en secours. Une prise d'air de dilution permet de réduire le débit extrait de l'enceinte.

Filtres et pièges Schneider Pœlman: pour chaque groupe, il y a une cage de 40 dièdres et une cage de 16 cartouches.

3.4. Bâtiments associés au réacteur RAPSODIE (fig.4)

Bâtiment actif pour la décontamination et le stockage du combustible, ADAC (examen et conditionnement du combustible avant son expédition à l'usine de retraitement).

Dans le bâtiment actif, il y a deux groupes «filtres + ventilateurs» dont un seul en service, l'autre habituellement en secours. Les deux groupes sont utilisés ensemble en période de décontamination. Chaque filtre Sofiltra comprend quatre éléments F5A (désignation actuelle AB506).

Dans le bâtiment ADAC, on a un filtre pour le circuit des sas et des cellules, et un filtre pour les autres locaux. Le débit total de 27 000 m³/h est rejeté par un ventilateur (avec un ventilateur identique en secours). Lorsqu'il y a risque de libération de l'iode, l'air des cellules traverse un piège à iode avant d'être rejeté dans le circuit général par un ventilateur particulier. Quand on ouvre la porte d'une cellule, un débit supplémentaire est extrait à travers un filtre, et rejeté à la cheminée par un ventilateur indépendant.

Les filtres sont constitués par 18 éléments Sofiltra, type F5A, dont quatre pour le circuit des sas, 12 pour les autres locaux et deux pour le circuit d'extraction porte ouverte. De plus, les bouches d'extraction normale dans les cellules sont équipées de 26 éléments Sofiltra, type F2A (désignation actuelle AB301).

Le piège à iode Schneider Pœlman comprend 16 cartouches.
FIG. 4. Bâtiments associés au réacteur RAPSODIE, épuration d’air.

REFERENCES


DISCUSSION

P.J. LINDER: I can see from your flow-sheets that you have some ducts with valves by-passing the absolute filters or other high-efficiency cleaning devices. Have you any special arrangements to avoid leakage through the valve, because leakage here - if of the same order as the penetration through the filter - would destroy the effect of the filters?

J. GUIRLET: No special action has been taken for the moment to prevent losses through the valves operating in parallel on the filter system. All we do is ensure that the valves have loss rates lower than the efficiency of the filter system.
AIR-CLEANING OPERATIONAL EXPERIENCE IN THE BHABHA ATOMIC RESEARCH CENTRE, TROMBAY

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BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

Abstract

The details of the operational experience gathered in the Bhabha Atomic Research Centre on various aspects of the problem associated with the control of pollutants from the operation of nuclear facilities housed therein form the subject of this report. A short account of the standards for radioactive gaseous waste management and the general practices concerning the prevention and control of air contamination is given. Studies on airborne radioactivity and the operational experience of the ventilation systems connected with some of the installations at Trombay are reviewed. The cost aspects of a typical ventilation system of an operating plant are presented.

1. INTRODUCTION

This report presents a review of information concerning the pollutant control and operational aspects of the ventilation and exhaust systems in some of the major nuclear facilities of the Bhabha Atomic Research Centre (BARC) at Trombay. A short account of the standard for gaseous radioactive waste management, general practices concerning prevention and control of air contamination and details of operational experiences are also presented.

2. LOCATION OF BARC AND ITS ENVIRONMENT

The Centre is situated on Trombay Island. It is about 5 km East of Bombay Island and about 10 km North-east of the thickly populated city of Bombay. It is bounded by the Bombay Harbour Bay on the South-west, the low hill ranges of the Western Ghats on the North and by the Arabian Sea on the South-east. The micro-meteorological factors pertaining to such a site call for careful consideration with respect to the control of airborne radioactive pollutants.

3. STANDARDS FOR GASEOUS RADIOACTIVE WASTE MANAGEMENT

The standards for the management of gaseous pollutants are given in "Manual for Radiation Protection in AEET" [1] which stipulates that the release of radioactive gases and/or aerosols from any installation shall be done in such a manner that the concentration of radioactive gases or aerosols at any point of occupancy in the environment (including the site)
shall not exceed the maximum permissible concentration values for air for members of the public. The standards adopted are based on international basic safety standards for radiation protection.

4. GENERAL PRACTICES CONCERNING PREVENTION AND CONTROL OF AIR CONTAMINATION

The design of installations is incorporated with systems of dilution ventilation with an appropriate number of air changes in addition to the normal comfort ventilation, to achieve the required standards of radiation protection in the working areas. The ventilation system of the active areas is planned so that the direction of flow is from the area of least activity to areas of increasing activity. All operations which are likely to produce radioactive contamination of air through production of gases or aerosols are carried out in airtight enclosures kept below atmospheric pressure (such as glove boxes or dry boxes) or in well-ventilated fume-hoods. Exhaust air from active areas and local enclosures such as glove boxes, dry boxes, fume-hoods or from the general ventilation of active laboratories is discharged into the atmosphere with appropriate filtration. Regular monitoring in the working areas and the environment is maintained to keep a check on the airborne radioactivity.

5. STUDY OF AIRBORNE RADIOACTIVITY AND OPERATIONAL EXPERIENCE CONNECTED WITH VENTILATION SYSTEMS

5.1. CIRUS reactor [2-4]

The CIRUS reactor at Trombay is a 40-MW(th) high-flux research reactor. It is natural-uranium-fuelled, heavy-water-moderated, light-water-cooled reactor with the provision of air to cool the reactor structure.

5.1.1. Ventilation system

Figure 1 shows the simplified flow diagram of the reactor ventilation system. The reactor hall is provided with 10.4 m\(^3\)/sec of washed, conditioned air. The air passes through the reactor structure after prefiltration by roughing filters of 85% efficiency as evaluated by the standard NBS test. Exhaust air from all ventilated areas is filtered by high-efficiency filters before being discharged to the atmosphere through a 130-m high stack. The absolute filters used have an efficiency of 99.97% as evaluated by the standard DOP test and can withstand 500°F and 100% relative humidity. The installed iodine monitors will trip the reactor, cut off the main exhaust flow and close the inlet and outlet dampers on high activity. An emergency by-pass fan is provided to exhaust lower volumes of air from the reactor through absolute filters and an iodine confinement system.
5.1.2. Airborne radioactivity

The air picks up radioactivity during its passage through the reactor structure activation of the constituents of air and recoil from the surfaces, fission products, gaseous and particulates, as well as the activation products from the structural materials.

Induced activity due to the activation of nitrogen and oxygen is not of significance with respect to release through the stack as they are of short half-life, while $^{41}$Ar and $^{14}$C, among others, are of importance. At 40-MW operation, the output of $^{41}$Ar is experimentally estimated to be of the order of 640 Ci/d as against the theoretically estimated rate of 950 Ci/d. The
concentration of $^{41}$Ar in the effluent is estimated to be about 520 pCi/ml which is about 1300 times the occupational MPCa for $^{41}$Ar. The total quantity of $^{14}$C produced in the reactor when operating at 40 MW is calculated to be 19.831 mCi/d. The $^{14}$C concentration in the effluent air is found to be low compared to the MPCa of $10^{-6}$ $\mu$Ci/ml.

All daughter products of gaseous fission products have been detected except those which have either a short or a very long half-life. Among the daughters of gaseous fission products $^{88}$Rb, $^{89}$Rb, $^{91}$Rb, $^{138}$Cs, $^{139}$Ba, $^{140}$Ba and $^{140}$La are the prominent gamma emitters. The particulate activity analysis of the filter-paper air sample collected before the absolute filters has shown the presence of $^{95}$Zr, $^{97}$Zr, $^{99}$Nb, $^{99}$Mo, $^{103}$Ru, $^{131}$I, $^{132}$I, $^{140}$Ba, $^{140}$La, $^{141}$Ce, $^{143}$Ce, $^{147}$Nd, $^{149}$Pm, and $^{24}$Na. In this study the interest was confined to fission products like $^{90}$Sr, and $^{131}$I. The amounts of release of $^{90}$Sr and $^{131}$I from the stack are estimated to be $22 \times 10^{-2}$ and 200 $\mu$Ci/d at 40-MW operation.

The presence of $^{24}$Na activity is due to the activation of aluminium by neutrons, the $^{24}$Na escaping into the exhaust system by recoil. The release of fission products is attributed to the defects in the cladding and surface contamination of the fuel elements. The presence of $^{58}$Fe in the dust collected over the filter plenum is presumed to be the corrosion product of air-cooled cast-iron thermal shields.

The release rate of tritium when the moderator reaches saturation tritium activity is estimated to be 22 Ci/d if the heavy-water content in the exhaust air remains at 28 ppm above the background.

5.1.3. Absolute filtration system

Checks on the functioning of the absolute filters during operation of the reactor were carried out on a routine basis by testing the efficiency

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</table>

TABLE I. PERFORMANCE DATA OF THE ABSOLUTE FILTERS AT CIRUS REACTOR
of the banks of absolute filters. Filter-paper air samples have been collected before and after the absolute filters and the efficiency as evaluated by the particulate activity is given in Table 1.

The build-up of pressure drop across the filter bank during the complete life of the filters is presented in Fig. 2. Because of clogging of the filters by the dust collected, the pressure drop begins to rise steeply after a certain period.

The replacement of the absolute filters is effected after a period of about 12 to 15 months when the pressure drop across the filter builds up to a value of about 11.5 cm w.g.

The spent filters are treated as solid waste which does not pose any problem in handling because of the low external radiation levels.

5.1.4. Estimation of dilution rate factors for continuous release from the stack

The estimation of dilution rate factor \( K \) of the atmosphere at different locations around the facility, will enable the calculation of the permissible discharge rate for any radionuclide, which in turn will define the confinement to be provided for a nuclear facility. The estimation of such dilution rate factors is of importance to the Trombay Centre because of the peculiar topography of the site.

Estimation of the dilution rate factor for the continuous release from the CIRUS reactor stack using tritium release as a tracer has been made over a period of one year. This method involves the estimation of tritium in the air at different locations around the facility at various seasons. The maximum and minimum values of the dilution rate factor estimated from the release of tritium from the CIRUS reactor stack are given in Table II and the location of the sampling points around the CIRUS reactor stack are indicated in Fig. 3.

The lower values of \( K_{\text{min}} \) are probably due to the proximity of the stack to the Trombay hill which tends to reduce the effective stack height.
### TABLE II. DILUTION RATE FACTORS AT TROMBAY

<table>
<thead>
<tr>
<th>Sampling point No</th>
<th>Distance from stack (km)</th>
<th>Minimum value of $K$ ($m^3/sec$)</th>
<th>Maximum value of $K$ ($m^3/sec$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>$1.42 \times 10^4$</td>
<td>$3.69 \times 10^4$</td>
</tr>
<tr>
<td>2</td>
<td>0.69</td>
<td>$1.04 \times 10^4$</td>
<td>$2.88 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>0.85</td>
<td>$1.07 \times 10^4$</td>
<td>$3.0 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>0.91</td>
<td>$2.44 \times 10^3$</td>
<td>$6.59 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>$1.83 \times 10^4$</td>
<td>more than $10^6$</td>
</tr>
<tr>
<td>6</td>
<td>1.11</td>
<td>$1.07 \times 10^4$</td>
<td>$3.1 \times 10^4$</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>$5.78 \times 10^4$</td>
<td>$4.23 \times 10^4$</td>
</tr>
<tr>
<td>8</td>
<td>3.06</td>
<td>$6.85 \times 10^3$</td>
<td>more than $10^6$</td>
</tr>
</tbody>
</table>

5.2. Fuel reprocessing plant [5]

This plant is designed to treat irradiated fuel elements from the CIRUS reactor. The Purex type of process is employed for separation.

5.2.1. Ventilation system

The ventilation flow sheet is given in Fig. 4. The dissolver off-gas passes through a scrubber and a deep-bed glass-wool filter before it joins the masonry plenum into which the ventilation air from the cells is also exhausted. The air is passed through standard glass-fibre filters which are suitable for temperatures up to 500°F and 100% relative humidity. After filtration the air passes through an 180-m long underground concrete duct with bitumen-coated inner surfaces and is exhausted through a 135-m high reinforced-concrete stack. The total volume of air discharged through the stack is 2830 m$^3$/min.
5.2.2. Airborne radioactivity

The isotopic composition of the samples collected at the stack in particulate form has indicated that on the average 55% of the total activity is due to $^{144}$Ce. In addition $^{95}$Zr, $^{137}$Cs, $^{90}$Sr and $^{106}$Ru are also found to exist in average proportions of 15, 3, 1.5 and 25% respectively.

The long-lived fission product $^{85}$Kr is released to the atmosphere in significant quantities. The $^{85}$Kr release during the dissolution of irradiated uranium (700 MWD/t irradiation and 10-months cooling) is found to vary from 80 to 104 Ci, with an average of 95.7 Ci.

![Flow sheet of ventilation system in plutonium plant.](image)

5.2.3. Removal effected by plating of radioactivity along the duct

The study of the removal effected by plating of radioactivity is of importance because it provides information concerning the extent and nature of hazards likely to result in the accidental condition.

Iodine deposition along the duct and the removal effected by the filters. Radioiodine (100 mCi) has been released into the exhaust system simulating the actual conditions. To assess the deposition and the removal effected by the filters, air samples have been collected (during dissolution) before and after the filters and at two points along the length of concrete ducting. The plating that occurred in the 180-cm diameter concrete duct onto a surface of 1017 m² and at a flow rate of 2260 m³/min has been estimated to be 85%, while the average retention efficiencies of the deep-bed glass-wool filter and the absolute filters are of the order of 12.9 and 20.4% respectively.

Deposition of particulates along the duct. The deposition of particulate activity as evaluated by the standardized swipe method with a beta removal effectiveness of 66.4% for the first swipe has indicated that for a total release of 1140 μCi (over a period of three months), 17 μCi (1.5%) of particulate activity has been plated along the duct.
Except for $^{106}$Ru, the other isotopes do not show any discernible variation in their contents between air samples and swipe samples. The $^{106}$Ru content in swipe sample was more than in air samples (35 and 25% respectively). The deposition of $^{106}$Ru in the outlet was more than at the beginning of the duct.

5.2.4. Absolute filtration system

The fresh filter bank has been found to have 99 to 99.5% efficiency for particulate activity encountered in the plant. The filter banks have been found to lose their retention efficiency over a period of time due to the excess steam and nitrous oxide (particularly during dissolution). A typical filter bank has been found to have a retention efficiency of 80 to 85% after continuous use for a period of over three months. The loss in efficiency is attributed to possible collapse of packing material during installation.

6. COST ASPECTS OF A TYPICAL VENTILATION SYSTEM

To evaluate the various cost factors of the ventilation and air-cleaning system of a facility handling hazardous radioactive dust, the Centralised Decontamination Centre was studied. This Centre processes contaminated equipment, vehicles, rubber, plastic articles etc. It also includes a laundry for the decontamination of clothing. This facility is supplied with air, washed and filtered by washable coarse viscous filters. The system consists of five exhaust filtration units including the local exhaust systems.

Considering the economies that can result from the use of prefilters in conjunction with the high-efficiency filters, integral filter units with fixed frame and replaceable filter cartridges are used. The filters have a 99.97% efficiency as measured by the standard DOP test and are resistant to $500^\circ F$ and 100% relative humidity. Special provision has been made for the rapid replacement of the filter elements.

The capital cost details of the ventilation and air-cleaning system of the decontamination centre, which handles 1680 m$^3$/min air by two 50-hp exhaust fans, are given in the Table III.

**TABLE III. CAPITAL COST DETAILS OF THE VENTILATION SYSTEM OF THE DECONTAMINATION CENTRE**

<table>
<thead>
<tr>
<th>Item</th>
<th>Rupees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cost of the inlet air system (spray washers, viscous filters ducts and blowers)</td>
<td>45 000</td>
</tr>
<tr>
<td>Total cost of the exhaust system (including fans, ducts, filters etc )</td>
<td>165 000</td>
</tr>
<tr>
<td>Cost of filters including filter-retaining frames in exhaust system</td>
<td>67 500</td>
</tr>
</tbody>
</table>
TABLE IV. PHYSICAL AND RADIOCHEMICAL PROPERTIES OF DUST ENCOUNTERED IN DECONTAMINATION CENTRE

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Active laundry</th>
<th>Rubbers and plastics</th>
<th>Heavy equipment decontamination room</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>Mostly less than 20 μm</td>
<td>Mostly less than 20 μm</td>
<td>Mostly less than 20 μm with few as high as 100 μm</td>
</tr>
<tr>
<td></td>
<td>Few are as high as 1000 μm</td>
<td>with few as high as 100 μm</td>
<td>higher sizes are in the range 20 to 100 μm</td>
</tr>
<tr>
<td>Shape</td>
<td>Spherical, fibrous, irregular and agglomerated particles</td>
<td>Very small particles mostly spherical or elongated other mostly irregular or agglomerated</td>
<td>As in column 2</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless, pale pink, pink, white and black</td>
<td>Colourless, pale pink, pink and black</td>
<td>As in column 2</td>
</tr>
<tr>
<td>Dust load (mg/m³)</td>
<td>0.384</td>
<td>0.087</td>
<td>0.122</td>
</tr>
<tr>
<td>Radiochemical properties</td>
<td>Beta decay exponent varies from 0.3 to 0.9</td>
<td>Beta decay exponent varies from 0.07 to 0.6</td>
<td>Beta decay exponent varies from 0.03 to 0.3</td>
</tr>
<tr>
<td>Decayed</td>
<td>Alpha decay exponent varies from 0.6 to 1.2</td>
<td>Alpha decay exponent varies from 0.4 to 1</td>
<td>Alpha decay exponent varies from 0.07 to 0.6</td>
</tr>
<tr>
<td>Type of activity and max conc</td>
<td>Alpha, beta and gamma ( \delta y 18 \times 10^{-18} \mu Ci/ml ) ( \alpha 51 \times 10^{-12} \mu Ci/ml )</td>
<td>As in column 1 ( \delta y 21 \times 10^{-18} \mu Ci/ml ) ( \alpha 76 \times 10^{-12} \mu Ci/ml )</td>
<td>As in column 1 ( \delta y 525 \times 10^{-19} \mu Ci/ml ) ( \alpha 166 \times 10^{-19} \mu Ci/ml )</td>
</tr>
<tr>
<td>Radioactive elements</td>
<td>Mostly U, Th, Pu and fission products</td>
<td>As in column 1</td>
<td>U, Pu, old fission products, (^{60})Co, (^{54})Mn</td>
</tr>
</tbody>
</table>

\(^{a}\) This is the quantity \( x \) in the equation \( \frac{A_1}{A_2} = (t_2/t_1)^x \) where \( A_1 \) is the activity at \( t_1 \) and \( A_2 \) at \( t_2 \)
Investigations have been made to characterize the airborne pollutants [6]. The physical and radiochemical properties of the dust are given in Table IV. Operational experience has shown that for the type of dust encountered in the plant each of the 28.5 m$^3$/min prefilter elements requires a change after six months of continuous operation, while each of the 28.5 m$^3$/min absolute filter elements requires a change after a period of 18 months. The replacement of the filter cartridges is effected when the pressure drop across filter builds up to a value of 6.15 cm w.g.

The annual replacement cost of a 28.5 m$^3$/min filter is Rs.640/-. This replacement cost takes into account the costs of filter cartridge, replacement and disposal.

ACKNOWLEDGEMENT

The authors wish to acknowledge the work of Dr. A. K. Ganguly and his colleagues which has been referred to extensively in the preparation of this report.

REFERENCES


DISCUSSION

J.J. COHEN: Figure 2 of your paper indicates a pressure drop build-up of roughly a factor of 4. Does this build-up significantly affect the total volumetric flow rate through the system and, if so, how is this compensated for?

K.T. THOMAS: The pressure drop increases rapidly after it reaches 2.5 inches. The filters are changed immediately afterwards, because the pressure drops build up very rapidly within a matter of a few days and we do not operate at very high pressure-drops for reasons of economy.

R. GOULET: Are pre-filters used in front of the absolute filters and why did the absolute filters plug up so rapidly during the last month?

K.T. THOMAS: Pre-filters are used in the supply-air system. The absolute filter pressure builds up rapidly, as I said, after about 2.5 inches and, within a matter of 15 days or so, reaches a figure of 4.5 - 5 inches, although it may take almost a year initially to reach 2.5 inches. It is not
possible to explain this rapid plugging up after reaching a certain pressure drop.

C. CHEEVER: Did you correlate the calculated atmospheric dispersion with your experimental results?

K.T. THOMAS. If you are referring to dilution-rate factors, we have found that our figures are lower than the calculated figures obtained using Sutton's equation. This is explained by the peculiar location of the Bhabha Atomic Research Centre at Trombay, which has hills on one side and the harbour bay on the other.

P.J. LINDER. What was the sampling time when determining the dilution-rate factors?

K.T. THOMAS: Sampling was done for about one year. However, details of the sampling time for determining dilution-rate factors are not available for presentation at present.

P.J. LINDER: I just wanted to point out that the sampling time could influence the analysis of the values reported.
AIR CLEANING AT THE USAEC Y-12 PLANT

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Y-12 PLANT,
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Abstract

AIR CLEANING AT THE USAEC Y-12 PLANT This paper describes some of the air-cleaning requirements of production, research, development, and biological facilities in the Y-12 area. Problems and their solutions in hazardous-material containment, air cleaning, contamination control, and air pollution control are enumerated. Bio-clean and laminar-flow clean rooms, germ-free supply air systems, exhaust systems for handling toxic and radioactive materials, virus containment and exhaust facilities are described. The Plant's practices regarding air cleaning are discussed including standardization of specifications for high-efficiency particulate air filters and mounting frames, DOP testing of air filter systems, and the replacement of sub-standard filter installations.

INTRODUCTION

The Y-12 Plant (Figure 1) located in Oak Ridge, Tennessee is one of the largest and most versatile of the AEC plants. It is operated by the Union Carbide Corporation - Nuclear Division for the Atomic Energy Commission. The plant was built in 1943-1944, as part of the Manhattan Project, to separate the fissionable isotope of uranium, U-235, from normal uranium by the electromagnetic process.

Since those early years, Y-12 has developed into a highly sophisticated manufacturing, research, and development organization. Scientists work in most fields of research associated with physical and biological sciences. At the same time, nuclear production capabilities are maintained.

As a result of this wide divergence of activity in the Y-12 area, air cleaning is a major consideration—not only in protecting the employees within the plant and residents in surrounding areas from radioactive and toxic materials and infectious organisms, but in the protection of biological experiments and experimental animals from environmental contaminants.

Some of the radioactive materials processed in the Y-12 Plant are:

- Uranium-233
- Plutonium-239
- Uranium-235
- Thorium
- Uranium-238
- Americium-241

Toxic materials handled within the Plant include beryllium, lead, mercury, and organic solvents.

The Oak Ridge National Laboratory-Biology Division, which is also operated by Union Carbide and located within the Y-12 area, experiments with many hazardous biologicals. Such viable particulates of concern to the environmental control engineer include:

- Herpes Tumor-Producing Virus
- Rauscher Leukemia Virus
- Friend Leukemia Virus
- Human Leukemia Virus

Other requirements for air cleaning include:

1. Carbon machining,
2. Fly ash removal - Steam Generation Plant,
3. Clean rooms for high-purity metal research,
4. Clean rooms for instrument calibration,
5. Clean rooms for parts inspection, and

AIR-CLEANING INSTALLATIONS

To illustrate the variety and general arrangement of some of the air-cleaning facilities employed in the Y-12 Area, a series of schematic flow diagrams have been prepared.
Figure 2 depicts a typical exhaust air system serving a machine tool on which uranium-235 metal is machined into shapes. Here, the cutting tool and work part are entirely enveloped in a transparent enclosure designed specifically to contain, at the source, metal particulates and tool coolant which become airborne during the machining operation. The smaller particles are withdrawn through the exhaust system while heavier particles fall out in the hood and may be easily removed.

The larger airborne particles are separated from the hood exhaust by a coarse filter of bronze wool which is wetted by the entrained coolant, while a mechanical trap is used to remove the contaminated liquid coolant from the air stream.

Room air is not recirculated. To assure that airborne radioactive particles are captured, all room exhaust, as well as machine exhaust, is filtered through wool felt bags before release to the atmosphere. Dust particles, thus captured, drop into the hoppers and nuclear-safe receivers when released from the filter bags by the reverse-air, jet-cleaning action of the dust collector.

Beryllium processing presents one of the major air cleaning problems from a toxic-dust standpoint. The metal is machined dry. Chips must be recovered for salvage while maintaining safe working conditions. Figure 3 shows the basic design for beryllium chip pickup and recovery and the machine-hood exhaust systems as installed in a Y-12 shop that machines beryllium shapes. The one machine shown represents a group of such machines served by these contamination control systems. Room air is drawn into the hood, which encloses the machining operation, by two exhaust systems. The large-volume hood exhaust system entrains and filters out the smaller particles of beryllium that become airborne in the hoods.

The high-velocity chip recovery exhaust system, operating at a nozzle velocity of 6,000 ft/min, picks up the chips that are released by the cutting or grinding tools within the hoods. The chips are then separated from the air stream.
by a highly efficient cyclone separator and dropped into a dust-tight receiver. The high-efficiency final filters remove the fine dust particles not captured by the cyclone. Servicing of final filters without spread of contamination or system shut-down is accomplished by the use of multiple filter boxes and a special valving arrangement.

Thorium processing ventilation is handled in the manner shown in Figure 4. Hood exhaust from process equipment and room exhaust are combined and filtered through high-efficiency filters. This design prevents both the release of toxic materials to the atmosphere and the buildup of airborne concentrations of radioactive material within the room.
After the end of World War II, the Y-12 Plant's electromagnetic isotope separation facilities were superseded by the more economical gaseous diffusion process carried on at other AEC installations. The only remaining facilities associated with electromagnetic isotope separation are the original pilot plant and two of the 36-calutron installations. These facilities, while located in the Y-12 Plant, are operated by the Oak Ridge National Laboratory. Part of the latter facility was first modified to provide a separations capability for enriching the stable isotopes of most all elements in the periodic chart. More recently, a part of this facility (an eight-calutron system) has been altered to permit the separation of isotopes of such alpha-active elements as uranium, plutonium, and americium. One to one hundred-gram quantities of these enriched isotopes have been made available to the AEC and to AEC-approved research programs.

Figure 5 shows the general layout of the processing areas and the overall ventilation scheme. The room pressures are maintained automatically in relation to themselves and to the outside atmosphere. The entire facility is maintained below atmospheric pressure with the rooms having the greater possibility of contamination (namely, the Components Wash Area and the Dirty Change Room) being maintained at the lowest relative pressure. All rooms have a high rate of air change. All air exhausted from the rooms is filtered at least once through high-efficiency filters.

Double containment is provided in the Components Wash Area and in the Chemical Process Areas. The first containment is provided by the glove boxes (Figure 6) in which the alpha-emitting product is processed; the second containment is provided by the room in which the glove boxes are located. Transfer of materials within the room is made in sealed containers thereby maintaining the principle of double containment at all times. All glove boxes are ventilated and maintained at approximately a one-inch water-column pressure (wg) lower than that of the room in which they are located.
Figure 7 shows the arrangement used in the Chemical Processing Area to filter the ventilation air from the glove boxes through high-efficiency filters in series. This arrangement also serves the glove boxes in the Components Wash Area. All glove boxes are automatically protected against radical pressure changes, loss of fan power for ventilation, and fire occurring in the boxes.
Many biological experiments can be adversely affected by outside influences, particularly if germ-free animals are used. To reduce the risk of environmental contaminants, many laboratories of the ORNL Biology Division are provided with germ-free supply-air systems. Figure 8 shows the general arrangement of one such supply-air system. This system provides temperature and humidity control of a 100 percent outside air supply and, in addition, provides for the removal of dust and bacteria from the air stream by means of a bank of high-efficiency air filters. It is important that the high-efficiency filters be located so as to be the final element in the system. For supply-air systems requiring a higher degree of bacteria and dust removal, a second set of high-efficiency filters is sometimes installed in the laboratory air-diffusing assembly (as close to the experimental area as possible). In certain experiments, the supply-air system and the experimental area itself must be as free from airborne particulates, odors, fumes, and vapors, as is possible to obtain.

FIG. 8. "Germ free" supply air system.
A facility using both the clean-room principle of horizontal laminar flow and odor and organic fume removal by activated charcoal is shown in Figure 9. High-efficiency filters are installed in the end wall of the larger laboratory. Filtered air enters the room horizontally, passes through the work area, and exhausts through perforated metal return air grilles. Air flow through the laboratory is laminar horizontal at a velocity of approximately 60 ft/min. The small laboratory is equipped with ceiling-mounted high-efficiency filters providing a ceiling-to-floor air movement. The air, as supplied to the laboratories, is composed of approximately one-third outside air and two-thirds return air from the rooms. The exhaust system removes, through hoods, any concentrated odors, fumes, or vapors generated therein. Activated-charcoal filters remove all of the objectionable items if present in the room air or outside air supply. The intermediate filters extend the life of the high-efficiency filters by removing particles of charcoal that are released from the charcoal filters. The high-efficiency air filters assure clean, "germ free" supply air at low velocity.

![Figure 10: High-purity laboratory (arrangement of mechanical equipment and air distribution).](image)

Research on high-purity metals has resulted in the requirements of a clean-room facility that is as free of particulates as possible to design and construct. The air-flow diagram for the High-Purity Laboratory is shown in Figure 10. Supply air, filtered through two banks of prefilters and two banks of high-efficiency filters, is discharged through the final high-efficiency filters located in the room ceiling, downward through the room at a velocity of 65 feet per minute, and returned through a grated floor. The room is kept under positive pressure with exfiltration of air allowed only through the laboratory airlock. The makeup air is passed through a charcoal filter and cooled, as required for system temperature and humidity control, before mixing with the return air from the room. The bank of final high-efficiency filters were specially selected for 99.99 plus percent efficiency by the DOP (dioctyl phthalate) test. The bank of initial high-efficiency filters was tested and accepted at 99.97 percent (minimum) efficiency.
Determinations were made by particle counters of the total particle count in the High-Purity Laboratory when approximating operating conditions. In a test period extending nearly 400 hours, the particle counter detected one particle, 0.5 micron and larger, in each six cubic feet of air sampled. Subsequent biological and radiological tests resulted in zero bacteria count and zero fission fallout and radon daughter products counts. (1)

Figure 11 presents a view of a system designed to separate particulate matter exhausted with hot gases from an incinerator. Air at 1,800°F passes through a low-velocity duct, to allow settling of heavier particles, then continues to a water-cooled heat exchanger. An air-cooled heat exchanger receives the flow and exhausts it at 500°F to a primary cyclone and then to a multiclone. The air proceeds into the main exhaust stream where it is moved at 120°F to a bag collector, fan, and stack. The bag collector is made of wool felt and operates with air-pulse reverse jet cleaning. Geometric design of the containers, located beneath the cyclones at the left and below the bag collector at the right, prevents spontaneous fission of the material collected. A photograph of this facility is shown in Figure 12.

Some operating problems that have arisen include:

1. Buildup of tar-like substances within the system which causes decreased heat dissipation in the heat exchangers and premature plugging and overheating of ducts and filtration equipment with consequent high maintenance costs.

2. Corrosion of internal parts of the system caused by combustion of waste products that contain such corrosive agents as acids, bases, oils, and plastics.

3. Moisture formation in the system as the gases are cooled by contributing to filter-bag plugging, corrosion, and criticality problems involving the safe concentration of hygroscopic nuclear products.

4. Contamination of the room air in which the incinerator is located, whenever the ventilation through the hood becomes insufficient to remove radioactive particles from the room.

Other air-cleaning requirements at Y-12 are generally handled in a conventional manner. For example, carbon dust resulting from machining operations is separated from the exhaust air stream by bag filters, and fly ash is removed from the boiler-plant stack gas by means of 98 percent efficient electrostatic precipitators.

PROBLEM AREAS

The proper selection of prefilters to high-efficiency filters has been evaluated rather carefully over the years, since the efficiency of the prefilters is a major factor in determining the service life of the high-efficiency final filters. In exhaust air systems, consideration should also be given to such factors as pressure surges and air velocities in the system in order to select a prefilter with sufficient structural strength to withstand over-pressure conditions and disturbances in the air stream that might damage the filter element.
Figures 13, 14, and 15 show the results of a prefilter failure. The exact cause of this particular failure was never determined; however, it was thought to have resulted from an over-pressure condition as might have been created by improper damper operation at the fan. A contributing factor was the rather high-velocity air stream striking the face of the filters which failed. Failures of this nature not only result in the loss of the prefilter bank but also require the change-out of the final high-efficiency bank which is a more serious and costly situation. Figure 15 shows the high-efficiency filter bank almost completely blocked with parts of prefilter paper and separators. All future filters used in this service have been equipped with three reinforcing face bars attached to both the front and rear of each unit. This change in filter design results in satisfactory operation.
Figure 16 shows an operation which has produced another air-cleaning problem; namely, a billet grinding operation. The material is an alloy containing normal uranium. No attempt is made to capture the dust particles at the source since the parts are of many sizes and the operator is wearing a fresh-air mask and protective clothing. Air is drawn into the room through louvered openings which are baffled to prevent the exit of flying dust particles. The ventilation air is exhausted through cabinets containing roughing filters and high-efficiency filters in series. Tests indicate that the arrangement is effective in retaining radioactive particles in the filters. However, too frequent changing of the filters has been required. Consideration has been given to substituting a self-cleaning bag filter for this operation.

Prolonged storage of high-efficiency filters may present more serious problems than presently recognized. Figure 17 is a photograph of a high-efficiency filter that was manufactured in 1963, stored at the Y-12 Plant for over five years, but never installed in an air-cleaning system. Recently, the filter was removed from the warehouse and rechecked for efficiency under the standard DOP test at the AEC Filter Test Station in Oak Ridge. The filter media in this unit ruptured at an air flow of 1,000 cfm and one inch (wg) pressure differential, as shown in Figure 18.

Three additional filters of the same lot, design, and age, and stored under the same conditions were also retested for DOP penetration. Two of the three failed at one inch (wg) pressure in a manner similar to the one shown in Figure 18.
All failures were due to ruptured filter media with punctures occurring along the back knuckles of the pleats at points where the paper media folded around the aluminum separators.

Further investigation revealed the following:

1. All were of the glass-pack-sealant, metal-frame, high-temperature design.

2. The filter paper used in the manufacture of these four units was a non-waterproofed, fire-resistant media.

3. Storage was in an unheated warehouse.
FIG. 16. Billet grinding area.

FIG. 17. High-efficiency filter.
No definite conclusions have been made as to the one cause of these filter failures. It could be a combination of factors. The failures could have been the result of a shift in the position of the aluminum separators which stressed the filter media. It should be noted that these units were all high-temperature filters using glass-pack seals. This type of filter is particularly vulnerable to handling damage since there is no adhesive at the ends of the pleats to hold the separators and media in a fixed relationship with one another. The fact that the filter media was not waterproofed cannot be overlooked as a contributing factor to these failures. It is possible that the media may lose some of its tensile strength as a result of a reversal of the paper-making process when filters are stored under adverse environmental conditions.

In order to study the storage problem further (at the request of the AEC Headquarters Office), an additional lot of fourteen high-efficiency filters, representing four US manufacturers, were subjected to extensive tests at the Edgewood Arsenal.
Filters selected were ones which had been stored at the Y-12 Plant from 2 to 5 1/2 years. The tests included initial DOP penetration determinations, humidification at 95° F (dry bulb) and 95% relative humidity, moisture addition at the rate of 1 1/4 pounds of water per minute when operating at a ten inch (wg) static pressure, and DOP testing after each of three periods of wetting. The final test was a DOP penetration test made ten days later with the filters in a dry condition.

Results of the tests on the fourteen test filters may be summarized as follows:

1. Three of the fourteen filters received minor shipping damage between the Y-12 Plant and Edgewood as evidenced by a failure to pass the as-received DOP test.

2. Eleven of the fourteen test filters failed the final DOP test at Edgewood after having been subjected to the moisture-pressure tests.

The tests have not as yet been fully evaluated. However, some general conclusions might be stated:

1. High-efficiency filter media should be properly waterproofed. Three of the fourteen filters tested by Edgewood were not waterproofed. All failed the tests.
2. Prolonged storage of filters and unfavorable storage conditions should be avoided. Only three of fourteen filters passed the Edgewood tests.

3. The tensile strength of filter media is a factor in high-efficiency filters retaining their original filtration capabilities through the shipping, storage, and handling phases. Specifications for filters should require a media at least 15 mils in thickness, when measured in accordance with the TAPPI method, Specification T411 m-44, Technical Association of the Pulp and Paper Industry.

4. Degradation of high-efficiency filter systems for emergency service is likely to occur. It is recommended that such systems be operated at least once per week for a minimum of 15 minutes in order to assure satisfactory performance should the need for their use arise.

Further work is underway in order to arrive at a better resolution of problems encountered in the prolonged storage of high-efficiency filters.

Y-12 has been through a long development period concerning what would seem to be a very simple task—mounting high-efficiency filters. Over the years, each architect-engineer would have his own methods of designing filter frames, and before the days of in-place DOP testing, these frames held the filter in place very nicely. However, with the development of DOP generators and photometers, it was found through in-place testing that they lacked all the desired qualities of a good filter holding frame. In fact, they all leaked. So, one was designed and standardized which more nearly met all requirements.

Figure 19 shows a poorly designed, high-efficiency filter framing system. Seals are dependent on caulking between individual light-gauge aluminum filter frames. The gasket sealing flange is of the same light gauge. The holddown clips are 1/8-inch set screws—eight per filter. It is obvious that difficulty would be encountered in sealing these filters in place. Gasket compression was most inadequate; perimeter frame leaks were many. DOP tests were impossible to run because of excessive penetration. Satisfactory results were finally obtained by the liberal application of silicone building sealant to the gaskets and to all construction joints.

On past installations, attempts have been made to retain 24 by 24-inch high-efficiency filters with four 1/4-inch bolts per filter, four 5/16-inch bolts per filter, angle-iron retainers fastened only at the top and bottom of a filter bank, holddown clips, equipped with springs, and many other items.

One deficiency that many of the older frames have is the lack of a sufficient number of holddown clips. Figure 20 shows a system originally equipped with only corner holddown clips. To obtain a DOP-tight system, it was necessary to add the center channel to obtain the required gasket compression. Note, too, that these filters are stacked one upon the other. This design precludes the installation of top and bottom holddown studs which are believed to be necessary for a good system.
Although there are many acceptable designs, any prototype of an unproven device for clamping filters into a frame together with the frame itself, should be thoroughly tested and evaluated before use in any installation.

The high-efficiency particulate air filter holding frame that has been standardized for the Y-12 area is a simple design, fabricated with standard structural steel members, as shown in Figure 21. The basic features of this holding frame are its rigidity, its all-welded leak-tight construction, and its evenly distributed and generous clamping power. The frame is made of carbon steel with 3 by 3 by 1/4-inch perimeter angles and 2 1/2 by 2 1/2 by 1/4-inch interior angles. The 5/8-inch holddown studs, Figure 22, are stainless steel with brass hexagon nuts. Both interior and perimeter clips are of 1/4-inch-thick carbon steel. Inert-gas consumable electrode welding is used throughout. All welded joints on the face of the angles forming the seating surface for the filters are smooth, flush, and ground to a 64-microinch finish or better. The frame forming the seating surface for each filter
FIG. 21. Y-12 plant standard high-efficiency filter framing system.

FIG. 22. Section of high-efficiency filter framing system showing component parts (front view).
is flat within 1/16 inch. All stainless steel studs are continuously welded to the angle to prevent leakage. Figure 23 is a rear view of a section of the mounting frame showing in detail the welds made by the inert-gas consumable electrode process.

FIG. 23. Section of high-efficiency filter framing system showing components parts (rear view).

The next slide, Figure 24, shows an installed filter frame at the air-entering side. The stainless steel studs of this mounting system serve as both a filter-holding and filter-positioning device, and are adequately sized for their primary purpose of filter-gasket compression.

Figure 25 shows the first tier of a large filter bank installed in accordance with the Y-12 standard design details. Note the 95 percent NBS efficiency pre-filters on the left and the high-efficiency (in this case 99.99 percent DOP test) filter bank on the right. Also note the service platform near the top of the photograph.

Based on experience at Y-12, and the experience of others who have used this particular filter frame, it has been concluded that a basic design criteria for HEPA filter mounting frames should include the following:

1. Have an all-welded construction.

2. Permit no rivets, screws, rubber seals, or caulking.
3. Provide one pressure point for gasket compression for each foot of filter perimeter.

4. Have holddown clamps capable of compressing the neoprene sponge filter gasket evenly to obtain 80 to 90 percent compression of the gasket.

5. See that all points of possible leakage are accessible for pin-point probing and repair.

6. Have no field joints between individual filter-holding frames.

7. Be free of leaks when tested with DOP.

The next several slides are photographs of clean rooms at the NASA’s Goddard Space Flight Center. Note that Y-12’s frame design was used throughout this re-
FIG. 25. Air plenum showing prefilters (left) and high-efficiency filters (right).

cently completed facility. Figure 26 shows the ceiling view of the vibration test cell. The room is a vertical laminar-flow clean room with the final high-efficiency filter bank located at the ceiling level. Figure 27 shows the prefilter and final-filter holding frames installed in the air plenum above the ceiling of the vibration test cell. Figure 28 shows a horizontal laminar-flow clean room with the end-wall-mounted high-efficiency filters in place. This view shows the clean-air side of the filter bank which serves a radio-frequency-interference test area. Figure 29 is a view looking into the fifty-foot-high, high-efficiency filter bank serving Goddard's Vacuum Optical Bench Test Facility. The Space Craft Checkout Area is shown in Figure 30. This bank containing over 350 filters is thirty feet high. All of these systems were DOP tested, probed for leaks, and are now operating at near-zero particle-count levels.

DESIGNING A CONTAMINATION CONTROL FACILITY

What are the major factors in the design and construction of a successful contamination control facility?
The primary factor is basic—to contain the contaminant. Without a means of limiting the diffusion of the contaminant throughout the area, there is little chance of successfully maintaining the desired working conditions. Where filters are used, it is most important that they be specified and selected to do the necessary air-cleaning job. Prefilters must be adequate to remove the bulk of the particulates from the air stream. The high-efficiency filters should be of noncombustible media, tested at two flows (100 and 20 percent) for total penetration (gaskets, frame, and media). Y-12 generally uses filters having fire-retardant plywood frames, aluminum separators, and glass or glass-asbestos paper. Of equal importance is the selection of the filter holding frame. It should have zero leakage (DOP) under all normal conditions of air flow and system pressures. Each filter system should be thoroughly checked out; first, visually, by the strong-light technique and, finally, by the DOP or similar test.
FIG. 27. Air plenum showing high-efficiency filter framing system.

FIG. 28. Horizontal laminar flow clean room showing high-efficiency filters installed in the end wall.
FUTURE OF AIR CLEANING

What does the future hold in air cleaning?

Experience with the Y-12 High-Purity Laboratory has proved that all particulates 0.3 micron or larger can be removed from the air stream. This degree of efficiency has been made possible by improved filters, methods of installing filters, and testing techniques for proving air-cleaning systems. In fact, large systems are now being designed in Y-12 that involve air recirculation from and returning back to areas in which toxic and low-radioactive materials are to be processed. The double high-efficiency filter concept is now used to clean up these recirculating air streams, then mix the return air with a minimum amount of makeup air. In the past, the design would have called for 100 percent once-through, outside air for such facilities. Savings should result not only in capital equipment for heating and cooling but in operating costs, both summer and winter.
Figure 31 shows an air system serving a beryllium area in which recirculation is planned. Total supply air to the area of 100,000 cfm, of which 86,000 cfm is recirculated air, provides approximately 30 air changes per hour. Filtration of the recirculated air utilizing double banks (two in series) of high-efficiency air filters
assures a supply of beryllium-free air. The process exhaust air from glove boxes and washdown stations is filtered by high efficiency filters in the normal manner before being discharged above the roof.

Double high-efficiency filtration accomplishes several important objectives:

1. There is greater assurance of complete air filtration. One is protected even if failure occurs in either bank of filters.

2. Maintenance can be done on the first bank without contaminating the entire duct system. The second bank of filters may operate ten years or more between changes as evidenced by experience with clean rooms designed on this basis.

3. In biological work, double high-efficiency filtration permits the final filter placement to be at or very close to the work area—the point of chief interest. This not only guarantees cleaner air to the laboratory but is a biological barrier eliminating cross contamination between areas as might be possible through the ventilation systems.

![Diagram](https://via.placeholder.com/150)  
**FIG. 32.** Radon adsorption system.
One of the more interesting design and startup jobs in Y-12 was a radon adsorption system. Figure 32 is a flow diagram of this system.

Basically, the system removes radon, a radioactive gas resulting from the decay of radium and thorium, from the makeup air stream that is used to pressure a low-level counting laboratory located some 50 feet below ground level. To accomplish this, the makeup air (60 cfm maximum) is dried to a -100°F dew point, filtered, cooled by liquid nitrogen to -180°F, passed through an activated charcoal adsorber at -112°F, reheated to 75°F, and admitted into the hermetically sealed air-conditioning system serving the counting laboratory. At low temperatures, activated charcoal will adsorb radon. The high-efficiency filters capture the radon daughter products (particulates to which radon decays) resulting in acceptable environmental conditions necessary for low-level radiation counting of materials.

CONCLUSION

Clean air for breathing is vital to people within, or outside of, a plant that processes radioactive or toxic materials or infectious biologicals.

Close attention must be paid to the design, fabrication, testing, and operation of air-cleaning systems to achieve the required results, if the health and safety of the people are to be maintained.

There is one important conclusion that should be emphasized: Attention to details is very important in the design, fabrication, and testing of air-cleaning systems. Do not leave vital design decisions and construction details to an architect-engineer unfamiliar with your special requirements or to a contractor's imagination to install air-cleaning equipment or associated components upon which the health and safety of many people depend. Assist these people by furnishing good design criteria, engineering details in cases where dependable and tested systems are available, and, after construction, always prove the system by detail efficiency and preoperational tests.

DISCUSSION

J.F. Fish. Is it possible to identify more fully "favourable" or "desired" storage conditions for HEPA filters?

J.C. Little: A guide to proper inspection, handling, storage and installation of high-efficiency filters was published by the USAEC in 1961. This report, TID-7023 by H. Gilbert of the USAEC and J.E. Palmer of General Electric, is still applicable today. The chief requirements for proper storage, as set out therein, should be consulted by anyone needing details. If factors not covered in that report, such as length of storage, prove to be a problem, I am sure that the necessary information will be published by the USAEC.

V. Prodi: What are the specifications for filter efficiency in a germ-free environment?

J.C. Little: Tests for germ-free air supply systems and virus exhaust systems must be at least equal to those for radioactive and toxic material filtration systems. DOP tests must not produce leaks greater than the leak rate of the absolute filters themselves.
H. CANTELOW: Why do you specify a minimum thickness of 0.015 inches for the filter media?

J.C. LITTLE: HEPA filters for all three Union Carbide installations in Oak Ridge have to comply with one standard specification, which stipulates for the media: "0.015 inch thick minimum fiberglass or fiberglass and asbestos having a minimum basic weight of 48 pounds per 3000 square feet".

We believe that a more consistent grade of media, having fewer pinholes, will result with the use of 15 mil or thicker paper. Other advantages of 15 mil paper over thinner media are extra strength to resist a shift of the separators and possible rupture of the media at the folds. Moreover, a more firmly packed filter will be obtained, a factor which increases the filter's resistance to damage due to improper handling, storage, or installation. In addition, a firmly packed filter resists the tendency of separators to vibrate during operation.

R.E. KRATEL: You stated a "zero point count level" on the clean-air side of HEPA filters. Does this mean the level of 0.03% penetration (DOP) or a higher demand (no particles more than 0.3 microns in diameter)?

J.C. LITTLE: Clean rooms which operate at near zero particle count levels are usually superior to the normal contamination control filtration systems. The usual high-efficiency, contaminated-air filtration system is generally considered acceptable if the overall efficiency is 99.95% under a DOP test. More sophisticated clean rooms may employ filters which show 99.99% efficiency or higher under the DOP test. In some installations, two HEPA filters are placed in a series for even higher efficiency. The highest possible performance from such systems calls for a leak test by the DOP method, rather than an overall efficiency test. All leaks in gaskets, framing system, etc., are repaired to a point such that the leaks in the framing and gasket, under a DOP test, are no larger than the leaks in the HEPA filters themselves.

The final tests on such systems are made with a particle counter used under operating conditions. A properly designed and tested HEPA filtration system can operate at near zero particle count levels when particles exceeding 0.3 microns in diameter are considered.

D.J. KEIGHER: In late 1958 and early 1959, fatigue cracks were found in HEPA filters in warehouses at various USAEC installations. It was a subject of considerable discussion at the 1959 USAEC Air Cleaning Conference. Much of the failure was found in papers, usually fire resistant, that were considerably thinner than 15 mil (some were 10, even 8 mil!). Those interested in this subject, and now inclined to question the USAEC 15 mil minimum, are referred to the Proceedings of the 1959 (Sixth) Conference.

Do you advocate that HEPA filters stored for an extended time - one or two years or more - be sent back to the Quality Assurance Station for recheck? Would this have made a difference in the case of the 5-year-old filter you mentioned? The HEPA filters shown at the NASA Clean Room do not appear to have screens or hardware cloth. Would this aid in their protection?

J.C. LITTLE: In answer to your first question, I do not advocate returning all HEPA filters stored for extended periods to the Quality Assurance Stations for recheck. It is not yet certain that prolonged storage is in itself a factor in the filter failures which we experienced. In fact,
a review of the data shows that two of the three filters passing the recent Edgewood tests (as explained in the paper) were manufactured in November 1962. At our particular plant, we are going to make a greater effort to use the older filters first and not hold a filter in the warehouse for longer than one year. Our present methods of testing HEPA filter banks, i.e. by pinpoint probes for leaks and overall efficiency determination by the DOP method, assure us high-efficiency filtration on newly installed systems. Stack sampling and routine DOP tests assure us continued satisfactory operation of the HEPA filter system.

Regarding your second question, face protection was provided on the downstream sides of NASA's vertically installed clean-room filter banks, not as individual filter screens, but as a 70%-free area grille extending from the floor to about the 10-ft level. No face protection was provided on the air-inlet side, as this is an air plenum and protection was not considered necessary. Care was exercised in the initial installation of these filters. There were only two or three damaged filters in about 900 units. Given clean-room dust loads, the life of these filters is estimated at ten years.

Face guards on high-efficiency filters serve three functions, as a protective device against damage to media during handling and installation; protection against damage after installation; and protection against shock overpressure. We do not use face guards in the Y-12 area, because we do not have shock overpressure possibilities that would justify this added filter core reinforcement, and we have not found face guards to be economically advantageous. Our filter change crew is thoroughly trained in the handling and installation of the relatively fragile HEPA filters, and over the years our losses due to damage during installation have been very low. Damage to the filter units after installation is not a problem since the filters are located within a restricted access enclosure.

J. PRADEL: Does the use of white rooms, with air supplied over a large surface and with horizontal laminar flow, really give better results than a system in which air is supplied by many ducts, as in hot laboratories? Isn't the flow perturbed by turbulent diffusion?

J.C. LITTLE: The laminar concept of air flow within a laboratory has one definite advantage - that of fast clean-up of the room in the event of a release of particulate contaminant. In work areas employing this design concept, the air flow through the room is usually between 65 and 125 ft/min. This represents an air change rate of between 200 and 400 changes per hour. If the laboratory is designed on a vertical air flow (ceiling-to-floor air flow, with final filters in the ceiling), the operator is assured of having clean air in the breathing zone under most conditions. In the case of horizontal, laminar air flow, turbulence caused by equipment within the room could be a factor in the diffusion of a contaminant within the area. However, with a high air flow rate, clean-up to normal conditions would be rapid.
CONTROLE RADIOLOGIQUE DES REJETS GAZEUX DE L'USINE UP2

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Abstract — Résumé

RADIOLOGICAL CONTROL OF GASEOUS WASTES AT THE UP2 PLANT. The authors first give a brief account of the organization and purposes of the La Hague Centre, and more particularly of the UP2 industrial facility. An inventory of possible sources of air contamination due to the Centre’s activities is drawn up and the characteristics of extraction and removal in the UP2 stack are described. The local weather conditions are briefly discussed and the results of an experiment in which a uranum aerosol (the sodium salt of fluorescein) was released through the UP2 stack in September and October 1965 are examined. In the second part of the paper the authors describe the methods of control adopted at the La Hague Centre and the different types of equipment installed at the monitoring points. Finally, the results of control of gaseous effluents released from the UP2 unit during several operational runs are analysed.

1 DESTINATION ET CONSTITUTION DU CENTRE DE LA HAGUE :

Le Centre de LA HAGUE, de la Direction des Productions du Commissariat à l’Energie Atomique, est implanté à l’extrémité Nord-Ouest de la presqu’île du Cotentin, sur les landes de JOBOURG qui constituent à cet endroit un plateau culminant à environ 180 mètres au-dessus du niveau de la mer.

Les installations du Centre sont groupées schématiquement en trois zones :

- Une zone Sud (gardiennage et sécurité générale, Sécurité, Administration, Service médico-social et Laboratoires inactifs).

- Une zone Nord où sont implantées les différentes utilisités (centrale vapeur, centrale électrique, ateliers mécaniques et électriques) indispensables au fonctionnement du Centre.

- Une zone centrale, industrielle, qui abrite actuellement les bâtiments nucléaires de l’ensemble de production UP. 2, de la Station de Traitement des Effluents et ceux des ateliers ci-après :


La vocation essentielle du Centre de LA HAGUE est cependant le traitement chimique, à l'échelle industrielle, des combustibles nucléaires irradiés, traitement qui permet l'extraction du Plutonium et, éventuellement, de certains radioéléments, tout en récupérant l'Uranium appauvri.

À ce titre, l'ensemble industriel UP 2 (Usine de Plutonium n° 2) constitue de loin l'unité la plus importante du Centre de LA HAGUE, avec une surface d'emprise au sol d'environ 2 ha : UP 2, dont une chaîne de traitement seulement est en service, a été conçue et réalisée pour traiter par voie chimique le combustible, à base d'Uranium naturel, irradié dans les Centrales de puissance de l'Electricité de France ; ce traitement, classique, comprend schématiquement les étapes suivantes :

1. Stockage en piscine
2. Dégainage mécanique
3. Dissolution
4. Premier cycle solvant (décontamination PF)
5. Concentration
6. Stockage des produits de fission
7. Deuxième cycle solvant (partition U - Pu)
8. Troisième cycle (extraction de l'Uranium (1))
9. Unité de stockage
10. Élaboration du Plutonium métallique

Précisons, à titre documentaire, que les eaux résiduaires radioactives sont, après traitement et contrôle, rejetées en mer, dans le Raz Blanchard, par une conduite sous-marine de 5 km de long environ

(1) Stocké actuellement sous forme de Nitrate d'Uranyle.
2 INVENTAIRE DES SOURCES POSSIBLES DE CONTAMINATION ATMOSPHERIQUE

Du point de vue de l'objet du présent colloque, il est évident que l'on peut dénombrer, sur un Centre comme celui de LA HAGUE, plusieurs sources possibles de contamination radioactive de l'air ; nous allons en dresser ci-après l'inventaire :

a) Pour mémoire :

LEAG : en cours de construction
ELAN : en cours de construction

b) Mise en exploitation active imminente :

AT. 1 : dans cet atelier, le circuit des effluents gazeux du procédé (cellules mécaniques, dissolution, etc...) est indépendant du circuit de ventilation générale du bâtiment. Ces effluents gazeux sont, après passage sur colonnes de lavage et filtration sur des batteries de filtres absolus, incombustibles, rejetés vers la cheminée UP 2, par l'intermédiaire d'un carneau souterrain

L'apport prévu à la cheminée UP 2 sera de 1 500 m^3/h, pour une activité de :

\[ 0,7 \times 10^{-6} \text{ Ci/s en } ^{131}\text{I} \]
\[ 0,012 \times 10^{-2} \text{ Ci/s en } ^{85}\text{Kr} \]

La ventilation générale du bâtiment aboutit, après filtration absolue, à une cheminée classique, propre à AT. 1 et dont le débit prévu est de 47 000 m^3/h.

c) En exploitation actuelle :

Bâtiment Décontamination :

L'air de ventilation passe à travers des batteries de filtres absolus, incombustibles, avant rejet à la cheminée propre à ce bâtiment ; dans le cas des cuves de traitement par voie humide, l'air extrait passe au préalable dans une chambre de lavage et de neutralisation.

Les caractéristiques d'extraction sont les suivantes :

Section de la cheminée : 3,6 m^2.
Vitesse d'éjection de l'air : environ 10 m/s
Débit moyen : 132 000 m³/h.

Ce bâtiment ne peut être qu'une source accidentelle de contamination atmosphérique

Station de Traitement des Effluents :
L'installation de ventilation de ce bâtiment compte deux circuits d'extraction (moyenne et haute dépression) ; dans les deux cas, l'air passe, avant rejet à la cheminée du bâtiment, par des batteries de filtres absolus incombustibles ; le débit de la cheminée est en moyenne de 70 000 m³/h.

Ensemble industriel UP.2 :

Caractéristiques d'extraction et de la cheminée UP.2 :

Chacun des bâtiments constituant cet ensemble comporte deux circuits d'extraction d'air : un "haute dépression" pour les zones actives (cellules procédé en particulier), et un "moyenne dépression" pour les zones peu actives ; chacun de ces circuits aboutit dans le bâtiment lui-même, à un ensemble important de filtration absolue, puis à une série de ventilateurs d'extraction. Tout l'air extrait est ensuite dirigé par un carreau vers la cheminée UP.2 dont voici les caractéristiques principales :

Hauteur géométrique : 100 m
Diamètre : 6,50 m
Vitesse d'éjection de l'air : environ 10 m/s
Débit moyen actuel : 810 000 m³/h.

Compte tenu de la vitesse de dissolution des barreaux et du pourcentage d'iode volatile (≤ 4%), les estimations de l'activité émise à la cheminée sont de l'ordre de :

\[ ^{85}\text{Kr} \quad A < 3 \times 10^{-2} \text{ Ci/s} \]
\[ ^{131}\text{I} \quad A < 1,5 \times 10^{-6} \text{ Ci/s} \]
\[ ^{131}\text{mXe} \quad A < 6 \times 10^{-5} \text{ Ci/s} \]

avec du combustible ayant subi un refroidissement d'au moins 140 jours.
3 ETUDES PRELIMINAIRES DE DIFFUSION ATMOSPHERIQUE :

Conditions météorologiques locales :

Parmi les différents facteurs pris en considération pour le choix du site de LA HAGUE figurent les conditions météorologiques locales, assurant une bonne dilution des effluents gazeux, et que nous allons décrire rapidement.

Par sa situation à l'extrême Ouest de la presqu'île du Cotentin, le site de LA HAGUE est soumis à un climat maritime tempéré, influencé par les vents de Sud-Ouest, souvent très forts, et accompagnant les perturbations pluvieuses.

Vents :
Le vent dominant est du Sud-Sud-Ouest avec débordements du Sud-Sud-Est à l'Ouest-Sud-Ouest.
La vitesse moyenne annuelle est de 6,9 m/s, le "coup de vent" (vitesse \( \geq 16 \) m/s) étant relativement fréquent.

Précipitations :
Les précipitations ont généralement un caractère stable, c'est-à-dire qu'elles se présentent rarement sous forme d'averses ; leur intensité est habituellement \( \leq 1 \) mm/h.
La hauteur moyenne annuelle est de 1100 millimètres.

Températures :
Les variations diurnes sont faibles : il est fréquent de ne pas avoir une différence \( \geq 2 \) °C entre le minimum et le maximum d'une même journée.

Visibilité et humidité relative :
La visibilité est souvent réduite à quelques dizaines ou quelques centaines de mètres (1 jour sur 3 ou 4 environ) par un brouillard parfois dense : il s'agit en fait, la plupart du temps, de stratus qui accrochent la falaise entre 100 et 120 mètres d'altitude (le point culminant de la presqu'île est le pied de la cheminée avec 184 mètres).
Liée à ce brouillard, l'humidité relative moyenne est de 90% ; à noter qu'environ 1/5 des observations annuelles relèvent une humidité relative saturante (100%).

Inversions de température : (Sol - 1000 mètres)
D'après les renseignements fournis par la Météorologie Nationale, on peut dire que, en moyenne, dans 1/5 des cas, la situa-
tion météorologique est celle d'une inversion de température dont la base se situe habituellement dans la tranche des 900 à 1000 mètres ; les vents ont alors une vitesse moyenne de 11 m/s à 1000 mètres et de 7 m/s au niveau du sol ; les "vents calmes" sont pratiquement inexistants.

Ces inversions sont créées par l'approche de fronts chauds de l'Ouest "escaladant" en quelque sorte la masse d'air froid continentale.


**EXPERIENCE DE REJET A LA CHEMINEE UP 2 D'UN TRACEUR FLUORESCENT :**

Le Service d'Etudes de Sécurité Radiologique du C E A. a réalisé entre le 2 Septembre et le 14 Octobre 1965 une série d'expériences de rejet d'un traceur fluorescent à la cheminée UP 2 ; le traceur utilisé a été le sel disodique de la fluorescéine en solution aqueuse.

Caractéristiques de l'émission :

L'émission s'est faite au niveau de l'orifice supérieur de la cheminée UP 2 (+ 100 mètres au-dessus du sol) par pulvérisation pneumatique froide d'une solution contenant 4 kg d'Uranium pour 50 litres d'eau, la durée d'émission étant de 1 heure environ ; elle s'effectue par 5 gicleurs disposés en couronne et alimentés sous une pression d'air de 5 kg/cm².

Les gouttelettes émises s'évaporent et les particules résultantes ont un diamètre moyen de l'ordre de 10 μ.

Prélèvements :

Deux types de prélèvements ont été effectués pour déterminer :

a) la concentration par unité de volume d'air : trompes d'air fonctionnant sur bouteilles de 6 l gonflées à 200 kg/cm² et aspirant à travers un filtre Delbag microsorban de Ø 11 cm ; le débit filtré est de 5 m³ en 40 minutes. Le filtre se trouve à 1 mètre du sol.

b) le dépôt au niveau du sol : boîtes de Pétri plates.

Mesures :

Les filtres et les boîtes de Pétri sont lavés dans 20 cm³ d'eau permutée pendant 10 mn ; la fluorescence des eaux de rinçage est mesurée à l'aide d'un Photovolt Multiplier Fluorescence Meter Model 540 sur des échantillons de 4 cm³.
Paramètres météorologiques :
La station météorologique du Centre a fourni les éléments suivants :
- Direction et vitesse du vent à 10 et 50 mètres.
- Gradient thermique entre le sol et 50 mètres.
- Humidité de l'air au voisinage du sol et à 50 mètres.
Le vent en altitude a été fourni par la Météorologie Nationale à Cherbourg.

Conditions de diffusion :
Elles ont toujours été assez bonnes car :
- les nuits claires sont assez rares sur le site.
- aucune expérience n'a été réussie en inversion thermique, en raison sans doute de la grande turbulence dynamique de l'atmosphère : il régnait, en effet, toujours un vent assez fort, atteignant parfois 20 m/s.

Rotation des panaches :
On a relevé l'habituelle rotation des panaches due au vent en altitude, rotation malgré tout peu importante : environ 10° à 9000 m.

Résultats :
Les mesures faites ont pu être classées géographiquement, ce qui permet de distinguer deux zones de terrains : (Fig 1)

**Zone 1** : Elle comprend le plateau et les parties doucement inclinées vers la mer ; les valeurs de concentration trouvées restent inférieures à celles calculées à partir des formules de Sutton.
La distance de concentration maximum est assez nettement définie : elle se situe à environ 1000 m du pied de la cheminée.

**Zone 2** : Elle comprend les parties encaissées ou situées sur les fortes déclivités ; les valeurs de concentration trouvées sont plus faibles que pour la zone 1, mais la distance de concentration maximum ne peut pas être fixée de façon valable.

Calcul d'un coefficient de lavage :
L'émission n° 8 s'est faite sous une pluie d'environ 5 mm/h et par un vent de Est-Sud-Est de 6 m/s ; les dépôts maximums dans le lit du vent, ramenés à une émission de 1 g, ont été les suivants :
à 900 m : $2,3 \times 10^{-7}$ g/m$^2$,
à 2 500 m : $3,5 \times 10^{-8}$ g/cm$^2$,
à 4 100 m : $2,2 \times 10^{-8}$ g/cm$^2$

Le coefficient de lavage correspondant, compte tenu des difficultés de manipulation, a été trouvé égal environ à $10^{-4}$ g.m$^{-1}$, valeur généralement admise dans la littérature [3].

5 SURVEILLANCE DES EFFLUENTS :

a) Généralités :

La définition des points de rejet et les études préliminaires ont donc précédé la mise en place d'une surveillance permanente des émissions gazeuses. Il aurait été possible, d'un strict point de vue économique et réglementaire, de se contenter de déterminations au niveau de la cheminée principale UP 2, et des évacuations des bâtiments annexes précédemment indiqués.

D'une part, devant la difficulté d'effectuer un prélèvement continu satisfaisant dans un débit de plus de 800 000 m$^3$/h, la multiplication des points de prélèvement était souhaitable.

D'autre part, il était intéressant de se rapprocher des diverses sources possibles de radioéléments dans le circuit d'extraction, permettant ainsi de les identifier et d'en apprécier l'importance.
Pour atteindre ce but, plusieurs points de surveillance ont été définis en dehors de la surveillance cheminée. Des dispositifs ont donc été installés au niveau de l'extraction de chacun des bâtiments formant l'ensemble UP 2.

b) **Installations** :

Les éléments dont le rejet est prévisible sont, dans un premier temps, essentiellement le $^{131}$Iode et le $^{85}$Krypton. Les contrôles étant situés après les batteries de filtres, il était aussi très important de s'assurer en permanence de l'intégrité de ces derniers et de leur efficacité.

Une station type de contrôle a donc été définie. Elle comprend (Fig 2 et 3) :

- un dispositif de contrôle de la radioactivité des poussières, soit en prélèvement sur filtre ruban mobile et mesure continue comme l'Enregistreur d'Aérosol Radioactif (EAR 640), soit en prélèvement continu sur filtre fixe et mesure discontinue en Laboratoire,
- un dispositif de piégeage de l'iode en continu, à plusieurs étages permettant d'apprécier le rendement du prélèvement.

La mesure est discontinue et effectuée en Laboratoire.

- un dispositif de mesure de l'activité $B$ des gaz constitué par une chambre différentielle à circulation de capacité 12 litres (Type CD. 22 et CD. 23),

- un dispositif de mesure de débit

Cet ensemble léger mais suffisant peut être complété par des pièges à vapeur d'eau pour piégeage de l'eau tritée ou par un Moniteur à Iode renseignant en continu sur les évolutions de l'activité rejetée due à cet élément.

Néanmoins, cet équipement est allégé en fonction de l'installation contrôlée

Les diverses stations sont ou seront ainsi équipées :

Station cheminée UP 2 . . .
Piège à Iode
Filtre à poussières fixe
Chambre d'ionisation différentielle avec enregistrement
<table>
<thead>
<tr>
<th>Station Bâtiment</th>
<th>Produits de Fission</th>
<th>Piège à Iode</th>
<th>Filtre à poussières fixe</th>
<th>Chambre d'ionisation différentielle avec enregistrement</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station Bâtiment</th>
<th>Moyenne Activité</th>
<th>Filtre à poussières fixe</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station Bâtiment</th>
<th>Haute Activité</th>
<th>Piège à Iode</th>
<th>Filtre à poussières fixe</th>
<th>Chambre d'ionisation différentielle avec enregistrement</th>
<th>Enregistreur d'Aérosols Radioactifs</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station Bâtiment</th>
<th>Traitement des Effluents</th>
<th>Piège à Iode</th>
<th>Filtre à poussières fixe</th>
<th>Enregistreur d'Aérosols Radioactifs</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station Bâtiment</th>
<th>Décontamination</th>
<th>Enregistreur d'Aérosols Radioactifs</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station Bâtiment AT 1</th>
<th>Piège à Iode</th>
<th>Enregistreur d'Aérosols Radioactifs</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Station ELAN II B</th>
<th>Filtre fixe avec mesure continue</th>
</tr>
</thead>
</table>

Les dispositifs de prélèvements proprement dits sont, en général, un compromis entre les possibilités économiques de réalisation et le désir des responsables du contrôle.

Au niveau de la cheminée par exemple, le prélèvement est effectué par l'intermédiaire d'un tube terminé par un entonnoir dont l'ouverture est perpendiculaire au flux d'air. Dans les stations des divers bâtiments de l'ensemble UP 2, des tubes percés comme une clarinette ont été introduits dans les gaines et permettent en principe un prélèvement dans l'ensemble de la veine gazeuse. Enfin, dans les autres unités, les prises d'air ne sont souvent que des simples tubes de Pitot.

Un effort est tenté pour améliorer et uniformiser, lorsque cela est souhaitable, la technique de prélèvement.
Cet ensemble de points de contrôle peut être très facilement modifié ou complété suivant les travaux effectués dans le bâtiment. Les informations obtenues permettent de situer avec précision le lieu d'émission des divers éléments rejetés par la cheminée.

c) Techniques de mesures :

L'étalonnage des appareils de mesure continue et l'exploitation des prélèvements tiennent évidemment compte des caractéristiques du point de contrôle. Les chambres différentielles mesurant l'activité des gaz sont étalonnées par rapport au $^{85}$Krypton constituant la majeure partie des radioéléments rejetés.

Les appareils de mesure continue des poussières donnent des indications par rapport à un mélange type de produit de fission.

L'exploitation des pièges à Iode et des filtres de prélèvement de poussières est effectuée en Laboratoire.

La mesure des radio-isotopes collectés met en jeu les techniques classiques de spectrométrie gamma et de mesure par compteur proportionnel et à scintillation. Comme on le verra plus loin, la spectrométrie gamma met en évidence et a permis de mesurer des émissions assez inattendues dans une usine de traitement de combustibles irradiés.

d) Surveillance extérieure :

Parallèlement à cette surveillance des effluents, trois stations ont été implantées autour du Centre tant dans des buts techniques que psychologiques (Fig 4).

La station principale des HAUTS-MARAIS est située à 500 m du pied de la cheminée, dans le 90° (Est).

En fait, elle a eu pour premier rôle celui d'une station de mesure de paramètres météorologiques. Pour des raisons de commodités d'implantation, le matériel de surveillance atmosphérique y a été implanté. Cette installation ayant été définie avant les expériences de rejet colorant, elle ne se trouve évidemment pas au point théoriquement le plus critique. Néanmoins, les extensions du Centre vers l'Est et l'Ouest permettront des contrôles aux points de re-tombées théoriques maximums.

Il est à noter également que la direction Est est couverte par la station de GREVILLE (105°). Le Sud est contrôlé par la station de VAUVILLE dans le Sud-Sud-Est (150°).

Ces stations ont un équipement de base standard:

- un dispositif de collection continue et, éventuellement, de mesure continue des poussières.
FIG. 4. Surveillance atmosphérique.
- Stations extérieures.
- un dispositif de piégeage de l'Iode,
- un dispositif de mesure d'activité des gaz (chambre différentielle CD 43 de I2O I).

Accessoirement, un ensemble collecteur de précipitations complète l'installation.

LA HAGUE est entourée de pâturages et la production laitière, assez importante, fait l'objet d'une surveillance permanente, et sur intervention lorsque des conditions météorologiques défavorables sont associées à un rejet d'Iode décelable.

Cet ensemble de surveillance de la radiopollution atmosphérique, associé à une information météorologique et à un contrôle continu des rejets, permet de connaître en permanence la situation radioactive locale.

Aucune détection positive reliable à un rejet atmosphérique du Centre n'a pu être mise en évidence

e) **Résultats des mesures** :

Les mesures à la cheminée UP. 2 ont débuté avec le démarrage de l'Usine en Juin 1966. Les mesures secondaires au niveau des
bâtiments ont été mises en place à la fin de cette première campagne. Les résultats concernent essentiellement la détection et la mesure des éléments attendus, c'est-à-dire le $^{85}$ Krypton et le $^{131}$ Iode. Mais également, la présence d'éléments moins attendus a été mise en évidence. Il s'agit de $^{203}$ Mercure et de $^{125}$ Antimoine. Le premier est notoirement un produit d'activation, le second étant évidemment un produit de fission. Enfin, la mesure de l'activité des poussières a toujours donné des résultats non significatifs.

Si ces résultats sont considérés par point de surveillance, on peut considérer que la quasi-totalité des mesures positives a été effectuée au rejet principal de l'Usine.

$^{85}$ Krypton :


L'émission du Krypton s'effectue en quasi-totalité au niveau du bâtiment Haute Activité, c'est-à-dire lors de la dissolution et des concentrations du premier cycle.

Les mesures effectuées au niveau du bâtiment Produits de Fission n'ont pas permis de détecter une variation dans le taux d'activité de l'air extrait lors des périodes de fonctionnement.

Les variations du taux de $^{85}$ Krypton rejeté ont toujours été fiables à l'évolution du traitement du premier cycle. Chaque incident de fonctionnement a eu fidèlement sa répercussion sur l'enregistrement de l'activité chambre au niveau de la cheminée (Fig 5). Le rapport des activités globales décelées au niveau bâtiment Haute Activité et à la cheminée n'est pas cependant égal à 1, ce qui indique qu'il est nécessaire de revoir ou de compléter les dispositifs de prélèvements.

$^{131}$ Iode :

Les autorisations de rejet sont provisoirement, pour ce radioélément, de $10^{-6}$ Ci/s. Les diverses campagnes de production ont conduit à des rejets qui ont atteint au maximum quelques pour cent de cette limite. Ils se sont situés, en moyenne, au niveau de $10^{-10}$ à $10^{-9}$ Ci/s.

Les rejets d'Iode $^{131}$, comme pour le $^{85}$ Krypton, proviennent essentiellement du bâtiment Haute Activité. Les activités mesurées ont paru élevées compte tenu des publica-
Contrôle à la cheminée UP2. Evolution des rejets de $^{85}$Kr en fonction des conditions d'exploitation.

Dans le cas de l'Iode également, les activités respectives mesurées aux divers niveaux de prélèvements conduisent à considérer que les dispositifs de prélèvement doivent être améliorés. Une source non négligeable d'émission de ce produit de fission a été mise en évidence au niveau du bâtiment de Traitement des Effluents. La libération de l'Iode peut intervenir lors de la neutralisation des effluents nitriques.

A titre d'exemple, pour une période donnée, et correspondant à un traitement de combustible moins refroidi, l'émission au niveau de la Station de Traitement des Effluents a été égale à 10% de celle du rejet principal de la cheminée UP. 2

Les contrôles particuliers de l'atmosphère et de la production laitière du secteur pouvant être concernés par ces rejets se sont avérés négatifs. Il faut considérer que ces rejets étaient néanmoins très faibles (une dizaine de milli­curies pour une période de 1 mois).
Mercure

Dès le début du fonctionnement de l'Usine, la présence de Mercure $^{203}$ a été mise en évidence. Cet élément à l'état de vapeur traverse les filtres en papier, protégeant les filtres à Iode, et s'absorbe sur les étages charbon.

Ce produit d'activation est couramment détecté dans le circuit de refroidissement des réacteurs, que ce soit dans le $\text{CO}_2$ pour le circuit fermé, ou dans l'air pour les circuits ouverts.

Il est cependant assez surprenant de le voir atteindre le niveau du traitement du combustible.

Le contrôle différencié qui est effectué au Centre de LA HAGUE a permis, d'autre part, de constater que le Radio-Mercure est émis principalement au niveau du bâtiment Haute Activité. Néanmoins, la concentration des produits de fission provoque également le départ de l'élément considéré.

Enfin, le contrôle des rejets gazeux de la Station de Traitement des Effluents a permis également de mesurer des rejets de Mercure voisins de ceux de ces dernières unités. Il est possible de supposer un dépôt de Mercure sur les gaines de combustibles mais plus difficile à admettre est son transfert au niveau de l'Uranium, qui semble pourtant évident.

D'autre part, la nature sous laquelle cet élément se volatile n'a pu être encore identifiée.

Les rejets de Radio-Mercure $^{203}$ ont souvent été du même ordre de grandeur que ceux de l'Iode $^{131}$ en admettant que les conditions de piégeage sont comparables. Une étude particulière de sa provenance et de son transfert au niveau du procédé sera entreprise.

Antimoine :

Le $^{125}$ Antimoine a été mis en évidence lors de périodes de très faibles rejets d'Iode. Le même phénomène de traversée de filtres papier a été mis en évidence. L'Antimoine a été détecté sur le charbon actif mais son aptitude à y être absorbé est inconnue. De ce fait, les activités rejetées de l'ordre de $10^{-12}$ à $10^{-11}$ Ci/m$^3$ sont très approximatives. Dans ce cas, également, le rejet essentiel a lieu à partir du bâtiment Haute Activité.

Le processus de volatilisation de l'Antimoine est également une question non résolue. L'hypothèse suivant laquelle cet élément se trouve sous forme d'oxyde (Anhydride Antimoine $\text{Sb}_2\text{O}_5$) est difficile à admettre, compte tenu des conditions initiales du traitement.
L'organisation économique et sûre qui a été mise en place au Centre de LA HAGUE répond aux nécessités de sûreté du Site. Elle permet, d'autre part, de fournir aux autorités du Commissariat à l'Energie Atomique les informations qu'est en droit de leur réclamer le Ministère de la Santé Publique.

Enfin, les mesures et détections effectuées ont mis en évidence des émissions de radioéléments dont les origines devront être recherchées dans la chimie du procédé et le comportement des combustibles irradiés.

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Abstract — Resumen

EXPERIMENTS BY THE MEXICAN NNEC ON THE CONTROL OF AIRBORNE RADIOACTIVE CONTAMINATION. The installations of the Mexican National Nuclear Energy Commission have to deal with the problem of environmental contamination caused by dust and aerosols suspended in the air and originating mainly with such uranium-bearing ores as tyuyamunite, carnottite, betafite, technical-grade sodium uranate, ammonium uranate concentrate, uranium tetrafluoride and uranium dioxide.

To prevent environmental contamination by these radioactive materials, the Commission has experimented with three different systems, based on the principle of extracting the dust from the environment, passing it through a cyclone system, separating the particles of larger size and controlling the small particles or aerosols by means of filtration, dilution in liquid columns and dilution in liquid curtains.

On the basis of the results obtained, plans have been made for supplementing the systems with an adsorption column and an ion exchange column, depending on the specific requirements of each laboratory.

El problema existente en las instalaciones de la Comisión Nacional de Energía Nuclear de México, con respecto a la contaminación ambiental, es el que se presenta actualmente en los Laboratorios de molienda del programa de exploraciones, en la Sección de molienda del mineral uranífero del programa de combustibles nucleares, en los Laboratorios de obtención de concentrados de uranio y en la Sección de quebrado y molienda del material para alimentar a la planta piloto, lugares donde se estudia el beneficio de los minerales de uranio con que cuenta nuestro país.

Para resolver este problema de la contaminación del medio ambiente por aerosoles y polvos que normalmente son arrastrados por el aire en estas zonas de trabajo, se instaló, en los lugares mencionados, un sistema integral consistente en la colocación de ductos por los cuales se extrae el...
El personal que trabaja en este local está equipado para su protección personal, como se puede ver en las figuras 1 y 2, con mascarilla, overol, guantes, botas y casco, además de un dosímetro de película, en esta figura...
también se pueden apreciar las campanas y los ductos por los cuales se extrae el aire contaminado con el polvo radiactivo existente en ese lugar, como se puede ver, las técnicas y los medios son un poco rudimentarios, pero en la actualidad se han mejorado.

Otra de las medidas de protección empleada para evitar la cantidad de polvos es el humedecimiento de los minerales que se están trabajando.

El aire contaminado con los polvos del material radiactivo se pasa por el extractor, que se ve en la figura 3, el cual envía todo el aire contaminado al sistema de ciclón.

Las primeras experiencias que se realizaron con este sistema se efectuaron con un equipo que constaba de un conjunto de forma cónica de 2,5 m de alto con un diámetro de 70 cm, la parte inferior tenía un recipiente de una capacidad de 50 l y la parte superior estaba abierta al medio ambiente. El funcionamiento de este equipo consiste en formar en su interior un ciclón con el aire descargado en él por el extractor para separar las partículas más pesadas, que son precipitadas y recogidas en el recipiente de la parte inferior. El aire, ya sin partículas, es expulsado al medio ambiente por la parte superior.

Mediante este sistema para separar los polvos radiactivos y evitar la contaminación ambiental, se escapaba una gran cantidad de cienos que se descargaban al medio ambiente presentando en un tiempo determinado una contaminación en las superficies de los alrededores, ello constituía una
FIG. 3. Extractor de la Sección de quebrado.

FIG. 4. Sistema de ciclón.
FIG. 5. Instalaciones en la Sección de molienda seca.

fuente de contaminación para el personal y ocasionaba un gran problema ya que el resultado de los análisis de uranio en orina eran elevados en personal que no intervenía en el trabajo de molienda ni quebrado.

Al hacer la investigación del origen de la contaminación, se concluyó que eran los aerosoles del material radiactivo que se habían precipitado en un tiempo determinado sobre la superficie de los alrededores del ciclón. El sistema fue reacondicionado para mejorarlo (figura 4). Hubo necesidad de colocar un segundo ciclón adaptado de tal manera que el aire proveniente del primer ciclón se inyectaba por la parte inferior y se descargaba al medio ambiente por la parte superior, lugar desde el cual se rociaba con agua a contracorriente que se depositaba en el tanque colocado debajo del ciclón. Mediante este sistema se efectuaba una última eliminación de aerosoles del aire, que se expulsaban al medio ambiente.

Con estas modificaciones se ha resuelto en gran parte el problema de la contaminación provocada por polvos de material radiactivo arrastrados por el aire.

En la Sección de molienda en seco para las muestras de laboratorio, que consiste en un local de 5,5 m de largo, 4,5 m de ancho y 3 m de alto, con una puerta de acceso y, en el lado opuesto de la puerta, una meseta de muestreo y dos molinos para la molienda del mineral uranífero, se instalaron unas campanas (figura 5) comunicadas por un ducto de 20 pulg. de diá-
metro a un extractor de una capacidad de 9800 m$^3$/h, que envía el aire contaminado extraído al equipo representado en la figura 6; éste fue calculado sobre la base de los datos técnicos siguientes:

<table>
<thead>
<tr>
<th>Volumen de aire</th>
<th>9800 m$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presión estática</td>
<td>179 mm col agua</td>
</tr>
<tr>
<td>Velocidad angular</td>
<td>2000 rev/min</td>
</tr>
<tr>
<td>Altura de operación</td>
<td>2240 m s/nivel mar</td>
</tr>
<tr>
<td>Temperatura</td>
<td>23°C</td>
</tr>
<tr>
<td>Potencia necesaria</td>
<td>11,5 HP</td>
</tr>
</tbody>
</table>

Este equipo consta de una serie de mamparas entrampadas por donde pasa el aire serpentean y entre cada mampara circula una corriente de agua que depura el aire que pasa entre ellas antes de descargarse al medio ambiente.

Este sistema nos ha dado buen resultado, no obstante, hubo necesidad de hacer unas transformaciones en la descarga al medio ambiente, así como en el flujo del líquido rociado en el interior para la depuración del aire.
Las pruebas que se hicieron en el laboratorio, para la estimación de los polvos que contaminaban el medio ambiente, fueron:

a) pruebas granulométricas de los diferentes minerales tratados en la planta piloto,

b) muestreo del medio ambiente de los lugares de trabajo,

c) muestreo de los lugares adyacentes a las descargas de los equipos empleados para la purificación del aire.

El cálculo del equipo instalado y experimentado en esos laboratorios se basó en las pruebas siguientes:

1) La prueba granulométrica tuvo como fin determinar en qué porcentaje se encontraban las partículas de polvo, considerando su diámetro y determinando su actividad. Se empleó un juego de tamices que variaba de 100 a 325 mallas. El promedio de todas las pruebas efectuadas fue el siguiente (se clasificó a través de las siguientes mallas):

<table>
<thead>
<tr>
<th>Datos Finales</th>
<th>Tara (g)</th>
<th>T. + M. Seca (g)</th>
<th>M. Seca (g)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracción mayor de 100 mallas</td>
<td>497,9</td>
<td>502,32</td>
<td>4,45</td>
<td>1,852</td>
</tr>
<tr>
<td>&quot; 100 a 200 &quot; &quot;</td>
<td>514,9</td>
<td>527,70</td>
<td>12,80</td>
<td>5,329</td>
</tr>
<tr>
<td>&quot; 200 a 270 &quot; &quot;</td>
<td>500,9</td>
<td>519,90</td>
<td>19,00</td>
<td>4,163</td>
</tr>
<tr>
<td>&quot; 270 a 325 &quot; &quot;</td>
<td>558,5</td>
<td>574,10</td>
<td>15,60</td>
<td>6,496</td>
</tr>
<tr>
<td>&quot; menor de 325 &quot; &quot;</td>
<td>500,9</td>
<td>665,05</td>
<td>164,15</td>
<td>79,500</td>
</tr>
<tr>
<td>Total</td>
<td>207,00</td>
<td></td>
<td></td>
<td>95,340</td>
</tr>
</tbody>
</table>

Análisis de % U₃O₈ en las diferentes mallas:

- mayor de 100 mallas: 0,13% U₃O₈
- entre 100-200 " " : 0,165% U₃O₈
- " 200-270 " " : 0,18% U₃O₈
- " 270-325 " " : 0,36% U₃O₈
- menor de 325 " " : 0,70% U₃O₈

El U₃O₈ está en mayor cantidad en las partes más finas del mineral, en este caso tyuyamunita.

2) La cantidad de aerosoles que quedaban suspendidos en el medio ambiente fue determinada tomando muestras del lugar de trabajo media hora después de haberlo concluido, empleando un equipo muestreador de aire como el representado en la figura 7.

También se tomaron muestras del medio ambiente en que se trabajaba, empleando el mismo equipo representado en la figura 7, el cual era trans-
portado por el trabajador durante la operación de molienda; este mantenía el tomador de muestra lo más cerca posible de su cara con el fin de tener una muestra representativa del aire aspirado por él.

Durante la operación se conservó un flujo permanente de 2 l/min, por medio del rotámetro con que cuenta el equipo.

El tiempo de muestreo fue variable: las primeras muestras fueron tomadas durante las 5 h que duraba la molienda, la segunda serie de muestras fueron tomadas a las 50 h de trabajo, la tercera serie fue tomada a las 100 h de trabajo y la cuarta serie a las 200 h de trabajo.

Los filtros que se recogieron en cada caso fueron radiomedidos y determinada la cantidad de sólidos detenidos por el mismo.

3) Los aerosoles que lograban salir del sistema y que finalmente se precipitaban en los alrededores de la descarga del aire del equipo contaminando toda esa zona, se determinaron empleando bandejas de 50 × 50 × 10 cm de altura en las que se colocó agua y después una solución de carbonato de sodio, manteniéndose siempre el mismo volumen y dejándose durante períodos de un mes. La muestra de 30 días de los aerosoles que se precipitaron fueron recogidos en ese líquido, concentrados y radiomedidos. También se determinó la cantidad de sólidos totales.

Los muestreadores fueron colocados a diferentes distancias del escape de aire del equipo.

De los resultados obtenidos de este estudio se puede observar que el sistema empleado es efectivo ya que elimina casi la totalidad del polvo producido por la acción de quebrado y molienda y que, además, la cantidad de sólidos expulsados y precipitados en los alrededores es poco variable y su actividad varía grandemente dependiendo de la ley o concentración de los minerales uraníferos quebrados o molidos.
Con la experiencia del equipo que se ha instalado en esos lugares se ha planeado reacondicionar la Sección de secado de concentrados de uranio, adaptando un sistema para la separación de los polvos radiactivos y empleando, en lugar de agua como en los equipos experimentados, una solución de carbonato de sodio en el interior del sistema de depuración del aire, para la dilución del uranio, y recuperando posteriormente el uranio por medios químicos.

Para recuperar este uranio contaminante se pretende hacer esta experiencia y utilizar la instalación, en un futuro próximo, para establecer normas de seguridad que nos permitan un medio ambiente poco contaminado en los lugares donde se trabaja con polvos de material radiactivo.

DISCUSSION

W. SCHIKARSKI: What are the particle sizes or size ranges that you are dealing with?

E. BRAVO S.: The smallest particles coming under consideration are of the order of 0.7 microns in diameter.
OPERATING EXPERIENCE WITH AIRBORNE ACTIVITY CONFINEMENT SYSTEMS AT THE SAVANNAH RIVER PLANT*

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Abstract

OPERATING EXPERIENCE WITH AIRBORNE ACTIVITY CONFINEMENT SYSTEMS AT THE SAVANNAH RIVER PLANT. Equipment has been installed in the ventilation exhaust system of each reactor building at the Savannah River Plant to collect and confine airborne radioactive particles and halogen vapours that might be released in a reactor accident. The equipment is continuously on-line and has been in service five years. The activity collection system in each reactor building consists of four active compartments and one spare. Each compartment contains banks of 20 moisture separators, 32 filters, and 32 beds of activated carbon in series and is designed for 32 000 cfm air flow. The moisture separators, which prevent moisture damage to the filters, are woven Teflon stainless steel mats and are steam cleaned approximately every nine months to remove accumulated oily materials and particles. No moisture separators have required replacement. The filters are pleated glass-asbestos felt, protected against mechanical damage by wire mesh on both filter faces. Upon installation, each new filter is tested with a 0.6-jm dioctyl phthalate aerosol. Any filter with a leak greater than 0.05% is replaced. Service life for filters is approximately 16 months. The condition of the moisture separator and filter banks in each compartment is determined weekly by measuring the pressure drop across each bank and the air flow rate through the bank.

The activated carbon beds in each compartment are for removal of iodine-131. Carbon bed banks are leak-tested with Freon-112 annually and after replacement. After about four years of service, seventeen of the 20 banks tested in 1967 were within the maximum leakage specification of 0.09%. Three banks, with leakage up to 0.16%, were replaced in 1967. Five of the 17 with satisfactory leakage rates were replaced because of corrosion of the enameled or cadmium-plated mild steel frames. Replacement carbon beds now have stainless steel frames.

INTRODUCTION

The activity confinement system for production reactors at the Savannah River Plant (SRP) is designed to collect airborne radioactive particles and halogen vapors that might be released to the atmosphere in a reactor accident that damages the reactor fuel. Other protection systems are provided to prevent activity release to the atmosphere by terminating the accident prior to fuel damage and by providing multiple, reliable cooling systems to remove nuclear decay heat.

The confinement system consists of moisture separators, filters, and halogen adsorbers to remove airborne activity (primarily solid particles and iodine-131 vapor) from the reactor area exhaust air. Noble gas activity is not removed by this system. The air passes through the filters and carbon beds before being discharged to a 200-foot stack. Since the system is always on-line, no manual or instrument action is required to assure confinement at the time of an accident.

This paper summarizes operating experience during five years of continuous operation (Reference [1] summarized operating experience during the first three years).

* Information in this article was developed during the course of work under Contract AT(07-2)-1 with the US Atomic Energy Commission.
FIG. 1. Schematic of ventilation system.

FIG. 2. Reactor building showing filter compartments near stack.

FIG. 3. Filter compartment - photograph and schematic diagram.
DISCUSSION

Ventilation System

In the design for the reactor building, a large ventilation exhaust system (300,000 cfm) was provided to ensure negative pressure in the vicinity of the reactor system, to dilute any radioactive material and sweep it from the building, and to direct all exhaust air to the stack. Seals were added at door and other openings to each reactor ventilation system in 1962 to allow use of less exhaust air flow during reactor operation and still maintain similar pressure differentials in the building. Under test conditions, air flow rates as low as 10,000 cfm were shown to maintain the proper air balance between personnel zones and reactor system zones (no personnel enter during operation) with this seal system.

During typical operation of the present system (Figure 1), two of three available exhaust fans are operated to provide a flow of 128,000 cfm air (one fan can provide about 96,000 cfm). This air flow ensures exhaust of any radioactivity at the 200-foot stack height and provides cooling to remove decay heat generated by collected activity. For example, with a 100 degrees F increase in air temperature, 250,000 Btu/min (or 3.8 MW) of heat would be removed.

Operating experience with the fan system has been satisfactory. During scheduled yearly maintenance periods, worn parts (e.g., belts and bearings) are replaced as needed. In 15 years of operation, one fan bearing failure occurred, but normal air flow was restored immediately by startup of the spare fan.

Two separate electrical feeders are provided to supply power to the fans. In addition, a backup diesel generator source will provide power within one minute after total loss of electric power. A transformer failure and malfunction of an automatic switching breaker in 1966 resulted in loss of power to the two on-line building exhaust fans. The reactor was not operating at the time of the failure. Power to the fans was restored within 30 minutes, and there was no adverse experience with building contamination during this period. A backup diesel system that will power a separate motor on the fan drive for two operating systems is being added in each area to make the fans even more reliable and less dependent on switchgear.

Filter Compartments

The confinement system consists of filtration-adsorption units installed in four active compartments and one spare compartment that are operated in parallel (Figure 2). Each compartment contains banks of moisture separators, filters, and activated carbon beds (Figure 3). The compartments are located on the roof of the reactor building between the reactor room exhaust ducts and the exhaust fans (Figure 1) and thus operate at less than atmospheric pressure. Each compartment can be remotely delatched and removed by a crane if it becomes highly contaminated or if extensive repair is required.

Operating experience with the compartments has been good. Minor corrosion of the aluminum walls caused by nitrogen compounds has been observed. The maximum depth of pitting is five mils and does not affect the integrity of the compartments.

Moisture Separators

The moisture separators ("Demisters") are designed to remove about 99% of entrained water particles of 1 to 5 microns, so the particulate filters would not be plugged by water and fail if a reactor accident were accompanied by a large amount of steam generation [2]. The separators (Figure 4) consist of woven "Teflon" yarn and stainless steel wire, forming mats about 24 by 24 inches by two inches thick. Each bank consists of 20 individual separators. The

1 Registered trademark of Otto H York Co
2 Du Pont's registered trademark for its tetrafluorethylene and fluorinated ethylene propylene yarn
FIG. 4. Mixture separator with heaters.

FIG. 5. Particulate filter, segments are 2 ft × 2 ft.
case, mat, and support mechanism are designed and tested to withstand air flows equivalent to ten times the rated air flow through the separator.

Each individual separator has a rated flow of 1600 cfm with a pressure drop of 0.95 inch of water and will remove eight pounds of water per minute without flooding.

The only problem with the separators has been gradual pluggage with a resulting reduction in air flow. Pluggage has been caused by accumulation of an oily substance (probably hydrocarbons from nearby diesel and power plant exhausts) and dust on the upstream face. The units are removed and cleaned when weekly flow—differential-pressure measurements show the flow resistance has increased to three times the original value. Cleaning has been necessary about once every nine to ten months for each separator bank.

Cleaning is done with steam at a nozzle pressure of 15-20 psig, the front face is cleaned for three minutes in a vertical position and the back face is cleaned by blowing steam downward into the back for three minutes with the separator in a horizontal position. Cleaning does not damage the mats. Rated flow—differential-pressure relationships are restored by cleaning. No mats have required replacement since original installation.

The filters (Figure 5) are designed to remove 99%+ of all solid particles. The filter medium is a glass-asbestos felt sheet that is fire-resistant, water-repellant, and that has 60% of its dry tensile strength when wet. Each bank of filters consists of 32 individual units each measuring 24 by 24 inches by 111/2 inches thick. The filter is constructed by folding the felt sheet over corrugated aluminum inserts into closely-spaced pleats in a steel frame.

The rated flow is 1,000 cfm per unit with a differential pressure of 0.9 inch of water. Normal face velocity is about four feet per minute.

Each filter must meet a penetration test not to exceed 0.03% of 0.3-micron diameter dioctyl phthalate (DOP) at 20% and 100% of rated air flow, performed by the vendor before installation in the filter compartment. Filters are tested after installation with 0.6-micron DOP prior to placing the compartment on line. Any filter with a detectable leak greater than 0.05% is replaced. The in-place DOP test is performed on individual filters in the bank. The sample hood (Figure 6) covers approximately one-third of the filter surface area and the gasketed surface at the frame, sampling is repeated until the entire bank is leak-tested.

Filters are replaced every 15 to 16 months when weekly measurements show the flow resistance has increased to six times the original value. The reduction in flow capability is normally caused by wet fly ash from nearby powerhouses. Improved ventilation system intake filters and drying of the exhaust filters have not lengthened exhaust filter life. Studies of methods for increasing filter life are being continued.

Prior to 1967, damage to the filter medium caused about 1% of the units to be rejected after installation. The defective filters were found by examinations and by DOP tests. Damage was caused by punctures resulting from work in the compartments. In early 1967, galvanized hardware cloth was put on both sides of new filters and the rejection rate from damage decreased to less than 0.3%.

Approximately 100 new filters received from the vendor in 1966 were found to leak excessively at the joint between the filter medium and frame when DOP tested in the filter compartments. The manufacturing process was revised to obtain a good seal at the frames and vendor tests were revised to include a test of the seal at the frame in addition to a test of the filter medium. There have been no further problems of this type.

Activated Carbon Beds

Activated carbon beds (Figure 7) were designed to remove more than 99.9% of the elemental iodine vapor that might be released from a reactor if an accident should occur. A carbon bed consists of a one-inch-thick layer of activated carbon enclosed between perforated metal sheets. Each bank consists of 32 individual beds, 24 by 24 inches by 11 1/2 inches thick.

Major design features are shown in Figure 8. The rated flow is 1,000 cfm per unit with a differential pressure of 0.86 inch of water. The carbon beds are made with 12 separate pleats installed horizontally to retard the settling of carbon and to minimize leak paths caused by
FIG. 6. Particulate filter; DOP test sampling hood.

FIG. 7. Activated charcoal beds.
settling. Each bed is packed with about 57 pounds of dust-free, activated coconut shell carbon. A sample from each batch of carbon used is tested and certified by the vendor and by the Savannah River Laboratory (SRL).

Prior to installation, each carbon bed is leak-tested with "Freon-112" and those with leaks greater than 0.1% of the total flow are rejected [7]. In-place leak tests of the carbon beds are completed after installation (before placing in service) and annually thereafter. These tests are for leaks on the carbon beds or gasket surface. The test technique was developed by SRL [8] using "Freon" as a tracer. Seventeen of twenty carbon banks tested in 1967 and five of seven in 1968 had less than the specified maximum leakage of 0.09%. Five banks had leakage of 0.10% to 0.16% because of corrosion of the enameled or cadmium-plated mild steel frames.

Corrosion of the mild steel frames was first noted in 1965 and was caused by nitrogen and sulfur compounds that are present in trace quantities in the reactor building exhaust air and are concentrated by adsorption on the carbon bed. Frames in six filter compartments (about 20 beds total) have failed (perforated screens separated from frames) in the past two years. Loss of carbon from these beds has been negligible, however, the loss was sufficient to cause leakage paths in four of the banks. Even with the leak paths detected, no reactor confinement system had total leakage greater than 0.1% of the flow for the four on-line compartments. Carbon-steel-frames were replaced with stainless-steel-frames in 40% of the filter compartments in 1967 and 30% of the compartments so far in 1968. The replacement program will continue until all beds have units with stainless steel frames.

Permanent electrical heaters have been installed in each filter compartment to permit drying the carbon beds for 24 hours preceding the annual "Freon" leak test (Figure 4). Drying removes adsorbed water which causes the "Freon-112" used in the leak test to desorb too quickly [8]. In addition to removing moisture prior to the leak test, drying at about 60 degrees C increases the service life of the carbon by desorbing impurities. Even with the yearly drying, impurities adsorbed by the carbon will gradually decrease the adsorption efficiency for iodine.

A continuing program for determining the adsorption efficiency of the carbon with age is being conducted by SRL. Tests indicate that the carbon should be replaced after about five years to ensure an iodine adsorption efficiency greater than 99.9%. The beds with stainless steel frames will be repacked with fresh charcoal when the iodine adsorption efficiency decreases to or below 99.9%.

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3 "Freon" and combinations of "Freon" or "F" with numerals are Du Pont's registered trademarks for its fluorinated hydrocarbons.
REFERENCES


DISCUSSION

G. van der LUGT: What is the reason for using 0.6-micron DOP particles for the in-place test?

J.H. HINTON: This is a standard method moulded upon the technique used by the Naval Research Laboratory and the Army Chemical Centre. The DOP smoke generated has a mass mean diameter of about 0.6 microns. The in-place test is performed after installation to ensure that there are no leaks in the filter medium or gasketed surface as the result of installation. A high rate of efficiency can be maintained even though the filter may contain a considerable number of holes. A bank of four filter compartments can contain about 1000 1/4-inch holes and allow only about 1% of the air stream to pass through the holes at normal flow (see Ref. [8] of the paper).

P.J. LINDER: Have you considered the possibility of letting the emergency ventilation plant operate only during accident conditions, so as to avoid ageing of the charcoal? And have you investigated the ageing of the charcoal filter from the point of view of efficiency of methyl iodide removal?

J.H. HINTON: Ageing of the carbon in the Savannah River Plant (SRP) system has not been found to be a real problem. Tests performed by the Savannah River Laboratory (SRL) have shown that the carbon retains its efficiency for adsorbing elemental iodine vapour for a period of about five years. The SRP system is exceptionally reliable; the system is
always on-line and no removal or instrument action is required to ensure confinement at the time of an accident.

I shall ask Mr. Merz of the SRL to answer your second question.

G.F. MERZ. The SRL's study of the effect of ageing on the efficiency of iodine adsorption by carbon is actually still in progress, as reported earlier by Dr. Milham\(^1\). All I can say regarding methyl iodide is that we plan similar tests using this compound.

\(^{1}\) These Proceedings (SM-110/49).
UNITED STATES EXPERIENCE IN MANAGEMENT OF GASEOUS WASTES FROM NUCLEAR POWER STATIONS

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Abstract

Management of gaseous wastes from nuclear power stations has been a matter of concern to the regulatory arm of the US Atomic Energy Commission and to the electric utility companies responsible for the safe operation of these stations. Operating experience for eight nuclear generating stations has been accumulated and evaluated in terms of system performance, atmospheric dilution and environmental consequences. The results of this study show that the management of gaseous wastes from nuclear power stations has, without exception, been well below those levels of radioactivity which would exceed the standards of Title 10, Code of Federal Regulations, Part 20. The major factor influencing waste gas emissions has been the performance of fuel cladding, with stainless-steel-clad fuel exhibiting a significantly greater tendency for defects and consequent escape of fission gases. The significance of meteorological parameters for specific reactor sites is also examined.

INTRODUCTION

There are some fifteen operable nuclear power stations within the United States and over 30 under construction or in the planning stages. In all of these stations consideration has been given to the management of gaseous wastes which may be created. This has been expressed in three different areas: first, a limitation of fuel-cladding defects, thus restricting the gaseous radioactivity available for release from the plant; second, the provision of processes and facilities within the plant to reduce the quantity of airborne emissions; and third, the provision of facilities to enhance atmospheric dispersion of the emitted wastes.

The majority of U.S. nuclear generating stations fall within one of two categories: pressurized water reactors (PWR's), in which the energy released to the reactor coolant is transferred to the turbine working fluid through an intermediate heat exchanger; and second, boiling water reactors (BWR's), in which steam generated within the reactor coolant circuit also serves as the turbine working fluid. The difference in the heat cycles for these two types of plants create major differences in the nature of gaseous wastes and the provision made for their management. In both cases, however, the basic reliance is placed upon the integrity of the fuel cladding to minimize the fission gases or other volatile fission products released to the reactor coolant. In the sections that follow these two reactor types are treated separately. For each reactor plant a description of the facilities provided is included as well as a summary of waste gas discharge experience. In the final section this experience is analyzed and the significance of the releases is examined in the light of atmospheric dispersion.
FIG. 1. Gaseous waste management system at Indian Point Station.
PRESSURIZED WATER REACTORS

A. Design Parameters

In a pressurized water reactor the light water coolant is pumped under high pressure through the reactor core where heat is transferred from the fuel rods. The reactor coolant passes to a steam generator where heat is transferred to a secondary water system prior to return of the reactor coolant to the bottom of the reactor core. The secondary water is boiled in the steam generator and the steam passes to the turbine where it is condensed and returned to the steam generator. Since the reactor coolant circulates in a closed loop, the only normal route for release of the coolant or its contained gases is via the by-pass purification system or the coolant letdown system used to control chemical and radionuclide concentrations in the coolant. Any leakage from the reactor coolant components (valve stems, seals, etc.) occurs into the reactor containment building.

Since large volumes of radioactive gases are not generated, all pressurized water reactors provide storage tanks to permit the retention for decay of these radioactive gases extracted from the reactor coolant system or the liquid waste processing system. Since hydrogen is normally employed in the reactor coolant to suppress radiolytic decomposition of the water, control must be exercised to prevent explosive mixtures in the auxiliary systems. This may be accomplished by use of hydrogen recombiners or by inert gas blanketing of tanks containing hydrogen. Since the gases can be stored their release can, if necessary, be timed to coincide with the meteorological conditions most favorable to dispersion. Present PWR's are not normally being supplied with tall chimneys since the quantities of waste gases involved are quite small and controllable without dependence on atmospheric dilution, although earlier units do use stacks.

B. Specific Plant Features and Experience

1. Indian Point #1

The prime source of gaseous waste at Indian Point is the primary coolant which releases hydrogen and traces of radioactive material when the coolant is cooled and depressurized. The primary loop deaerator is a major point of release; a second point of release is the waste gas stripper and the waste evaporator. The flow sheet is shown in Figure 1. The gases are passed through a condenser and a surge tank to a catalytic hydrogen recombiner. In the recombiner the water vapor from the $H_2-O_2$ combination is condensed and separated, the moisture-free gas entering the fission gas surge tank. Two parallel compressors pump the gases from this tank to four surge tanks designed to provide storage for 120 days. Release to the atmosphere is via the stack at a controlled rate through a 35 cfm absolute filter.

Primary coolant system equipment is vented to a sweep gas system which is also used to control the concentration of hydrogen in the waste tanks and piping. This system contains 2-5,000 cubic foot surge tanks that can be pressurized to 75 psig. The gas can be re-
FIG. 2. Gaseous waste management system at Yankee-Rowe Station.
TABLE I. RADIOACTIVE GASEOUS WASTE DISCHARGES AT INDIAN POINT

<table>
<thead>
<tr>
<th>Period</th>
<th>Gaseous Releases Average Rate</th>
<th>Gross Electricity Generated (Mwh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug. 2, 1962 - Jan. 31, 1963</td>
<td>0.001</td>
<td>185,300</td>
</tr>
<tr>
<td>Feb. 1, 1963 - July 31, 1963</td>
<td>0.13</td>
<td>543,400</td>
</tr>
<tr>
<td>Aug. 1, 1963 - Jan. 31, 1964</td>
<td>0.001</td>
<td>444,700</td>
</tr>
<tr>
<td>Feb. 1, 1964 - July 31, 1964</td>
<td>0.71</td>
<td>14,300</td>
</tr>
<tr>
<td>Aug. 1, 1964 - Jan. 31, 1965</td>
<td>0.58</td>
<td>623,100</td>
</tr>
<tr>
<td>Feb. 1, 1965 - July 31, 1965</td>
<td>0.52</td>
<td>634,000</td>
</tr>
<tr>
<td>Aug. 1, 1965 - Jan. 31, 1966</td>
<td>1.52</td>
<td>364,400</td>
</tr>
<tr>
<td>Oct. 1, 1966 - Mar. 31, 1967</td>
<td>0.36</td>
<td>1,102,000</td>
</tr>
<tr>
<td>Apr. 1, 1967 - Sept. 30, 1967</td>
<td>1.10</td>
<td>1,120,000</td>
</tr>
<tr>
<td>Oct. 1, 1967 - Mar. 31, 1968</td>
<td>1.08</td>
<td>522,800</td>
</tr>
</tbody>
</table>

*Compiled from Consolidated Edison Company Semi-Annual Operations Reports for Indian Point Station.

The waste gas releases are summarized in Table I. In operation to date it has been unnecessary to holdup the waste gases for decay. All gases reaching the fission-gas surge tank have been released through the stack without compression and storage. Thus, the compressors have been run only for testing purposes. The annual average release rate limit for noble gases is 50,000 µCi/sec; thus, the maximum releases to date, without holdup, have been only 0.003% of the limit.

2. Yankee-Rowe

The bulk of activity processed in and discharged by the off-gas system at this plant is released from the liquids discharged to the waste disposal plant from the primary coolant system. Most of the gaseous radiotopes and hydrogen are released when the coolant is depressurized; the remaining gases are released in the liquid waste evaporator. The waste gas flow sheet is shown in Figure 2.

A completely closed header system, serving all reactor liquid effluent receivers, collects all hydrogen-bearing gases. This system is purged with nitrogen before waste is discharged from the primary plant to
prevent the accumulation of explosive hydrogen-air mixtures. The gases are compressed and collected in a 4160-ft\(^3\) steel surge drum. Three 60-ft\(^3\) decay drums may be filled from the surge drum for additional decay before release to the primary 150-ft stack. The gases are released at a controlled rate through deep-bed filters, mixed with 15,000 cfm of air, and discharged through the stack.

The containment sphere purge system exhausts directly to the primary stack without filtration and is operated only when personnel access is required. The internal air filtration system controls the normal content of airborne particulate activity within the containment building. The total flow of purge and dilution air is 15,000 cfm. The main condenser air ejector effluent is also exhausted to the primary building exhaust fan.

The flue gases from the incinerator are passed through a wet-gas scrubber, filtered through a deep-bed-glass-wool filter, and discharged through a separate stack.

Gaseous release history is summarized in Table II. The activity released from Yankee is generally less than that of any other plant studied.

<table>
<thead>
<tr>
<th>Period</th>
<th>Total Activity (curies)</th>
<th>Percent of Limit</th>
<th>Gross Electricity Generated (Mwh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1961</td>
<td>0.002</td>
<td>Nil</td>
<td>961,350</td>
</tr>
<tr>
<td>1962</td>
<td>21.7</td>
<td>0.03</td>
<td>740,125</td>
</tr>
<tr>
<td>1963</td>
<td>7.4</td>
<td>0.01</td>
<td>1,004,100</td>
</tr>
<tr>
<td>1964</td>
<td>1.0</td>
<td>0.001</td>
<td>1,257,000</td>
</tr>
<tr>
<td>1965</td>
<td>1.3(^d)</td>
<td>0.002</td>
<td>1,028,000</td>
</tr>
<tr>
<td>1966</td>
<td>2.4(^e)</td>
<td>0.004</td>
<td>1,371,000</td>
</tr>
<tr>
<td>1967</td>
<td>2.3(^f)</td>
<td>0.004</td>
<td>1,348,425</td>
</tr>
</tbody>
</table>

\(^a\) Compiled from sources 6 and 7

\(^b\) Excluding tritium

\(^c\) Based on a maximum permissible concentration at discharge of \(3 \times 10^{-4}\) \(\mu\)Ci/cc, averaged over 12 months

\(^d\) In addition, 16 curies of tritium were released

\(^e\) In addition, 11 curies of tritium were released

\(^f\) In addition, 15 curies of tritium and 139 \(\mu\)Ci of beta particulates were released
The total activity (exclusive of H\(^3\)) discharged in gaseous wastes has been typically less than 10 curies/year, and was never greater than 0.03% of the limit. In the case of Yankee, a dilution factor of 1000 for atmospheric diffusion, averaged over the entire year, is used with a MPC of \(3 \times 10^{-7}\) \(\mu\text{Ci}/\text{cc}\) in establishing the limit.

### 3. San Onofre

The major quantity of gaseous radioactive waste originates with the liquid generated either at shutdowns or by the continuous dilution of boron contained in the reactor coolant during the core cycle. The concentration of fission gases in primary coolant is expected to approximate 230 \(\mu\text{Ci}/\text{ml}\) with 1% defective fuel. Most of the waste gas volume consists of hydrogen and nitrogen. The coolant contains about 45 cc of hydrogen gas (at standard temperature and pressure) per kilogram of coolant. The volume of xenon and krypton gases in one system volume of coolant would be less than 1 ft\(^3\), compared to 300 standard cubic feet of hydrogen. Nitrogen is used as a cover gas in the waste system flash tank and hold-up tanks shown in Figure 3.

It is estimated that about 50% of the volatile activity will be removed from the coolant in the flash tank. These gases flow continuously to a gas surge tank.

The gas surge tank receives gaseous activity from the flash tank and waste system gas stripper, as well as from the vent header within the containment sphere during normal operation. As waste gas pressure rises in the gas surge tank, the waste gas compressor starts and compresses the gas into one of the decay drums where it can be stored for decay prior to release to the vent stack. Before reaching the vent stack fans, the gas is passed through a roughing pre-filter and a high-efficiency filter.

### Table III. Radioactive Gaseous Waste Discharges at San Onofre\(^a\)

<table>
<thead>
<tr>
<th>Period</th>
<th>Volume, ft(^3)</th>
<th>Activity, Ci</th>
</tr>
</thead>
<tbody>
<tr>
<td>June, 1967</td>
<td>2,236</td>
<td>0.0015</td>
</tr>
<tr>
<td>July, 1967</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>August, 1967</td>
<td>4,722</td>
<td>0.002</td>
</tr>
<tr>
<td>September, 1967</td>
<td>7,761</td>
<td>0.96</td>
</tr>
<tr>
<td>October, 1967</td>
<td>11,748</td>
<td>1.43</td>
</tr>
<tr>
<td>November, 1967</td>
<td>8,712</td>
<td>1.07</td>
</tr>
<tr>
<td>December, 1967(^b)</td>
<td>3,052</td>
<td>0.44</td>
</tr>
</tbody>
</table>

\(^a\)Compiled from Monthly Operation Reports for San Onofre Nuclear Generating Station

\(^b\)Total Power Generation through December 31, 1967 was 386,500 Mwh
FIG. 3. Waste flow sheet at San Onofre Nuclear Power Station.
Gaseous releases are tabulated by month in Table III. As of December 31, 1967, gaseous releases had totaled 3.90 curies with an average concentration in the stack of $1.2 \times 10^{-8} \, \mu\text{Ci/cc}$, without compression and decay storage. This can be compared to the annual average license limit of $2.86 \times 10^{-3} \, \mu\text{Ci/cc}$.

4. Connecticut Yankee

Gaseous wastes derive from the vent and drain system, as off-gases from the boron recovery system and as gases evolved from liquid in the primary drain collecting tank and boron waste storage tanks. These wastes consist almost entirely of hydrogen and the fission product gases although nitrogen used for purging the air from the system may also be present in the gaseous wastes.

The gas piping shown in Figure 4 is arranged as a cascade system. All gases enter the system via the waste gas header near the primary drain collecting tank and flow to the vapor space of one of the boron waste storage tanks. The gases then flow to the vapor space of the second boron waste storage tank and finally to the waste gas surge sphere.

The gas sphere has a polyurethane-coated nylon cloth diaphragm attached at its equator. The sphere receives the gas displaced from the waste liquid tanks upon filling and restores the gas to the tanks upon emptying. Off-gases continuously accumulate in the waste gas surge sphere due to plant operation and the operation of the boron recovery system. When a quantity of off-gas has accumulated in the waste gas surge sphere it is sampled to determine its activity. The off-gas is then gradually drawn from the sphere by one of the waste gas blowers and discharged through a fiber-glass decay gas filter to the suction of two 35,000 cfm ventilation and purge fans. An interlock prevents discharge of the waste gas while an insufficient ventilation discharge flow exists. The diluted mixture is discharged to the atmosphere via a 175-ft primary vent stack.

Gaseous waste experience is summarized in Table IV by month, and is well below the permissible limit of 10,000 $\mu\text{Ci/sec}$, averaging 0.032 $\mu\text{Ci/sec}$ in the 70,000 cfm vent exhaust over the initial eight months of operation.

BOILING WATER REACTORS

A. Design Parameters

In a boiling water reactor (BWR) the light water coolant is circulated, usually by forced convection, up through the reactor core where it boils under high pressure; the steam passes to a turbine where it condenses and is returned to the reactor core. An ejector removes air and non-condensable gases from the turbine-condenser and then discharges them to the plant stack through an off-gas system generally comprising a delay line and filters.
TABLE IV RADIOACTIVE GASEOUS WASTE DISCHARGES
AT CONNECTICUT YANKEEa

<table>
<thead>
<tr>
<th>Period</th>
<th>Gross Gaseous Waste Releases (Volume, ft³)</th>
<th>Activity, μCi</th>
<th>Electricity Generated (Mwh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug. &amp; Sept., 1967</td>
<td>--</td>
<td>--</td>
<td>3,840</td>
</tr>
<tr>
<td>October, 1967</td>
<td>1,100</td>
<td>9.1</td>
<td>56,340</td>
</tr>
<tr>
<td>November, 1967</td>
<td>2,000</td>
<td>11.4</td>
<td>150,630</td>
</tr>
<tr>
<td>December, 1967</td>
<td>--</td>
<td>None</td>
<td>350,700</td>
</tr>
<tr>
<td>January, 1968</td>
<td>8,100</td>
<td>624.8</td>
<td>240,210</td>
</tr>
<tr>
<td>February, 1968</td>
<td>--</td>
<td>None</td>
<td>335,670</td>
</tr>
<tr>
<td>March, 1968</td>
<td>4,104,000b</td>
<td>36.5</td>
<td>19,950</td>
</tr>
</tbody>
</table>

aInformation received in personal correspondence with D. E. Vandenburgh, Connecticut Yankee Atomic Power Company.

bReactor containment purge.

Under normal operating conditions, corrosion products and activated gases constitute the main source of radioactive wastes from a BWR. In the absence of leaking fuel rods, nitrogen-13, nitrogen-16 and oxygen-19 are the primary activated gases. These are stripped from the reactor core by the steam flow and carried via the condenser air ejector and a delay line to the stack. Nitrogen-13 is by far the predominant activity with a calculated release rate of approximately 400 μCi/sec for a nominal 1000 Mw(e) station.

In addition to the corrosion products and activation products described, it is normally anticipated that small amounts of "tramp" uranium contamination on the fuel rod cladding will result in the presence of minor quantities of fission products in the reactor water and the air ejector discharge from the turbine condenser. The turbine gland seal is also normally fed with primary steam and the gland seal condenser is exhausted into the plant stack via holdup piping. When fuel rod defects occur, fission products diffuse into the reactor water. The fission gases, krypton and xenon, are stripped from the water by the steam and travel via the turbine gland seal and the turbine condenser air ejector to the plant stack. The volume of gas to be handled is largely determined by the air in-leakage to the turbine condenser. Since this is usually on the order of tens of cfm, provision of significant delay time for the air ejector discharge is impractical, and waste gas storage is not feasible for these plants.

In general, waste systems are designed to handle the maximum expected activity levels without exceeding applicable government regulations for waste discharge. The design objective for BWR waste management systems is to maintain average radiation doses beyond the plant...
boundary from routine plant operation to 1% or less of the permissible exposures. In general this design objective has been achieved in the boiling water plants operating at the present time.

B. Specific Plant Features and Experience

1. Dresden Unit #1

The principal source of activity release from the plant is the main condenser air ejector. This removes about 35 scfm of air, radiolytic decomposition products of water, and those fission gases and activation gases that may be present. These gases are passed through 130 feet of 30-inch diameter pipe, providing about 20 minutes for decay of short-lived radiogases, prior to filtration through a high efficiency particulate filter and discharge into a 300 foot stack.

The turbine gland seal condensate exhaust is provided with about 2 minutes decay by passing through 130 feet of 20 inch pipe at 200 scfm prior to introduction into the stack.

The average annual release rates for noble gas fission products during reactor operation are presented in Table V. These releases range up to only 3.6% of the license limit of 700,000 μCi/sec. Instantaneous

<table>
<thead>
<tr>
<th>Period</th>
<th>Gross Electricity Generated (10^3 Mwh)</th>
<th>Gaseous Release Rate (μCi/sec)</th>
<th>Percent of License Limit(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>276</td>
<td>800 (maximum)</td>
<td></td>
</tr>
<tr>
<td>1961</td>
<td>555</td>
<td>3,020 (maximum)</td>
<td></td>
</tr>
<tr>
<td>1962</td>
<td>1250</td>
<td>24,300 (maximum)</td>
<td></td>
</tr>
<tr>
<td>1963</td>
<td>989</td>
<td>3,000 (average)</td>
<td>0.4</td>
</tr>
<tr>
<td>1964</td>
<td>1038</td>
<td>20,400 (average)</td>
<td>2.9</td>
</tr>
<tr>
<td>1965</td>
<td>1018</td>
<td>24,800 (average)</td>
<td>3.5</td>
</tr>
<tr>
<td>1966</td>
<td>1475</td>
<td>24,900 (average)</td>
<td>3.6</td>
</tr>
<tr>
<td>1967</td>
<td>853</td>
<td>11,300 (average)</td>
<td>1.6</td>
</tr>
</tbody>
</table>

\(^{a}\)Compiled from Commonwealth Edison Company Annual Reports for the Dresden Nuclear Power Station.

\(^{b}\)Licensed to release at an annual average rate of 7 x 10^5 μCi/sec.
release rates have not exceeded 80,000 $\mu$Ci/sec. The increase in activity discharged during 1964 through 1965 is attributable to the relatively large number of stainless steel fuel cladding failures that occurred during these years. The activities of halogens and particulates, originated from entrainment in the condensers, have averaged 0.002 to 0.003 $\mu$Ci/sec.

2. Big Rock Point

Non-condensables from the main condenser air ejector are released to a 240 foot stack through a high-efficiency filter after a hold-up of 30 min in an expanded off-gas line, while the turbine gland seals are vented to the stack after a delay of about 90 sec. Ventilation air from the chemical laboratory and counting room is filtered and released to the atmosphere through a roof exhaust vent.

TABLE VI. RADIOACTIVE GASEOUS WASTES DISCHARGED AT BIG ROCK POINT

<table>
<thead>
<tr>
<th>Period</th>
<th>Release Rate ($\mu$Ci/sec)</th>
<th>Gross Electricity Generated (Mwh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept. 1962-April 1963</td>
<td>&lt;20$^d$</td>
<td>~60</td>
</tr>
<tr>
<td>May 1963-Oct. 1963</td>
<td>20$^d$</td>
<td>115,300</td>
</tr>
<tr>
<td>Nov. 1963-April 1964</td>
<td>50$^d$</td>
<td>179,900</td>
</tr>
<tr>
<td>May 1964-Oct. 1964</td>
<td>54$^d$</td>
<td>103,400</td>
</tr>
<tr>
<td>Nov. 1964-April 1965</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>May 1965-Oct. 1965</td>
<td>5,000$^e$</td>
<td>19,000</td>
</tr>
<tr>
<td>Nov. 1965-April 1966</td>
<td>30,000$^e$</td>
<td>77,000</td>
</tr>
<tr>
<td>May 1966-Oct. 1966</td>
<td>40,000$^e$</td>
<td>80,000</td>
</tr>
<tr>
<td>Nov. 1966-April 1967</td>
<td>10,000$^e$</td>
<td>17,000</td>
</tr>
<tr>
<td>May 1967-Oct. 1967</td>
<td>11,400$^e$</td>
<td>not reported</td>
</tr>
<tr>
<td>Nov. 1967-April 1968</td>
<td>6,200$^e$</td>
<td>not reported</td>
</tr>
</tbody>
</table>

$^a$Compiled from Consumers Power Company monthly and semiannual operating reports for Big Rock Point Nuclear Plant.
$^b$Permissible continuous discharge (averaged over 12 consecutive months) is 1 curie/sec.
$^c$Permissible instantaneous rate of release is 10 curies/sec.
$^d$Principally $^{13}$N.
$^e$Greater than 99% noble-gas fission products. Halogens and particulates have averaged less than 1.2 $\mu$Ci/sec.
<table>
<thead>
<tr>
<th>Period</th>
<th>Average Rate</th>
<th>Peak Rate</th>
<th>Halogens, Range of Weekly Average</th>
<th>Gross Electricity Generated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μCi/sec)</td>
<td>(μCi/sec)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feb. 16, 1963 - Aug. 15, 1963</td>
<td>50</td>
<td>500</td>
<td>$6 \times 10^{-6} - 2 \times 10^{-3}$</td>
<td>41,600</td>
</tr>
<tr>
<td>Aug. 16, 1963 - Feb. 15, 1964</td>
<td>34</td>
<td>440</td>
<td>$9 \times 10^{-5} - 6 \times 10^{-3}$</td>
<td>171,100</td>
</tr>
<tr>
<td>Feb. 16, 1964 - Aug. 15, 1964</td>
<td>94</td>
<td>650</td>
<td>$2 \times 10^{-6} - 9 \times 10^{-6}$</td>
<td>214,400</td>
</tr>
<tr>
<td>Aug. 16, 1964 - Feb. 15, 1965</td>
<td>390</td>
<td>1,225</td>
<td>$1 \times 10^{-5} - 4 \times 10^{-4}$</td>
<td>182,200</td>
</tr>
<tr>
<td>Feb. 16, 1965 - Aug. 15, 1965</td>
<td>12,200</td>
<td>65,000</td>
<td>$8 \times 10^{-5} - 3 \times 10^{-2}$</td>
<td>175,400</td>
</tr>
<tr>
<td>Aug. 16, 1965 - Feb. 15, 1966</td>
<td>16,000</td>
<td>85,000</td>
<td>$3 \times 10^{-5} - 3 \times 10^{-2}$</td>
<td>62,500</td>
</tr>
<tr>
<td>Feb. 16, 1966 - Aug. 15, 1966</td>
<td>5,500</td>
<td>43,500</td>
<td>$3 \times 10^{-4} - 2 \times 10^{-2}$</td>
<td>84,400</td>
</tr>
<tr>
<td>Aug. 16, 1966 - Feb. 15, 1967</td>
<td>23,000</td>
<td>50,000</td>
<td>$1 \times 10^{-4} - 7 \times 10^{-2}$</td>
<td>123,200</td>
</tr>
<tr>
<td>Feb. 16, 1967 - Aug. 15, 1967</td>
<td>23,160</td>
<td>not reported</td>
<td>$4 \times 10^{-3} - 1 \times 10^{-1}$</td>
<td>133,703</td>
</tr>
<tr>
<td>Aug. 16, 1967 - Feb. 15, 1968</td>
<td>33,300</td>
<td>not reported</td>
<td>$9 \times 10^{-3} - 9 \times 10^{-2}$</td>
<td>213,004</td>
</tr>
</tbody>
</table>

*Compiled from Pacific Gas and Electric Company semi-annual operating reports for the Humboldt Bay Power Plant*
With a 240 foot stack and the annual wind distribution found at the site, it was calculated that an annual average stack release rate of 1 curie/sec, or a short-term release rate of 10 curies/sec, would not result in off-plant doses of less than 500 mrems/year; and the off-gas system was designed with the expectancy that emissions would be well below these permissible emission ratings.

The air ejector system radiation monitor, located near the beginning of the delay system, alarms if the emission rate after 30-min decay exceeds 1 curie/sec, and automatically initiates valve closure with a 15-min time delay if the emission rate after 30-min decay should exceed 10 curies/sec. In the event that the valve closure actually occurs, plant shutdown within a few minutes would be required due to loss of condenser vacuum.

A summary of the releases of radioactive gaseous wastes is presented in Table VI. Average gaseous releases through April 1965 ranged from less than 20 to 54 \( \mu \text{Ci/sec} \) and consisted mainly of \(^{15}\text{N}\). Since that date, noble gases from defective fuel elements have resulted in substantially higher releases although never more than 4% of the license limit.

3. Humboldt Bay

The principal sources of gaseous wastes are the main condenser air ejector and leakage from the turbine gland system. Other sources are air from purging the drywell and from the refueling building. The drywell is purged only when access to the reactor, for refueling or other purposes, is required. The design of the expanded off-gas lines provides an 18-min delay for the air ejector waste and a 50-sec delay for the gland seal exhaust stream before filtration and release through a 250-ft stack.

The air ejector gases are monitored by two ion-chamber gamma detectors (one an operating spare) designed to detect radioactive noble gases. A release rate of 0.05 curie/sec is sustained for 10 min, the off-gas isolation valve closes and the reactor is shut down. The stack gas is monitored for halogens and particulates with charcoal and particulate filters, and for gamma radiation with two scintillation detectors (one an operating spare). Calibrations of the off-gas and stack-gas monitoring systems are based on periodic isotopic analyses of "grab" samples, using a 256-channel gamma spectrometer (scintillation detector) system. Both systems permit evaluation of noble gas and gaseous activation product release rates over the range \( 10^2 \) to \( 10^7 \mu\text{Ci/sec} \).

Radioactive waste discharges (Table VII) have been consistently within the license limits. The annual stack release rate for fission product noble gases is 50,000 \( \mu\text{Ci/sec} \), with a peak rate limit of 500,000 \( \mu\text{Ci/sec} \). The license rate limit for halogens and particulates is 0.18 \( \mu\text{Ci/sec} \). Prior to February 15, 1965, the average and peak noble gas release rates were consistently less than 1% of the plant limits. During the periods since that time, which were typified by an increasing number of fuel element failures, the release rate has been in the range of 10 to 50% of the limits.

*actual delay at full load is approximately 40 minutes.*
It is expected that the release will remain in this range until all the stainless-steel-clad fuel is replaced with Zircaloy-clad fuel and residual contamination from "tramp" uranium in the primary system is eliminated. Maximum weekly average particulate and halogen release rates also increased, from about 1% to almost 40% of the average annual limit.

![Graph of nuclear power plant average gaseous emission rates.](image)

**DISCUSSION**

The experience in gaseous waste management reported in the previous section has been normalized and summarized in Figure 5. This figure presents the average discharge rate in $\mu$Ci/sec per $10^3$ Mwh of energy generated over the reporting periods for each of the stations. It can be noted that the normalized gross discharge rates for the two types of steam supply systems are widely separated; the BWR units have ranged from about 2 to 300 $\mu$Ci/sec per $10^3$ Mwh and the PWR units from about 3 to $400 \times 10^{-5}$ $\mu$Ci/sec per $10^3$ Mwh.

There is no apparent relationship between power level and gaseous emission rate for these plants. Considering the average emission rates over their power production lifetime to date, PWR's average between about $2 \times 10^{-5}$ and $2 \times 10^{-3}$ $\mu$Ci/sec-Mwt; BWR's range from 24 to 80 $\mu$Ci/sec-Mwt, with the smaller plants producing the higher rates. For a given plant type, the gaseous release rate depends primarily upon the integrity of the fuel cladding. In the case of PWR's the extent of use of the waste-gas storage facilities also appears to have a significant effect on release rates.
It should be re-emphasized that the radionuclides represented by these gross activity release rates differ between the two plant types. The PWR gaseous releases generally consist largely, if not exclusively, of $^{133}$Xe and $^{85}$Kr while the BWR releases are predominated by the very short-lived fission product and activation gases. However, considering that the permissible concentrations for these mixtures differ by about one order of magnitude, the PWR releases are, on a dose-equivalent basis, about $1/10,000$ those of the BWR's. These gaseous release rates lead to the incorporation of tall stacks in BWR facilities to provide for dispersion and dilution.

Although tall stacks have also been provided for earlier PWR plants, including those reported here, present designs of PWR plants do not generally include a distinct, separate chimney structure. Instead, a short vent pipe is usually attached to, and extends only a short distance above the top of the reactor building for this purpose. The ability of the gases discharged from such a vent to escape the "cavity" effect induced by winds flowing around the building is uncertain. The analysis employed for these plants thus usually assumes the gases are brought down to ground level by this effect and mixed in the turbulent wake of the reactor building prior to downwind transport.

This effect can be considered mathematically by a number of means including the "virtual source" and "volume source" models. In the latter, the gas released per second is assumed to be mixed initially into some fraction of the volume defined by the projected building area and the mean wind speed. Growth from this initial size is determined by the atmospheric dispersion conditions. Thus, using a Gaussian plume model, one obtains

$$
X = \frac{Q}{(cA + \pi \sigma_y \sigma_z) \bar{u}}
$$

where $X =$ plume centerline ground level concentration at $x$, $\text{Ci}/\text{m}^3$

$Q =$ source release rate, $\text{Ci}/\text{sec}$

$c =$ building shape factor, usually between $\frac{1}{2}$ and $2$

$A =$ projected area of reactor building, $\text{m}^2$

$\sigma_y, \sigma_z =$ lateral and vertical plume dimensions, $\text{m}$, respectively, at downwind distance, $x$

$\bar{u} =$ mean wind speed, $\text{m}/\text{sec}$

Using as typical values; $c = 0.5$ and $A = 1800 \text{ m}^2$, under neutral conditions at $1000$ m with a $5$ m/sec wind, a plume centerline concentration of $2.7 \times 10^{-5}$ $\text{Ci}/\text{m}^3$ is obtained for a release rate of one curie/sec. Considering the plume to be represented by a semi-infinite cloud of the centerline concentration, the corresponding dose rate would be about $4.8$ mR/h for an effective gamma energy of $0.2$ Mev/disintegration.
For a BWR, chimneys of 250-300 feet in height to promote dispersion of released gases are not uncommon. For this case:

\[ X = \frac{Q}{\pi \bar{u} \sigma y \sigma z} \exp \left( -\frac{h^2}{2 \sigma z} \right) \]

where \( h \) = effective height of release, m

Using the same diffusion and source parameters the ground level concentration at 1000 m for a 100 m release height is only \( 2.2 \times 10^{-7} \) Ci/m\(^3\) or a factor of 100 less than the previous example. However, in this case, the dose rate from the elevated plume must also be considered. At this distance, this contribution would be about 2 mR/h, assuming an effective gamma energy of 1 Mev/disintegration for the short-lived gases.

In both of these approaches the diversity of wind and stability conditions at a particular site as well as the location of plant neighbors are considered in arriving at annual average short period release rates appropriate to the plant. Additionally, operating license restrictions are usually also applied to other potential emissions, such as halogens and "particulates". Experience to date however has confirmed the much greater radiological significance of the noble gases.

**SUMMARY**

The gaseous wastes released from seven operating power reactors, ranging in thermal power from 210 Mw to 1473 Mw, have been summarized for a total of about 35 reactor-years of operation resulting in the generation of over 26 millions of Mwh of electricity. During this period, no BWR plant exceeded 4.5% of its licensed limit except for the Humboldt Bay plant which averaged about 50% of its annual average limit for one 12 month period when a number of defective fuel elements were in the core. During this period the maximum potential exposure in the plant environs was determined to be about 50 mrem. PWR plants have experienced gaseous release rates which are less than a tenth of one percent of license limits, in some cases without using existing gas storage facilities.

The experience cited in the preceding sections has been restricted to those plants presently operating which represent types currently under construction or planned. Such historic units as Shippingport, Hallam, Fermi, Piqua, Pathfinder, Peachbottom and Elk River have been excluded from consideration due to their unique designs which are not represented in the current generation of power plants. In these plants also, however, the excellent waste management performance noted for the PWR and BWR plants has been duplicated.
SOURCE MATERIAL

INDIAN POINT #1


YANKEE-ROWE


SAN ONOFRE


CONNECTICUT-YANKEE


DRESDEN #1


BIG ROCK POINT


HUMBOLDT BAY


DISCUSSION

O.L. CORDES: Do you use yearly averaged meteorological conditions in computing the licensed yearly output?

M.I. GOLDMAN: Yes, average meteorological conditions over a year are used to compute the average annual gaseous waste release rate for a reactor license. The amount and quality of the meteorological data determine the margin of conservatism in the waste release limits established by negotiation with the USAEC regulatory authority.

H. ISBIN: In seeking to express a management-performance characteristic of the gaseous radioactive waste discharges, it is convenient to use the ratio of the number of microcuries released (averaged over a year) to the limits prescribed in the licensing process. Have you considered developing more specific criteria, taking into account the individual radio-nuclides present?

M.I. GOLDMAN: The gaseous release rates for BWR and PWR plants are based on different gas mixtures. BWR mixtures generally consist
largely of short-lived fission gases resulting from the short delay between release from the fuel and discharge from the plant stack. PWR waste gases are composed primarily of the longer-lived fission gases $^{131m}$Xe, $^{133}$Xe and $^{85}$Kr, due to the hold-up inherent in the closed-loop primary system and the waste decay tanks provided at all PWRs. These mixtures and their dose-equivalent factors are taken into account in establishing the emission limits for a particular plant under consideration.

W. SCHIKARSKI: What is the principal reason for the large differences between BWR and PWR off-gas releases? Is it mainly differences in primary system design or in fuel performance, or is it management decisions that are involved?

M.I. GOLDMAN: The main difference in off-gas releases between BWR and PWR plants is due to the direct flow route for fission gases in a BWR from the reactor coolant via the turbine and condenser through the air ejector to the plant stack. Thus, the discharge consists primarily of short-lived fission and activation gases. In a PWR, the reactor coolant circulates in a closed loop providing considerable opportunity for decay of short-lived gases released from the fuel. Further, if the gaseous release is large, additional decay can be provided by the gaseous waste storage tanks. Similar fuel performance in the two types of reactors would give much higher releases in BWR. Management approaches do not have a significant effect on the releases, which depend mainly on design differences in reactor-coolant behaviour.

R.E. HOLMES: Would you summarize the position on tritium releases in terms of curie release, percentage of the licence level, and whole-body dose to exposed persons?

M.I. GOLDMAN: Tritium releases have been monitored only recently (i.e. within the past four years), since it was not anticipated that they would be significant for light-water reactors. From the few data available, releases of tritium in waste gases are in fact consistent with the estimates. For example, at Yankee-Rowe (see Table II in paper SM-110/42), tritium releases via the plant stack averaged $11-16$ Ci per year from 1965 to 1967. Using the same basis of calculation for noble gases, the tritium releases would average $0.02-0.03\%$ of the permissible discharges, resulting in estimated whole-body doses of about $0.1$ mrem per year.

C.G. AMATO: Can you state whether changes in waste-gas management for a PWR would result in significant financial savings? I define significant economic advantages as 1 per cent or higher of the capital cost, or unit cost, of the product.

M.I. GOLDMAN: On the basis of this definition, changes in waste-gas management for a PWR (by elimination of gas-storage facilities) would not result in a 1 per cent change in the capital or operating costs of the product. Nevertheless, I do not believe that any additional benefit accrues from operation of gas-storage facilities by a reduction in the fraction of the licence limit released. The data provided in the paper indicate quite clearly that those plants choosing not to store wastes still have release rates which are but a few thousandths of 1 per cent of the licence limits. The question remains as to what benefit is obtained from further reduction of these fractions in accordance with the ICRP regulations.
CONTROL OF AIRBORNE WASTES FROM UNITED KINGDOM GAS COOLED POWER REACTORS

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Abstract

CONTROL OF AIRBORNE WASTES FROM UNITED KINGDOM GAS COOLED POWER REACTORS. The United Kingdom has in operation 23 carbon-dioxide-cooled nuclear power reactors. The main features of a typical reactor are described, and the ways in which airborne wastes arise are detailed. The first eight power stations employ reactors in steel pressure vessels and the biological shield is air cooled. This air becomes activated by the action of thermal neutrons and radioactive isotopes of both true gases and finely divided particulates are produced. Additionally some leakage of the coolant gas takes place and this, as well as the ventilation of active handling facilities, adds to the main source of effluent. In the case of reactors with prestressed concrete pressure vessels the cooling is achieved by circulating water through pipes close to the internal steel liners, and cooling-air problems are thus eliminated. The quantities, isotopic composition and origins of the various contributions to the final discharge are given. Treatment consists of filtration and dispersal through stacks at reactor roof height. The filters used are described.

Measurements are made by sampling the main gas circuit which is continuously filtered, by sampling a fraction of the exhaust gases before discharge to the atmosphere and as a precaution a minimum programme of environmental samples are checked. In the event of an emergency where relatively large quantities of fission products may be involved extra equipment is provided to reduce the emission of radioactive materials to acceptable levels.

1. Introduction

There are at this time in the United Kingdom 24 gas cooled power reactors operating to generate electricity feeding into the national grid. These reactors are basically the same and differ chiefly in power output varying from 50MW(e) at Calder Hall to 313MW(e) at Oldbury. (Figure 1 is a photograph of Berkeley).

The fuel in all cases consists of cylindrical rods of natural uranium totally enclosed in finned cans made from a magnesium alloy, with a melting point of 645°C. Figure 2 shows a typical fuel element. These fuel elements are stacked vertically in channels in the graphite moderator. The primary reactor coolant is carbon dioxide at pressures varying from 100 p.s.i.a. to 365 p.s.i.a.

The reactor core is contained in a steel pressure vessel with the exception of Oldbury where the containment is prestressed concrete, with a steel liner. The concrete biological shield round the steel pressure vessel is cooled by air or in the case of the prestressed concrete pressure vessel, the liner is insulated and water cooled.

Other common features are the ability to refuel on load, and the provision of equipment to sample the carbon dioxide from every channel which is sensitive enough to detect very small leaks of fission products into the gas should these occur.
FIG. 1. Berkeley Nuclear Power Station.

FIG. 2. Magnox polyzoal fuel element.
2. Shield Cooling Air

The main source of radioactive gaseous effluent expressed in terms of radioactivity is carried by the shield cooling air. This air is exhausted through glass fibre filters and data for three stations is given in Table I. The bulk of the air passes between the outer face of the steel containment vessel and the inner face of the concrete biological shield. Since this space is maintained at a slight negative pressure with respect to atmosphere, leakage round the edges of the many penetrations through the biological shield occur and provide cooling and ventilation. For example, each boiler has an inlet and outlet duct each of several feet diameter passing through labyrinths into the pressure vessel. There are 250 standpipes through which fuel is changed and control equipment is operated. Figures 3 and 4 show the layout diagrammatically.

As the cooling air passes inside the biological shield it is subjected to a thermal neutron flux which activates any elements present. These are oxygen, nitrogen, noble gases, carbon dioxide and any impurities present including particulates.

The main radioactive constituent which is emitted to atmosphere is $\text{A}^{41}$ with a half life of 110 minutes and this is, of course, undiminished by the filters. A figure of 6 millicuries per second per reactor is typical. Activation isotopes of sodium, manganese and steel corrosion products which pass the filter are emitted and the normal full power values are a few tens of millicuries per year.

TABLE I. DATA ON SHIELD COOLING AIR DISCHARGES AT BERKELEY, BRADWELL AND HINKLEY POINT 'A'

<table>
<thead>
<tr>
<th>Station</th>
<th>Berkeley</th>
<th>Bradwell</th>
<th>Hinkley Point 'A'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of flow of Air per Reactor (cu.ft/minute)</td>
<td>100,800</td>
<td>216,000</td>
<td>212,000</td>
</tr>
<tr>
<td>Air Temperature of Filter</td>
<td>35°C</td>
<td>38°C</td>
<td>70°C</td>
</tr>
<tr>
<td>Filtration</td>
<td>Bonded glass fibre blanket, oil impregnated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Efficiency</td>
<td>99% at 10 (at 35°C)</td>
<td>97% at &gt; 10 at 38°C</td>
<td>84% at 2 - 10μ (at 70°C)</td>
</tr>
<tr>
<td>No. of Discharge Point (per Reactor)</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Height of discharge point above ground</td>
<td>52 metres</td>
<td>41 metres</td>
<td>54 metres</td>
</tr>
<tr>
<td>Millicuries per reactor per year</td>
<td>4</td>
<td>2</td>
<td>16</td>
</tr>
</tbody>
</table>
FIG. 3. Elevation of a gas cooled reactor.
It is worth noting that reactor produced fission products, if they are present at all are below the detection levels of 10 μc/day.

The method of estimating these discharges is to pass a sample taken from the stack through a filter paper and to count the radioactivity as total beta against a Cl\textsubscript{36} standard, first allowing a 72 hour decay period to eliminate the major radon and thoron and daughter products normally present in air.

In order to obtain a truly representative sample careful consideration is given to the positioning of the sample take-off point, flow kinetics and type of sample paper used. Since the levels measured by stack sampling are so low, it has not been considered necessary to devote much effort to analysis of the small quantities involved. One of the isotopes which has however received special attention is S\textsubscript{35} which is detected from time to time and some correlation with boiler leaks into the gas side exists. The probable source is an (n,p) reaction on Cl\textsubscript{35} and this may be released into the gas stream by the action of the moisture. Some of the S\textsubscript{35} is believed to exist as sulphur dioxide and ordinary glass fibre filter papers have a low efficiency for stopping this gas. The charcoal backed papers designed primarily for iodine sampling have an improved efficiency. If for instance the unwarranted assumption were made that all the emissions were I\textsubscript{131}, probably the most hazardous potential emission in a milk producing environment, it has been estimated that up to 20 millicuries per day could be released without exceeding the maximum levels in milk, currently recommended in the United Kingdom.

In the case of A\textsubscript{31}, the quantities discharged in terms of curies/second are measured during commissioning by direct means. Since the maximum permissible levels of exposure for this isotope are limited by whole body exposure the long term control is effected simply by means of integrated gamma dose measurements taken around the power station site. It should be remarked that there is also a dose contribution from the coolant in the gas ducts and boilers, particularly the top ducts. For routine monitoring no differentiation is made with respect to the
partition of dose from the various sources. In no case does the annual dose at the nearest inhabited location exceed 0.4 rem/year.

3. Gas Circuit

Although theoretically the carbon-dioxide coolant is totally contained within the pressure vessel and associated boilers, nevertheless there is a small leakage of about 0.1% per day on average which would be a potential source of effluent. There is also a small discharge made on a day to day basis by reason of:

(a) Fuelling machine and ancillary equipment operations.

(b) Controlled purging of the pressure circuit to relieve slight over-pressure and control levels of undesirable chemical contaminants.

(c) De-gassing of circulator seal oil to remove carbon dioxide absorbed from the circuit.

Occasionally it is necessary for operational reasons to empty a boiler or less frequently the whole system by blowing down through particulate filters from a stack which is sampled in the same way as for shield cooling air. In the full blowdown over 100 tons may be involved and the time taken is several hours.

The carbon dioxide as fed to the reactor has a rigid specific action with regard to impurities, but the yardstick for chemical purity is very different from that required when activation is to be considered. Of particular importance is $^{40}$Ar, which produces, as in the case of the shield cooling air, $^{41}$Ar in the coolant. $^{16}$N with a few seconds half life is produced by an (n,p) reaction on $^{16}$O.

Similarly, the graphite moderator, although of high purity by engineering standards, contains sufficient impurities to lead to measurable radioactive isotopes. For example, impurities of less than 0.5 p.p.m.

<table>
<thead>
<tr>
<th>TABLE II. BYPASS AND BLOWDOWN FILTER MEDIA AT CEGB MAGNOX STATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Station</strong></td>
</tr>
<tr>
<td>Bradwell</td>
</tr>
<tr>
<td>Hinkley Point 'A'</td>
</tr>
<tr>
<td>Sizewell</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Typical Filter Efficiencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclones</td>
</tr>
<tr>
<td>Ceramic Candles</td>
</tr>
<tr>
<td>Sintered Metals</td>
</tr>
<tr>
<td>Charcoal Bed</td>
</tr>
</tbody>
</table>
of lithium produce a few thousand curies of tritium per annum. A further source of radioactivity comes from the constructional materials within the reactor and almost any common metallic isotope has been found. The predominant species and quantities vary, as one would expect, from reactor to reactor.

Drier beds are used to control the moisture level in the coolant to a few parts per million. The drier material is usually activated alumina in pellet form. The liquors are collected in the process of periodic regeneration and about a litre a day is typical. The main radioactivity is tritium, which is discharged as a liquid into the station condenser cooling water outfall.

The particulate activity is controlled by continuous cycling through filters in the pressure circuit and sample take-off points are provided to enable a sample to be passed through a filter which is assayed for beta activity.

The leakage of about 1% per day of carbon dioxide is the sum of a number of unspecified smaller leaks and it cannot easily be shown what fraction is entrained in the shield cooling air. There is a possibility, therefore, that some radioactivity is released unfiltered from the gas circuit directly to atmosphere and a daily maximum figure is calculated and shown to be at most a few millicuries per reactor per year.

4. Emergency Conditions

An emergency might exist if there is gross cladding failure of the fuel, such as may be caused by overheating. The quantity of fission products passing into the coolant is clearly very variable and may be a few curies from a crack in a single fuel element to a few thousand curies from gross failures.

The faults causing the release fall into two categories:

Firstly and potentially the more serious is a fire following depressurisation. The normal operating conditions are such that there is less than a 1 in 100 chance of a single channel fire following a major containment rupture and a more remote chance of more than one channel being involved. The emission of fission products, if it did in fact take place, would be at the end of depressurisation and an extract fan with a capacity of five tons an hour can be brought into action; the extract line incorporates a particulate filter followed by a charcoal filter. Fresh carbon dioxide can be fed into the core to match the extract and minimise air entry until the system has cooled down.

Secondly, if a serious breach of a fuel element can occur in an intact pressure circuit, fission products will escape into the gas and be carried round the circuit which brings the material into contact with large areas of metal boiler tubes and graphite. For example there is over 1000 tons of core in a typical reactor. This acts as an effective absorbing mechanism and so called "plate out factors" as high as 1000 in half an hour for iodine have been demonstrated. In general it would not be good practice to blow down the circuit and hence reduce cooling until core temperatures had been substantially reduced to a safe level. During this period some leakage would occur. Blowdown, when carried out, is through high efficiency filters followed by impregnated charcoal beds and vented at high level in some cases through the shield cooling air exhaust stack. Calculations assuming the time of blowdown commence-
ment to be pessimised show that the maximum release expressed in curies of I\(^{131}\) should not exceed 16 curies which it should be noted is spread over several hours.

5. Legal Control

In the United Kingdom no radioactive waste may be disposed of unless an authorization by an appropriate Government Department has been granted.

In granting such an authorization the Minister may and usually does specify conditions governing the disposal.

In the case of airborne wastes the difficulty of relating measurements from known discharges and leakage to direct hazard has led to conditions being imposed to monitor the environment rather than the source. Gamma doses both dose rate and integrated are made round the station out to a few miles from the reactors. Special samplers are exposed at different distances and assayed by beta counting and gamma spectrometry. Where appropriate milk is collected and analysed.

6. Conclusions

Experience totalling over 120 reactor years of operation has shown that the gaseous radioactive effluents from gas cooled reactors with high integrity canned fuel elements are predictable and can be maintained at orders of magnitude below acceptable levels. It is not necessary to discharge through stacks significantly above the reactor buildings, nor to utilize extra high efficiency filters. Under foreseeable emergency conditions any emission of fission products will not, it is believed, be intolerable and resultant doses should be within those acceptable to competent authorities.

DISCUSSION

W.G. BELTER: In section 3 of the paper, you mention that tritium is the main radioactivity and that it is discharged as a liquid into the station condenser cooling water outfall. Could you indicate the average total quantity of tritium which is discharged by these power reactors each year, and state how this quantity relates to the permissible limits?

G.C. DALE: The permissible limits vary from station to station. A typical figure for discharge into the River Severn is 5000 Ci per annum. To date no station discharge has exceeded 3000 Ci per annum.

L. F. FRANZEN: Did I understand you to say that the activity of the shield cooling air was measured during the commissioning period only?

G.C. DALE: As far as \(^{41}\)Ar is concerned, that is the case. Particulate activity is measured continuously during operation.

M.D. THAXTER: Did your remarks in the last paragraph of the paper refer to your experience in the past or to your expectations for the future?

G.C. DALE: They refer to our past experiences, but these augur well for the future.

M.D. THAXTER: In speaking of 120 reactor years of successful operation I take it you mean, since the Windscale incident?

G.C. DALE: Yes, that is so.
PANEL DISCUSSION ON
ASPECTS OF THE CONTAMINATION OF THE AIR
BY RADIOACTIVE GASEOUS EMISSIONS
FROM THE GROWING NUCLEAR POWER INDUSTRY
SUGGESTIONS FOR ACTION BY THE IAEA
Members:

D.W. MOELLER (Chairman) United States of America
J. PRADEL France
W. JACOBI Federal Republic of Germany
K.T. THOMAS India
V. PRODI Italy
T. MURATA Japan
G.C. DALE United Kingdom
M. TOMŠIČ Yugoslavia
D.W. MOELLER (Chairman): The purpose of this Panel is to develop a list of suggestions for action by the IAEA in managing radioactive emissions from the nuclear power industry. It is intended that the Panel should cover all types of emissions resulting from the peaceful applications of nuclear power. This includes the nuclear reactor industry as well as the application of nuclear energy for major earth-moving projects, underground engineering and space exploration.

As most of you know, the International Atomic Energy Agency (IAEA) was established in 1957 as an autonomous intergovernmental organization under the aegis of the United Nations with the objective of seeking inter alia "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world". In the particular area of responsibilities concerned with contamination of the atmosphere by radioactivity, the Agency has developed a program oriented toward discussion, instruction, collection and dissemination of information. This program has comprised various symposia dealing wholly or partly with airborne radioactive wastes, panel meetings, international and regional training courses in waste management and a research co-ordination meeting on the treatment of aerosols and volatilization compounds in waste processing operations; in addition the Agency regularly collects and publishes abstracts of research studies and awards contracts for research on problems relating to the treatment of gaseous radioactive wastes. Finally a visiting seminar comprising several Agency experts has recently toured a number of Latin American countries, giving lectures and advising on general health physics topics, including environmental monitoring.

Airborne contamination is also covered of course in the Agency's more general programs, such as those for the award of fellowships and the provision of highly qualified experts to assist and advise on an ad hoc or longer-term basis. It will also naturally be covered in the International Nuclear Information Service (INIS) which the Agency is currently developing as an international store-house of information relating to nuclear science and technology.

Our purpose this afternoon will be to offer comments on further improving this work. In this regard, the Panel members have been asked to make suggestions for present work that might be altered or additional work that might be added, and to provide guidelines as to priorities on each of these programs since all of us recognize that the program, in the final analysis, is restricted by the amount of financial support available.

I will now call on the Panel members in turn.

J. PRADEL: One of the Agency's activities which we find particularly useful is its work in arranging symposia. In our view it would be desirable if Member States could make more use of the Agency's resources in this field. Would it not be possible for the skilled simultaneous interpreters on the Agency's staff, together with the necessary simultaneous interpretation equipment, to be made available, on terms that would have to be laid down, to countries which requested such services in order to arrange highly specialized meetings with limited participation, including even bilateral meetings?
There is another field in which it seems to me that the Agency could play a useful role: increasingly, we feel the need for arranging in-service training, and the common United States practice of the Sabbatical year, or other similar practices, will probably be adopted in the near future. It will therefore be necessary to arrange for exchanging personnel between laboratories in different countries. It seems to me that a solution to this immense problem might usefully be sought by the Agency.

Finally, I have noted a desire that our studies should extend to the general realm of atmospheric pollution. I am sure that most of the scientists gathered here are in favour of this suggestion and I propose that the Agency should use the different means in its power to remove the obstacles there may be to such extension in certain countries.

W. JACOBI: It must be emphasized in our discussions that the radiation effects resulting from the release of radioactive material in air do not only concern the country in which the emission takes place, but other countries also. From this it follows that international collaboration is required in this field. As this Symposium has revealed, there are a number of crucial points where the Agency should seek to exert an influence by promoting research, facilitating the exchange of information and assisting in the establishment of international safety standards. Some of these problems I will mention here, as I see them from my point of view.

First, the generation and behaviour of aerosols during a reactor accident. A lot of simulating experiments were done last year; however, it is my opinion that the experimental conditions should be adapted more to the real processes occurring during an accident. Only in this way can we get results which are transferable to the accident case. Moreover, an understanding of the phenomenological results is also needed. For this reason basic research on aerosols should be promoted by the Agency, quite apart from its importance for other air pollution problems.

Second, methods and regulations for in-place testing of filters. Although high-efficiency filters for aerosols are available, only the in-place testing of filters gives us that filter efficiency which we can insert into the hazard analysis.

Third, the release behaviour and filtration of iodine and its compounds. This problem was already discussed during the Symposium and further remarks are therefore unnecessary.

Fourth, filtration methods for noble fission gases. To the extent that the filtration problem for iodine is solved, the importance of noble gas release is increased. This problem will be of special interest for reactors in an environment with high population density as in Europe.

Fifth, estimation of the distribution of and hazard from tritium released during normal operation and in case of accidents from reactors or fuel processing plants. I think some work must be done here; in particular, practical methods for the measurement of tritium in the atmosphere and total biosphere must be worked out, and this should be encouraged by the Agency.

Sixth, establishment of values for the maximum acceptable activity release under normal reactor operation conditions. The ICRP has recommended maximum permissible concentrations of radionuclides in air, but these values concern the air inhaled by human beings. However, what we need is the maximum acceptable release rate and its time distribution, and the Agency should encourage any attempt to work out internationally accepted values in this respect.
Now, how can the Agency contribute to the solution of all these problems? We know and we regret that the budget of the Agency is too small to give financial support for all of these research projects. However, the Agency can draw up a catalogue of research projects which are of importance in this field and distribute this catalogue to the Governments of Member States with an indication of the urgency of these projects and the recommendation that competent laboratories be given the financial support they need to carry them out. Independent of this, the exchange of information should be continued in meetings organized by the Agency. In addition it is my opinion that informal panel meetings are especially fruitful. It should not be the task of these panels to come to decisions or to draw up a report, but simply to provide a forum for discussion. I hope the Agency will arrange more meetings of this character.

K. T. THOMAS: I should, if I may, like first to venture a general assessment of the problem, considering the great quantities of radioisotopes that are likely to be released in the future. Clearly, the agencies responsible for protecting the welfare and physical well-being of all will need to approach the problem with forethought and wisdom. The hazards associated with noble gases, particularly krypton-85 and radioiodine, which may lead to permanent pollution of the atmosphere, warrant special consideration. These radioisotopes are those most likely to be released in large amounts from reactors and processing plants during normal conditions as well as in the event of accidents, and so create a hazard to man.

The necessity of considering the international aspects of the pollution of the atmosphere by gaseous pollutants can be emphasized by estimating the total likely build-up in the atmosphere, considering the growth of nuclear power industry and the extent of the associated hazard. For one developed country alone it has been estimated that roughly 700 megacuries of $^{85}$Kr and 37 000 megacuries of $^{133}$Xe will be released to the atmosphere from the country's power reactors by 2000 A.D. It has also been shown that if $^{85}$Kr is allowed to accumulate at the above rate in the air surrounding the earth ($3.1 \times 10^8$ cubic metres at s.t.p.) to a height of ten miles, the background could increase by 4.2% or more (background assumed to be 0.015 mR/h).

This gives an indication of the magnitude of the problem and shows the necessity for a detailed assessment of its extent and for taking steps to devise ways and means to limit the release of activity to the atmosphere. The IAEA will be the appropriate co-ordinating body to make a realistic assessment of the problem, in association with WHO or WMO wherever necessary.

In view of the possible practical difficulties likely to be encountered in undertaking such a program of work, it may as a first stage be easier to evolve suitable procedures on a regional or national basis, especially where the concentration of nuclear facilities is relatively high. In this connection, a study of the work already done on similar lines in certain countries will provide useful guidance.

The problems associated with power reactors and reprocessing plants are of primary importance. Although considerable research and development work on the removal of gaseous radioisotopes from such sources has been reported, there is no slackening in the demand for improved and more dependable processing techniques and equipment for the effective control of air pollution, particularly with reference to $^{85}$Kr and $^{131}$I.
For $^{85}$K, unless practical solutions are found for its removal, "isolation and containment" will continue to be practised to allow it to decay before release, so as to prevent slow build-up of atmospheric background.

For the removal of radioactive iodine from the air-stream, many methods have been in use for a long time. However, as has been pointed out earlier at this Symposium, problems of methyl iodide, etc. still exist. Investigations have been made in various places as to the possibility of impregnating the charcoal with some specific type of chemicals so as to increase the efficiency for the removal of iodine and its compounds. In addition, methods for the effective confinement of iodine and its compounds by the use of dilute hydrazine spray have been reported, though continued efforts are needed in this direction.

Now if I may turn to suggestions for action by the IAEA, I would say in general that the activities of the IAEA in the last few years have been more oriented towards the treatment of solid and liquid radioactive wastes and have covered only the broader aspects regarding the treatment of airborne wastes. Now a stage has been reached where the possible future course of action should lay stress on the problem of gaseous emissions in more specific detail.

As regards meetings, I suggest that the next symposium should be on the environmental aspects of the release of airborne contaminants from the growing nuclear industry. The 1963 Panel was helpful in bringing out the general principles of air pollution control, but future panel and research co-ordination meetings should be more applied and practical in scope, relating directly to well-defined systems of gaseous waste treatment and disposal. Such meetings, if found necessary, should be confined to the problems of radioactive gases and vapours formed in nuclear reactors and fuel reprocessing plants and plants for treatment of high-level radioactive wastes. Special emphasis could be given to the problems of release of $^{85}$Kr and $^{131}$I.

On training, it is gratifying to note that the Agency has organized international and regional training courses on general waste management processes. However, future courses might well be on more specific topics in this field. To provide a good background for personnel associated with gaseous waste management, short-term courses on the air-cleaning aspects of nuclear industry will pave the way for better understanding and appreciation of this problem. For this purpose, if necessary, the services of experts engaged in actual operations may be made available.

Finally, as regards the research contract program, further work can be initiated, as required, in the field of low-temperature and membrane separation processes for inert gases, radiiodine filter testing and removal methods and the study of plating effects of radioactive gases on duct surfaces under various conditions. Some of that work could possibly be carried out by Member States on a cost-free basis.

V. PRODI: First of all, I wish to express my appreciation for what the Agency has done up to now, and is doing, as pointed out already. I am referring in particular to the organization of symposia, fellowship programs and abstracts of research studies. With this, the Agency pursues the goal set out in the Statute to facilitate the exchange of information between scientists engaged in this field. I think that this is extremely useful and should by all means be continued. In this regard, I think that co-ordination should be sought also among scientists interested in the same
field of research, but approaching it from different points of view. For instance, in the field of gas and aerosol behaviour closer contacts with meteorologists and atmospheric physicists in general might be very useful in saving time and effort. This could be arranged, for example, with the World Meteorological Organization.

Also, better co-ordination between the nuclear organizations of the Member States is necessary; the Agency has also pursued this goal by convening panels on the co-ordination of research on specific topics. An example of this is the Panel on Aerosol Behaviour, held in Vienna in July 1967. Nevertheless, it would be desirable that the time required for publication and dissemination be much reduced, otherwise the conclusions reached by the Panel may end up by being obsolete. For instance, participants at this Symposium might have profited if the working papers of the 1967 Panel could have been made available to them for this meeting.

I have also been asked to suggest that the Agency should define recommended maximum levels for discharge into the air, as has been done for discharge into the sea and continental waters; to this end, an ad hoc panel would be desirable.

T. MURATA: Nuclear power plants have the advantage of causing less air pollution than conventional power plants. However, it will be necessary to control the radioactive gases released from nuclear power plants since the number of such plants and their power level are increasing. This problem will become especially serious in a country with high population density, such as Japan. For this reason, various investigations concerned with the control of radioactive gaseous waste have been carried out. The main projects now in progress in Japan can be summarized as follows:

1. Behaviour of iodine in reactor containments
   (a) Formation and decomposition of methyl iodide in water-vapour phase
   (b) Formation of methyl iodide in fuel
   (c) The reaction of fissioning iodine with methane
   (d) Formation of methyl iodide on the surface of a reactor vessel
   (e) Reaction of iodine vapour to aerosols

2. Removal of iodine and its compounds
   (a) By water spray
   (b) By a charcoal filter

3. Removal of radioactive noble gases
   (a) By adsorption on charcoal at low temperature
   (b) By liquid absorption
   (c) By trapping as clathrates

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1 Nippon Atomic Industrial Group
2 Mitsubishi Atomic Power Industries, Inc.
3 Japan Atomic Energy Research Inst.
Most of these investigations have been partially or completely sponsored by the Atomic Energy Bureau in the Science and Technology Agency, which comes under the Prime Minister's Office.

For the future, it will become more important to promote the research program covering basic design and engineering development, so as to ensure smooth development of the nuclear energy industry.

These are the reasons why I should like to recommend that the IAEA convene symposia on airborne radioactive waste more frequently. Furthermore, I sincerely hope that the IAEA will award more research contracts on the subject - especially on the removal of radioactive rare gases in the off-gas system of the plant - and will also pay special attention to the problem of plutonium aerosols resulting from fast reactors.

G.C. DALE: From available information it seems operators of nuclear power installations are able to control the gaseous emissions so that the limits of radiation exposure to both employees and members of the general public recommended by the ICRP are not exceeded. So far as the United Kingdom is concerned this control is not unduly expensive in design or running costs and the administrative controls imposed by the Government are effective and clearly defined. No need is felt for further Codes of Practice at the present time.

In the international field the subject of krypton-85 is from time to time raised, particularly with regard to irradiated fuel processing plants, and whilst the present contribution of dose to the world population is very small, estimates for the future measured in decades predict that some control of release may be required. A relevant problem is the fate in the biosphere of gaseous releases of widely differing densities and solubilities such as tritium and krypton-85.

It is suggested that the IAEA should convene a research co-ordination meeting to find out what work is in progress; depending upon the conclusions, it should then sponsor research directed towards supplying additional information.

M. TOMŠIČ: My contribution to the discussion will be a suggestion for further work on the chemistry of the noble gases krypton and xenon and its implications for the problems of removal of these gases from radioactive gaseous wastes.

This problem is gaining in importance with the rapid growth of nuclear industry. A rough projection shows that by 1985 decisive measures will have to be taken for the retention of radioactive noble gases, particularly krypton. Krypton-85 has a relatively long half-life (10 years), and owing to its chemical inertness it remains in the atmosphere indefinitely; no deposition occurs. I should point out that the pollution with krypton has important international aspects due to its accumulation on the global scale. Locally the pollution is not and will not be critical. The International Atomic Energy Agency is particularly suited for instigation and support of research in the control of this radioactive pollutant.

The laboratory of Dr. Slivnik, who has presented a paper at this Symposium, has rare capabilities for fluorochemical research and has made some important contributions to the chemistry of noble gases. The recent developments in noble gas chemistry offer new possibilities for the treatment of radioactive wastes containing such gases.

Thus, krypton and xenon can be separated quantitatively. A solid xenon fluoride is obtained (di-, tetra- or hexa-). The short-lived xenon
may, after a sufficient cooling period, even be used commercially. The volume of the noble gas waste (now krypton only) that has to be stored is thus greatly reduced. This chemical reaction is quite well known and work could be started on scaling-up the equipment from the present laboratory size. Further simplification of krypton storage could be achieved by binding it into a solid compound. One stable compound of krypton has been discovered but its production is complicated and further research is needed.

In conclusion, I should point out that these chemical methods of noble gas treatment are complementary to the methods of concentration of noble gases which have been presented by Dr. Merriman and Dr. Rainey of Oak Ridge National Laboratory.

D.W. MOELLER (Chairman): On behalf of all participants I should like to thank the Panel members for their interesting contributions. Before calling for questions and suggestions from the floor, I would like myself to offer the following additional suggestions for action by the IAEA.

First as regards informational services, I believe that the IAEA should be given every encouragement in providing summaries of air-cleaning research and development under way within its member countries. As I mentioned previously, the Agency has recently established an International Nuclear Information System. If possible, I would urge that this activity be patterned along the lines of the Nuclear Safety Information Center located in Oak Ridge, Tennessee. This Center has proved very successful as a co-ordinator and digester of nuclear information in the United States. Examples of reports which it has published are:

1. A quarterly "Indexed Bibliography of Current Nuclear Safety Literature"
2. An annual and bi-annual "Compilation of National and International Nuclear Standards"
3. A quarterly technical progress review, "Nuclear Safety" (this journal will, for example, carry a summary of this Symposium)
4. Special reports such as:

The Center also prepares summaries of nuclear safety articles which are stored in a computer for retrieval and preparation of bibliographies for research workers. On the basis of benefits per unit funds expended, I believe it would be difficult to find any activity of greater interest and assistance to workers engaged in research on radioactive airborne wastes and I would recommend that this type of activity be given top priority within the IAEA program.

As a second area of interest, I believe the IAEA should be encouraged to provide international leadership in keeping abreast of airborne waste management problems associated with new developments in the applications of nuclear power. Such developments include:

A. **Peaceful applications of nuclear explosives**

   Nuclear explosives offer advantages in:

   (1) **Major land-moving projects**

   These include the excavation of harbours and canals, the cutting of highways and railway passes through mountains, the stripping of rock
layers from deep mineral deposits and the altering of watersheds for better
distribution of water resources. Specific examples of such applications
include the digging of a new, or improvement of the existing, canal in the
Central American isthmus between the Atlantic and Pacific Oceans; the
possible development of hydro-electric power in North Africa by cutting a
canal from the Mediterranean Sea to the Qatara Depression in Egypt or the
Chotts Depression in Tunisia; the excavation of harbours along the west
coast of Australia, Africa and South America; and the use of nuclear ex­
plosives to alter watersheds, interconnect aquifers and create under­
ground reservoirs.

In almost all these activities, the release of radioactive materials to
the atmosphere represents the primary public health consideration. Since
all these projects are essentially "one-time" events, it may be that there
is a need to develop new criteria for permissible releases to the environ­
ment. There is also a need to develop guidelines where the benefits to one
country might result in the release of potentially harmful radioactive
materials into another. This is particularly true where the releases are
of such a magnitude as to require countermeasures for the protection of
the population. Criteria for radionuclide releases and guidelines for
action in such situations might be developed through a co-operative program
involving the IAEA, the International Commission on Radiological Protection
and the World Meteorological Organization. The IAEA has touched upon
this subject in a broad sense in its recent Safety Series No.18, "Environ­
mental Monitoring in Emergency Situations" (1966);

(2) Underground Engineering

It has been proposed that nuclear explosives be used to increase the
flow of natural gas from "tight" underground rock formations. The "Gas­
buggy" experiment recently conducted in New Mexico is an example of this
type of application.

Such experiments will result in low-level contamination of the released
gas. For this reason, there is a need to establish permissible concen­
trations for radionuclide contaminants in such gas if it is destined for use
by the public. Here again, the necessary objective might be attained
through a co-operative program among several international agencies. The
removal of the contaminants might also represent a subject for air-cleaning
research.

B. Applications of nuclear power in space

Since space is "international", it is logical for the IAEA to play an
important role in establishing standards and offering guidance in the ap­
lications of nuclear power in this realm. Such applications include:

(1) Auxiliary power sources, including the use of radionuclide sources
to provide small amounts of power and small reactors to provide larger
amounts of power;

(2) Nuclear power for rocket propulsion. For interplanetary travel,
it has been estimated that nuclear power for propulsion is almost a neces­
sity. Consideration should be given to the air pollution problems associated
with both the application and testing of such systems;
(3) Nuclear powered airplanes. It is now feasible to build aircraft large enough to use a nuclear reactor as a power source. The air cleaning problems in this field need evaluation, especially with regard to accident planning.

C. Nuclear power

As this Symposium has indicated, there are still many air-cleaning problems remaining in the field of conventional nuclear power. There is a special need for reviewing and planning programs for the forthcoming liquid-metal-cooled fast power reactors. Many believe such reactors will represent much less of a problem in terms of airborne radionuclide releases. If so, this should be reviewed and the data made known throughout the world.

In past Symposia the IAEA has discussed air pollution problems in uranium mining and milling. Problems in this area are still not solved. If simple methods for the removal of radon and its daughter products could be found, then such techniques might be applied to the removal of naturally occurring radionuclides in air, especially in modern sealed air-conditioned buildings. Even in this era of nuclear power, natural background remains the major source of exposure to the population. If effective means for radon removal could be found, the lung dose to the population from natural background radioactive materials in air might be significantly reduced.

In the reactor power industry, there is still a need for new and simpler techniques for the removal of krypton-85 from gaseous effluents released by chemical processing plants. There is also a need for the development of emission standards for releases to the air. Although intake and dose standards constitute our basic goal, the engineering control of nuclear plants depends upon emission standards and these should be developed.

These, then, are some of the areas which the IAEA might consider in terms of its future programs. We will now open the discussion for questions and suggestions from the floor.

J. J. COHEN: Being associated with the Plowshare program for peaceful uses of nuclear explosives, it was gratifying to me to hear the Chairman’s remarks in this regard. Because of the potential for success of this program I also believe it would be of great benefit to investigate problems regarding release of radioactive materials from Plowshare projects. I have in mind specifically:

(1) Methods of measurement of quantities released under the conditions of specific Plowshare operations;
(2) Methods of minimizing quantities released;
(3) Establishment of standards for maximum tolerable releases. In this regard, we must be mindful of all other sources contributing to the biospheric burden.

W. SCHIKARSKI: It should be borne in mind that the systems and equipment used for reducing the airborne activity have to be completely reliable and available all the time. It is proposed that the Agency collect and distribute the reliability data which emerge from the various research programs and operational experience.

J. DADILLON: I should like to make two suggestions, one of which is fairly close in substance to that just made by Dr. Dale. Indeed each
country has experts engaged in a delicate task of analysis and synthesis which is probably the same everywhere but which does not always lead to the same results. I therefore agree with Dr. Dale that the Agency could co-ordinate this work by bringing together a small number of people concerned, after which it would be in a position to make as realistic proposals as possible to Member States concerning typical accidents and hypotheses in regard, for example, to the various factors contributing to a reduction in the contamination. Naturally this work would have to be repeated periodically in order to take into account the new results obtained.

This brings me to my second suggestion. I have often wondered why so-called experimental reactors never carried equipment enabling them to provide information on radiological safety. Admittedly such information can only be obtained, thanks, if that is the right term, to a radioactive incident or accident. However, even if such incidents and accidents have been very few in number, they have occurred and will occur again, the probability increasing as the number of reactors increases. I think it would therefore be desirable if the Agency could somehow or other encourage, as standard practice, the inclusion in all nuclear facilities of devices, distinct from the warning devices, which could in the event of an accident or an incident collect all relevant information with regard, for example, to the quantity of contamination emitted, its type, its diffusion through the circuits and the premises, its filtration, etc. This information could be centralized and disseminated by the Agency.

W.G. BELTER: I would like to make four points. First, the Agency should continue to publish Waste Management Abstracts, thereby providing the opportunity for research investigators to contact their counterparts in other countries to obtain up-to-date results on a regular basis.

Secondly, the time and effort which goes into the planning and conduct of panel meetings would in my view be better spent on providing technical advisory services to developing countries on specific waste management problems.

Thirdly, noble gas removal studies, such as have been suggested by some speakers, are being carried out in the United States on a scale commensurate with the importance of or need for this technology in the future.

Lastly, international symposia on air cleaning should be held once every five years. This would be more or less in accordance with the kind of time-schedule followed for other facets of the Agency waste management program.

L.F. FRANZEN: In the Agency's Safety Series there is a booklet (No. 17) dealing with environmental monitoring and safety requirements of air cleaning systems. In my opinion, the contents are to a certain degree outdated or else our knowledge has increased so far that a revised and enlarged edition should be issued. Are there specific plans to do so in the near future?

L.A. EMELITY (Scientific Secretary): I do not know of any specific plans for revising this booklet, which only appeared in 1966, but in general the publications in the Safety Series are regularly reviewed and revised as and when necessary, within the limits of the available resources.

D.W. MOELLER (Chairman): There being no additional comments from Panel members or participants, I will now attempt to present a summary of some of the highlights of what has been said.
First of all, it should be noted that all speakers have expressed appreciation for the many contributions of the International Atomic Energy Agency to the furtherance of the peaceful applications of nuclear energy. All of us have benefited from one or more of the Agency's activities and the Agency should be proud of the work it has accomplished. We endorse a continuation of these efforts. In terms of specific areas, the following points appear to be of special significance:

1. **Global aspects of airborne wastes**

   Panel members emphasized the international aspects of atmospheric pollution by radioactive materials and stressed that the International Atomic Energy Agency should do everything possible to make Member States aware of the global aspects of the problem. This is particularly true in regard to many of the airborne wastes discussed in this Symposium and potential future releases which may accompany applications of nuclear explosives in major land-moving projects and underground engineering and applications of nuclear power in space travel.

   In terms of the international aspects of airborne radioactive wastes, it was also suggested that the Agency assist in co-ordinating efforts of other international agencies which have a major interest in this problem and are in a position to offer helpful guidance and advice to Member States. Bodies specifically mentioned were the World Meteorological Organization (WMO), the International Commission on Radiological Protection (ICRP) and the World Health Organization (WHO). With regard to the ICRP, the need for internationally acceptable radioactive waste discharge limits was mentioned and it was suggested that a joint IAEA-ICRP program be undertaken to develop the necessary guidelines;

2. **Information distribution**

   The Agency was highly commended for the leadership it has shown in assisting in the interchange of technical information on the peaceful applications of nuclear energy among Member States. Its many excellent publications in this field were mentioned repeatedly and almost all Panel members commented favourably on one or more of the various symposia which the Agency has sponsored. Such symposia were highly endorsed by the Panel and maximum effort in continuing this work was encouraged.

   In this regard, it was suggested that consideration be given to making the specialized services of the Agency available for the sponsorship of specialized symposia on a regional basis. Where certain problems are of importance to only a few countries, their significance might be evaluated with a symposium involving only a few member countries. As secondary comments, the Agency was congratulated for recognizing the importance of keeping to a minimum the time-lag between the date of a symposium and appearance of the published proceedings, as well as the need to update its reports frequently so as to keep abreast of the latest developments;

3. **Research activities**

   One Panel member suggested that the IAEA consider convening a research co-ordination meeting to offer suggestions to Member States on
their research programs. It was also suggested that nuclear energy experts working on problems of airborne radioactive wastes recognize the fact that much of their knowledge can be directly applied to solving air pollution problems of a more general nature. With the increasing emphasis on air pollution by public health agencies, such assistance would undoubtedly be welcomed.

Several specific airborne radioactive waste problems were cited as deserving major research effort at the present time. These were the problems of radioactive iodine (arising both from reactor accidents and from the chemical processing of "spent" reactor fuels), the noble gases (particularly krypton), the release of tritium and, in certain cases, the release of aerosols of plutonium. New developments on krypton and xenon chemistry, by workers in Yugoslavia were reviewed by Mr. Tomšić and a more generalized review of research work in Japan was presented by Dr. Murata;

4. Evaluation of safety systems

Other speakers suggested that the Agency give attention to the need for better programs among Member States for testing the reliability of safety systems applied to the control of airborne releases from nuclear energy installations. This includes the work of developing programs for better quality control in the analysis of samples, developing models for guidance in accident evaluation and suggesting standardized approaches so that data obtained in different Member States would be comparable;

5. Training of personnel

Since it is universally recognized that nuclear energy personnel require refresher training at periodic intervals, it was suggested that the Agency not only continue its fellowship program but also give greater emphasis to the exchange of scientific personnel among Member States. Such exchanges might be an excellent means, for example, of finding suitable employment for university staff during periods of sabbatical leave.

In conclusion, then, we can say that the Panel endorses and commends the IAEA for its activities during the past decade and we hope that our comments this afternoon will be helpful in planning future activities on the problem of airborne radioactive wastes. I would again thank the Panel members for their comments and suggestions, as well as those participants who have attended and contributed to the discussions.
SYMPOSIUM ON
OPERATING AND DEVELOPMENTAL EXPERIENCE
IN THE TREATMENT OF
AIRBORNE RADIOACTIVE WASTES

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