Treatment and Storage of High-Level Radioactive Wastes
TREATMENT AND STORAGE OF HIGH-LEVEL RADIOACTIVE WASTES
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TREATMENT AND STORAGE OF HIGH-LEVEL RADIOACTIVE WASTES

PROCEEDINGS OF THE SYMPOSIUM ON TREATMENT AND STORAGE OF HIGH-LEVEL RADIOACTIVE WASTES HELD BY THE INTERNATIONAL ATOMIC ENERGY AGENCY IN VIENNA, 8 - 12 OCTOBER 1962

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A variety of radioactive materials having no immediate use result from the utilization of atomic energy. The manner in which these materials are handled has repercussions on reactor economy and technology, on the health and safety of persons and populations and on atomic legislation. Excellent progress has been made in developing a technology capable of safely and economically dealing with these materials so that no immediate problems exist.

The highly radioactive "wastes" arising from the reprocessing of irradiated fuel pose long-range problems, however, and methods for the ultimate disposal of these wastes must be developed and evaluated. Such development and evaluation can be materially assisted by providing the scientists doing the work with an opportunity of exchanging ideas and information on their experience. Therefore, the IAEA, as part of its programme of promoting nuclear technology, convened in Vienna from 8 - 12 October 1962 the Symposium on the Treatment and Storage of High-level Radioactive Wastes.

The Symposium was attended by 130 scientists from 19 countries and two international organizations. Thirty-three papers were presented and discussed in full and formed a background for a panel discussion of chairmen near the end of the Symposium. The papers and a record of the discussions are published in this single volume. It is hoped that the information thus recorded will achieve the desired purpose of assisting the peaceful development of atomic energy.

February 1963

SIGVARD EKLUND
Director General
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REVIEW OF PROBLEMS AND PRACTICES
PRESENT AND FUTURE PROGRAMMES IN THE TREATMENT AND ULTIMATE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTES IN THE UNITED STATES OF AMERICA

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UNITED STATES ATOMIC ENERGY COMMISSION, WASHINGTON, D. C.

Abstract — Résumé — Аннотация — Resumen

PRESENT AND FUTURE PROGRAMMES IN THE TREATMENT AND ULTIMATE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTES IN THE UNITED STATES OF AMERICA. The inherent restrictions of tank storage for high activity waste, such as potential leakage and the necessity of liquid-waste transfer for periods of hundreds of years, has resulted in a vigorous research and development programme in the United States directed at engineering practical systems for the ultimate disposal of these materials. The programme in the Atomic Energy Commission Reactor Development Division is described as it relates to the development of a future nuclear power economy. The long-range waste management programmes at the plutonium production centres, Hanford and Savannah River, with their particular site requirements, are briefly summarized.

Several "conversion to solids" methods, including the use of fluid beds, heated pots, radiant-heated spray columns, rotary kilns and ceramic sponges are under study. The addition of glass-forming materials to the waste for the purpose of providing a more stable final product is also being investigated. Some of the advantages and disadvantages of each process are noted. The present status of these development projects is summarized and the proposed future programme plans are stated.

The investigation of specific geologic formations such as salt structures, deep permeable basins, and impermeable crystalline rock for the ultimate storage or disposal of calcined solids or certain types of liquid wastes is described. Plans for a proposed field experiment in salt with full-scale activity are discussed. The exploratory drilling programme at the Savannah River Plant to determine the feasibility of storing aged, first-cycle wastes in the basement rock below SRP is briefly described and preliminary results noted.

Brief reference is made of the long-range engineering studies being conducted at Oak Ridge to evaluate the hazards and economics of various methods for handling, storage, and/or ultimate disposal of highly radioactive liquid and solid wastes. The role of this engineering evaluation programme in relation to future programme planning in waste management is discussed.
ploratoires que l’on exécute à Savannah River pour déterminer s’il est possible d’emmagasiner de vieux déchets du premier cycle dans le sol rocheux sous-jacent; il indique les résultats préliminaires obtenus.

L’auteur évoque les études techniques à long terme qui se poursuivent à Oak Ridge et qui ont pour objet d’évaluer les risques et les aspects économiques des diverses méthodes de manipulation, de stockage et d’élimination définitive de déchets liquides et solides hautement radioactifs. Il examine le rôle de ces évaluations techniques dans l’élaboration des futurs programmes de gestion des déchets.

TECNUAL Y BUDUAN PROGRAMAS OBRAS Y DE DISPLACIAMIENTO DE DESCHOS DE ELEVADA RADIACTIVIDAD

PROGRAMAS ESTADOUNIDENSES ACTUALES Y FUTUROS PARA EL TRATAMIENTO Y EVACUACIÓN DEFINITIVA DE DESECHOS DE ELEVADA RADIACTIVIDAD. Las desventajas inherentes al almacenamiento de desechos de elevada radiactividad en tanques, tales como el riesgo de escape y la perspectiva de tener que proceder durante tiempos muy largos al transporte de desechos líquidos han inducido a preparar en los Estados Unidos un programa intensivo de estudios y mejoras encaminado a establecer sistemas prácticos de evacuación definitiva de aquellos materiales. El autor describe el programa de la División de Desarrollo de reactores de la Comisión de Energía Atómica de dicho país en la medida en que se relaciona con la evolución futura de la energía nucleoeléctrica en sus aspectos económicos. Asimismo, presenta una síntesis de los programas a largo plazo para el tratamiento y la evacuación de los desechos radiactivos en los centros de producción de plutonio, en Hanford y Savannah River, señalando los requisitos impuestos por sus ubicaciones respectivas.

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THE TREATMENT OF HIGH-LEVEL RADIOACTIVE WASTES

INTRODUCTION

High-level liquid radioactive wastes have been generated for a number of years at United States Government installations such as the Hanford Works, the Savannah River Plant, and the National Reactor Testing Station. In the future, they will be generated at commercial fuel reprocessing plants associated with the developing US nuclear power industry. Such high-level wastes have been and will continue to be stored in tanks at the site of their origin, the reprocessing plant, for an interim storage period, to permit radioactive decay and artificial cooling.

An indication of the magnitude of the existing storage problem is noted by the fact that more than 75 million gallons of high-level radioactive solutions and slurges are presently being stored in nearly 200 underground tanks throughout the US Atomic Energy Commission complex. In addition to continued waste production at Government installations, and assuming that current aqueous chemical reprocessing methods are used, it has been estimated that the nuclear power industry will generate approximately 36 million gallons by 1980 and 300 million gallons by the year 2000 [1].

While it appears that interim storage can be accomplished economically in tanks of present-day design at sites having suitable geologic and hydrologic conditions, the inherent safety restrictions of this operation such as potential leakage and the necessity of liquid-waste transfer for periods of hundreds of years, has resulted in a vigorous research and development programme in the United States of America directed at engineering practical systems for ultimate disposal of these materials.

This paper summarizes the United States high-level waste management programme as it relates to the development of industrial chemical reprocessing and a future nuclear power economy; the research and development projects at the Hanford and Savannah River plutonium production centres and the long-range waste management programmes of these sites, which are an integral part of production operations and which utilize specific site conditions. The Reactor Development Division high-level waste-disposal programme has followed two general approaches, namely, (1) conversion of these wastes to a solid oxide form or fixation of the activity in an inert, non-leachable solid carrier, and (2) the direct disposal of these wastes into specific geologic formations, such as salt structures, impermeable crystalline rock, etc. (Fig. 1). During this meeting, representatives from United States Atomic Energy Commission installations at Oak Ridge National Laboratory, Hanford, National Reactor Testing Station, Brookhaven National Laboratory, and the Savannah River Plant discuss in detail the results of research and development work being conducted at their sites.
CALCINATION AND FIXATION

The calcination of high-level aqueous wastes to convert these materials to a stable solid form offers several important advantages in ultimate waste disposal, namely, a major reduction in waste volume and a general simplification of long-range waste management problems. Several "conversion-to-solids" methods are now under study and are briefly described in the following paragraphs. The work involving the addition of glass-forming materials to the waste for the purpose of providing a more stable final product is also summarized.

Fluidized-bed calcination

Calcination of aqueous waste to dry solids in a fluidized bed at 400° to 500° C is the most advanced technique at present in terms of engineering development. A hot demonstration plant facility of 60-gal/hr capacity has been installed at the National Reactor Testing Station, Idaho, which will allow initial demonstration and evaluation of the process with aqueous aluminium nitrate waste. The flow-sheet involves the injection of waste solution through spray nozzles into a fluidized bed wherein the water evaporates, the nitric acid decomposes to water and nitrogen oxide and the metallic nitrates decompose the corresponding metallic oxide [2]. Studies have been conducted in 6 and 12-in diam. electrically-heated beds and in a 24-in² NaK-heated bed. Although exploratory studies have demonstrated the feasibility of this process for stainless steel and zirconium fuel wastes, the ma-
The treatment of high-level radioactive wastes has been with aluminium-type fuel wastes. During the past 18 months, equipment acceptance tests and several cold runs have been conducted on the 48-in diam. Demonstration Waste Calcining Facility (DWCF) at the National Reactor Testing Station. Over 2000 hr of cumulative operating experience have been achieved during cold testing to date, resulting in significant improvements in process control and the development of operator proficiency. Several operational and certain equipment deficiencies have been encountered during these runs and are being corrected before "hot" operations can be started. Among the problems noted have been excessive solids carry-over in the calciner off-gas, feed-nozzle caking and erosion, dust leakage in the transport air blower system, and the formation of alpha alumina in the calciner product. All of these problems have been analysed for possible solutions, e.g. the use of boric acid in the feed solution has been studied as an inhibitor for alpha alumina formation. Satisfactory operation of the DWCF with either the alpha or amorphous form of product now appears possible [3]. The alpha form provides a higher density and requires much less atomizing air to achieve a stable particle size. However, the amorphous form provides a lower rate of solids elutriation from the bed and has a lower solubility rate in dilute acid solutions such as are used in the scrub system for off-gas clean-up. Results of cold testing runs are now being analysed to determine the preferable crystal-form of alumina. Several runs with tracer quantities of Na-24 are planned to provide a quantitative evaluation of the effectiveness of the off-gas clean-up facilities.

Pot-calcination process

Another calcination approach being investigated is the pot-calcination process being developed at ORNL. This process involves evaporation to dryness and calcination at temperatures of 700°-900° C of solids in a pot which would then serve as the final storage container [4]. After filling a pot with calcined solids, process lines are disconnected, permitting the pot to be removed from the furnace, sealed and shipped to a permanent storage site. Potential advantages of this system include its simplicity, its versatility in processing several waste types, minimal aerosol problems since the quantity of inert gases formed is low, and the use of a storage container in the process eliminates further packaging of the final product.

Approximately 25 runs have been completed with engineering scale equipment to obtain information required for the design of the Pot Calciner Pilot Plant at Hanford (Fig. 2). In these runs during the past year, the suitability of both a batch and continuous-type evaporator for use in the process was established [5]. Material and energy balance flow-sheets were completed for continuous and batch evaporation and calcination of Purex, TBP-25 and Darex-type wastes. Design and fabrication of hot-cell equipment for study of fission-product behaviour during evaporation and calcination of actual high-level waste has been completed and installation of a hot cell has been started. Design of the Pot Calciner demonstration facilities is now being completed at Hanford. Equipment procurement and cold mock-up testing
of the pot-calcination process will be conducted during the next 18 months, before installation and hot demonstration in the Fuels Recycle Pilot Plant, which is now under construction.

One of the major areas of investigation under study at ORNL during the past year has been the off-gas problems associated with pot calcination, i.e. physical entrainment of mixed waste solids and volatility of such waste components as ruthenium, sulphates, caesium and sodium. A major development has centred on the use of relatively small concentrations of phosphite and/or hyposphite for preventing volatilization of ruthenium from Purex, TBP-25 and Darex waste solutions during the evaporation period [6]. A series of glass products have been prepared with Purex and simulated aluminium waste by adding various combinations of phosphorous acid or sodium hypophosphite, lead oxide or sodium tetraborate and calcium or magnesium oxide (Figs. 3 and 4). Cold engineering work in these areas is scheduled for the coming year.
Radiant heat-spray calcination

Another calcination method which has shown considerable promise is the radiant heat-spray process which is being investigated at the Hanford Laboratories [7]. The process consists of feeding liquid wastes through a pneumatic nozzle into the top of a tower. The walls are heated to 850° C by
passing low voltage current through the entire column, with water droplets passing down the tower through successive zones of evaporation, drying and calcination. Separation of solids and gases has been effected by either filtration or cyclone separation. Laboratory runs have been conducted on a wide variety of wastes, including aluminium and stainless-steel-type wastes, as well as acidic and neutralized Purex waste (Figs. 5 and 6).

![Image of waste products]

Some of the potential advantages of the spray-calcination process are believed to be, (1) the operation is insensitive to changes in waste composition and is readily adaptable to many different types of feed, (2) remote operation and maintenance appear to be relatively simple when compared with
other proposed methods of calcination, (3) difficulties of foaming, low heat transfer through deposited solids, and widely varying flows through the associated gas clean-up system are minimal in comparison with batch processes, and (4) there appears to be less likelihood of hazardous reactions between HNO₃ and organic compounds, because of the short residence time and low hold-up period.

While laboratory investigations with simulated waste solutions have been encouraging, further development on an engineering scale is needed before the full capability of this process can be evaluated. Installation of a 1-gal/hr spray calciner unit in a high-level radiochemistry facility has been completed. During the coming year, engineering cold tests and hot-cell small-scale experiments with actual Purex plant wastes will be conducted to obtain further information on the process as a unit operation including off-gas treatment, fission-product behaviour, condensate and calcined waste characteristics.
Rotary ball-kiln calcination

Calcination in a rotary ball-kiln has been studied at Brookhaven National Laboratory as a means for the permanent disposal of waste from the reprocessing of aluminium and zirconium alloy fuels and in the reprocessing of fuels clad with stainless steel, or having stainless-steel matrixes. Basically, the unit consists of a slowly rotating horizontal tube or kiln externally heated by means of electric resistance heaters (Fig. 7). Feed is introduced into the kiln by means of a distribution nozzle and falls on a hot shallow bed of metal balls, which aid in heat transfer and prevent the formation of large agglomerates during calcination. The calcined solids overflow from the discharge end of the kiln into a powder receiver. The calciner is designed for continuous operation to give good transfer of heat to the interior of the kiln and to reduce problems of controlling radioactive dust to a minimum.

An engineering scale calciner (approximately 6 gal/hr of waste) has been constructed at BNL. Equipment and process development studies are scheduled for completion by early 1963. In addition to obtaining engineering process data, the development of a rotary gas seal and a satisfactory means of waste-feed injection, have been emphasized in recent studies. Results of these cold engineering studies will assist in determining whether the unit
will be installed with the pot-calcination facility under design and development for the Fuels Recycle Pilot Plan at Hanford.

Preparation of phosphate glasses

As briefly noted in the ORNL work on pot calcination, the formation of phosphate glasses as a means of incorporating fission products in stable, relatively non-leachable media, is of considerable interest in the over-all waste disposal development programme. During the past year at Brookhaven National Laboratory, a major emphasis has been placed on the development of a process in which the entire conversion from the raw aqueous waste to the final phosphate glass product would be carried out in an all-liquid system [9]. The process appears to be one of relative simplicity and readily lends itself to a continuous process in which the liquid media would be transferred by gravity flow from one process (temperature) step to another. Such problems as heat input to the system, removal of decomposition gases, and process materials handling are minimized in an all-liquid system. Laboratory studies have been conducted on the formation of Purex-phosphate glass and aluminium nitrate-phosphate glass at temperatures up to 1100°C (Fig. 8). Construction of an engineering pilot plant to investigate the feasibility of phosphate glass fixation on a continuous basis, has been completed. Engineering studies are being carried out to develop flow-sheet data and to determine corrosion effects on plant components.

Ceramic-sponge fixation

During the past two years, the Coors Porcelain Company and the Los Alamos Scientific Laboratory have participated in a joint study to investigate the absorption of liquid radioactive waste in ceramic sponges. The process involves the preparation of a highly porous clay body which is fired to approximately 1100°C [10]. This body is then soaked in the liquid waste, dried and re-soaked several times. It is finally fired at 1300°C to permanently fix the radionuclides in the ceramic material. Considerable laboratory work has been conducted by the Coors Company to develop an optimum ceramic sponge. Various three-component ceramic systems containing such raw materials as silica, feldspar, kaolin, clay, diatomaceous earth, nepheline syenite, talc and synthetic calcium silicate have been investigated. A 25-gal/d pilot plant has been installed at LASL and will be operated during the coming year with tracer quantities of radioactivity in simulated waste.

Figure 9 shows the soaking and drying section of the LASL ceramic sponge pilot plant. The ceramic sponges are first placed in a stainless-steel cage which is then lowered into the soaking and drying tank. Waste is pumped into the tank and held a sufficient length of time - approximately one-half hour - for the sponges to become saturated. The waste is then drained and the sponges are dried by means of a warm-air circulating stream. Upon completion of the drying cycle, liquid waste is again admitted to the tank and the cycle is repeated. Each drying and soaking cycle requires approximately three to four hours. After five soaking and drying cycles the spheres are removed from the tank and loaded into the tunnel kiln.
Figure 10 shows essentially the 45-ft long kiln and the control panels. The kiln has a useful firing cross-section of about 7 in X 9 in. The ceramic sponges are transported through the kiln on trays which are carried on a transfer car. Each tray holds about thirty-five 2-in sponges. The furnace is electrically heated and has a maximum operating temperature of 1600°C, with the unit operating at approximately 1300°C.

Off-gases from the kiln pass through a silica-gel bed and a condenser and finally through absolute filters; the silica-gel absorber beds are required since essentially all the ruthenium in the waste is volatilized during the firing step. The use of a reducing atmosphere and additives such as sugar and phosphate have been investigated in an effort to suppress the evolution of ruthenium. None of these approaches has been completely successful in retaining the ruthenium in the ceramic sponge. No difficulty has been
Soaking and drying facilities for Los Alamos scientific laboratory ceramic sponge pilot plant.

experienced to date with caesium volatility. Work is continuing on all phases of the project to develop higher sponge porosities and more nearly complete fixation and stability with various types of waste.

Calcination in molten sulphur

As a supporting function of plutonium production operations at the Savannah River Plant, the Savannah River Laboratory is developing a calcination process whereby aqueous wastes are fed into a vessel containing molten (150°C) sulphur so that the water and volatile acids are driven off and the chemical compounds, such as aluminium nitrate, are decomposed and/or chemically reduced [11]. The resulting sulphur-waste slurry is then heated at 400°C to 444°C for 1 to 5 hr, thereby driving off sulphuric acid and residual water and further calcining and/or reducing the chemical compounds in the sulphur-waste slurry. The slurry is then cooled to 115°C-120°C and transferred as a liquid to the final containment system where it is allowed to solidify. Molten sulphur serves as a liquid-heat transfer medium, substantially eliminates the entrainment of radioactive solids in gas streams and provides a reducing atmosphere which minimizes ruthenium volatilization.
Waste containing both stainless-steel nitrates and aluminium nitrate have been investigated in laboratory studies. These investigations have included tracer studies with caesium, strontium and ruthenium. Results of extensive leaching tests at room temperature (25°C) indicate that the products resulting from the sulphur calcination of both Al(NO₃)₃ and stainless-steel nitrate are very resistant to water leaching. Engineering scale-up studies are planned for the coming year.

DIRECT DISPOSAL

Preliminary evaluations by a committee in the Division of Earth Sciences of the United States National Academy of Sciences [12], and a sub-committee of the American Petroleum Institute [13] have indicated that the discharge of high-activity waste into selected geologic formations may be technically feasible. The types of formations recommended for investigation were: (1) salt domes or beds - space provided by mining or dissolution, (2) deep permeable formations (4000 to 15 000 feet) containing connate brine, and (3) excavation in impermeable formations.

Disposal in salt

A major portion of direct disposal development work accomplished to date in the United States has been studies on the possible disposal of li-
quid and/or solid high-activity wastes in salt structures. Salt was chosen because of unique geologic characteristics such as plasticity, dryness, imperviousness to water, good structural strength and thermal conductivity and its non-association with usable ground-water sources. Detailed laboratory and field studies have been conducted by ORNL on the structural aspects of salt in the presence of liquids, radiation, decay heat, chemical and radiochemical reactions between salt and waste mixtures and ion migration from the wastes into the salt formation. These studies, including field tests in actual salt mines (Fig. 11) have shown [14] that: (1) the thermal conductivity and diffusivity of impure rock salt in place are within 10 to 20% of the laboratory values for single-crystals; (2) elevating the temperature of 3000 gal of waste in a 7 1/2-ft square cavity to 65°C did not upset the structural stability of the mine room; (3) adsorption of the liquid-waste solution on to crushed salt appears to retard both cavity alteration and the production of radiolytic decomposition gases; and (4) radiation doses to be expected in an actual disposal operation do not appear great enough to significantly affect the structural stability of the room.

Initial studies have shown that gamma doses up to $1 \times 10^8$ r produce negligible changes in the compressive strength of rock salt [15]. A computer calculation of the gamma dose in salt from cylinders containing radioactive solid wastes stored in the floor of a salt mine indicated that the gamma dose would exceed $1 \times 10^8$ r only in areas close to the cylinder [16]. For example,
two-year-cooled, calcined, acidic Purex wastes contained in 6-in diam. cans and buried 7 ft below the floor of a 15-ft high, 50-ft wide, long room, have been considered. With an assumed can spacing of 5 ft, calculations have shown that the gamma dose of salt at the centre line between the cans, integrated over a period of $2 \times 10^6$ yr, would be only $3 \times 10^5$ rad. With an increase in the interim storage, from 2 to 14 yr, the dose would be reduced by approximately 50%.

Laboratory experiments have indicated that rock-salt samples from the Hutchinson Mine in Kansas shatter violently, with a subsequent release of steam, at temperatures between 250° and 300° C [17]. This occurs at about the same temperature regardless of the rate of heating and is apparently due to the water trapped in negative crystals. Additional tests are being run in the Hutchinson Mine to determine the effects of temperature above 250° C on the thermal and physical properties of salt. A simulated array, consisting of a large cylindrical heat source surrounded by six rod-type heaters, is being operated in the mine floor to obtain thermal data for comparison with computer calculations. The effect on the structural stability and plastic flow of the salt around the cans and in the walls of a mine room due to elevated temperatures will be determined.

Ultimate storage in deep bed-rock

The Savannah River Plant in South Carolina reprocesses spent fuel and has a relatively large inventory of high-level radioactive liquid wastes. It has been estimated that a total storage requirement of approximately 40 million gallons may be needed by 1975. Underlying the plant site, at a depth of approximately 1000 ft, is dense, crystalline bed-rock. A concept has been developed wherein it may be feasible to store aged high-level waste in tunnels mined out of the basement rock [18]. Though the economics of this approach appear attractive, the safety of the concept remains to be determined. Therefore, an intense investigative programme has been initiated to develop the basic information needed to make a rational safety analysis. Both the hydraulic and physical characteristics of the basement rock and the overlying aquifer are being determined, in addition to the compatibility of the rock with the waste to be stored.

A series of seven holes have been drilled 1000 ft into the basement rock in an area encompassing approximately 3 square miles. In the first four holes continuous core samples were taken. The last three holes were cored for the bottom 600 ft only. Core samples have been tested for various physical characteristics such as compressive strength, modulus of elasticity, density, permeability, thermal conductivity, specific heat and thermal coefficient of expansion.

The chemical tests involved the determination of the rate of attack on the rock of various types of simulated and actual wastes contemplated as being stored in the bed-rock tunnels.

The hydrologic portion of the investigation includes drill stem tests to determine bottom hole pressures, swabbing of the finished hole, pumping tests of packed sections of the hole and piezometer installation to the several main aquifers which overlie the bed-rock. This coupled with borehole
geophysical data is required to evaluate the hydrologic parameters governing the safety aspects of this concept.

Results to date indicate that the waste can be made compatible with the rock either before disposal, or by self-neutralization by allowing the waste to consume a small volume of the rock tunnel wall.

The physical tests on the core samples indicated that effects on these characteristics will have a negligible effect on the concept. The swabbing tests indicated the presence of connate water in the rock. Future tests will be made to determine the age of this water to see if any hydraulic connection with the overlying aquifer is of any significance.

A preliminary economic study utilizing an ultimate storage of 20 and 40 million gallons, indicated costs of approximately 58 and 37 cents/gal, respectively, for the tunnel concept only. If the cost of interim storage, pretreatment, etc. are added, the resulting cost compares favourably to the current method of tank storage and has the added advantage of reducing the perpetual monitoring requirements of tank storage.

Other research and development work in direct disposal includes:
(1) the injection of waste-cement slurry mixtures into shale formations by hydraulic fracturing, a technique utilized by the petroleum industry, and
(2) the injection of liquid wastes into deep permeable formations, as suggested by a committee of the American Petroleum Institute. The present objective of these studies is to determine the feasibility of these approaches for potential application to low and intermediate level waste, and therefore are not considered at the present time as part of the high-level waste-disposal development programme.

It is noted that the Hanford production site has been safely storing high-level chemical-reprocessing wastes as alkaline slurries in underground tanks during the past 17 yr [19]. This operation has been regarded as an interim measure only. As part of a long-range waste management programme, Hanford is actively investigating the recovery of certain fission products for beneficial use followed by in-tank immobilization of the remaining residue. In this programme, large volumes of essentially non-heating wastes (coating wastes, BiPO₄ wastes and some aged Redox supernates) would be evaporated to salt cakes by submerged combustion in the storage tanks. The smaller volume self-heating wastes would be fractionized to permit the storage of long-lived heat emitters in small volume, high-integrity containers. Included in this long-range programme would be the separation, purification and packaging of fission products such as strontium, caesium, cerium, promethium, and other radioisotopes for storage and utilization on market demand. The choice of chemical processing operations to be used for isotope removal is being investigated. Present plans call for an integrated fission-product-recovery waste management complex to be in operation by 1966.

WASTE MANAGEMENT ENGINEERING AND SAFETY EVALUATION STUDY

During the past two years a group at the Oak Ridge National Laboratory, composed of engineers from the Chemical Technology and Health Physics
Divisions, has been conducting detailed engineering, economic and safety evaluation studies to aid the Atomic Energy Commission in its future waste management programme planning. In this study, the objective is to evaluate the economics and hazards associated with the treatment of high-level radioactive wastes and their storage in ultimate disposal sites. A number of preliminary handling operations and final disposal methods are being studied in order to determine the optimum combination. Conceptual designs of ultimate storage methods are then prepared for cost estimation purposes for consideration in the development programme.

A hypothetical 6-t/d chemical reprocessing plant has been chosen as a basis for the study; it is estimated that this plant could process all the fuel from a 15 000-MWe nuclear economy, which might represent the entire United States in the 1970's. It is further estimated that this plant would handle 1500t/yr of uranium-converter fuel at a burn-up of 10 000 MWd/t, and 270 t/yr of thorium-converter fuel at a burn-up of 20 000 MWd/t.

The preliminary handling operations which are being evaluated include: (1) interim liquid storage; (2) pot calcination; (3) interim solids storage; (4) shipment of wastes as liquids or as calcined solids; (5) removal of significant fission products. It is planned to evaluate the following ultimate storage methods: (1) pot-calcined solids in salt deposits; (2) pot-calcined solids in surface vaults; (3) pot-calcined solids in deep vertical shafts; (4) liquids in salt deposits; (5) liquids by hydrofracturing; and (6) liquids in tanks.

It is noted that the effects of fission product recovery on waste disposal economics will also be assessed. The removal of long-lived heat-producing isotopes may reduce the cost of waste disposal, although this gain may be off-set by increased liquid and solid bulk of the wastes and by the addition of chemicals which interfere with calcination.

Preliminary cost studies of interim liquid storage, conversion to solids by pot calcination and shipping have been completed. Data from these studies and tentative costs for ultimate disposal of calcined solids in salt deposits are reported in these proceedings [20].

Following the engineering and economic studies, it is planned to carry out a detailed safety evaluation to consider the consequences of: (1) maximum credible accidents, (2) smaller but more probable incidents, and (3) routine fission-product releases associated with each preliminary handling operation and each ultimate disposal method. A particular site will be chosen in order that calculations of dispersion and dilution in the geologic, hydrologic and meteorologic environments and evaluation of the consequences can be made in terms of the natural and man-made conditions which exist at the site. Consequences of accidents, incidents and routine releases will be evaluated on the basis of fission-product accumulation and movement in the atmosphere, in surface water, in ground water, in the ground, and in simple, direct food-chains in relation to recommended permissible exposures to the population at large. An effort will also be made to express the hazards in terms of preventive and/or indemnity costs.
CONCLUSIONS

The economy of nuclear power depends in part on developing safe and economic methods for the disposal of the industry's waste. A comprehensive radioactive waste management development programme is being conducted in the United States in order to achieve this objective. In the high-level waste treatment and disposal programme, it is hoped that "conversion to solids" processes and ultimate disposal methods can be demonstrated and tested in the field with actual high-activity waste by the time industrial chemical reprocessing becomes a reality. Present indications are that this significant step in the development of the United States nuclear energy industry will occur in the 1965-66 period.

The fraction of nuclear power costs allowable for waste disposal has not been established and, because of the preliminary status of the development programme summarized above, no realistic cost estimate for the ultimate disposal methods is available at this time. However, the cost of storing wastes in tanks of present design on a "perpetual care" basis has been estimated to lie between 0.1 and 0.15 mil/kWh of nuclear electricity produced [21]. This cost approximates only 1 - 2% of the cost of nuclear power in an 8 - 10 mil/kWh economy. The ORNL engineering and economic studies indicate that the total cost of interim liquid storage, pot calcination, and shipping over a 3,000-mile round trip can be as low as 0.02 mil/kWh(e) [22]. Tentative costs for a large-scale disposal operation for calcined solids in salt deposits are estimated at 0.01 mil/kWh(e) [23]. Based on past laboratory and engineering scale cold-unit operation data, and on an expected successful field demonstration and testing programme with high-activity wastes, it is firmly believed that waste management operations should not constitute a major obstacle to the development of economical nuclear power.

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CURRENT PRACTICE IN THE MANAGEMENT OF HIGH-LEVEL RADIOACTIVE WASTES IN THE UNITED STATES OF AMERICA

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Abstract — Résumé — Аннотация — Resumen

CURRENT PRACTICE IN THE MANAGEMENT OF HIGH-LEVEL RADIOACTIVE WASTES IN THE UNITED STATES OF AMERICA. The need for assured containment of radioactive fission products and transuranic elements was met initially by constructing large underground tanks. This simple approach is still being used to-day, with more than seventy million gallons of radioactive solutions being stored in nearly 200 underground tanks throughout the USAEC complex.

A wide variety of tank designs has been used. This variety results from variations in the volumes and compositions of the wastes to be stored, in the environmental conditions of the different storage sites, and in engineering judgement factors. In each case, the particular tank design reflects a balanced judgement in which operational safety, long-term integrity, and cost are controlling factors.

The capital cost of the waste storage facilities in use ranges from $0.47 to $2.66 per gallon. The costs of surveillance, waste processing or transfer, and replacement facilities must also be included in the estimation of long-term costs. It is concluded that the available data are not yet sufficient to make accurate predictions.

At Hanford, reinforced concrete tanks, lined with carbon steel, are used to store radioactive solutions. Of 145 such tanks placed in service at various times since 1945, four developed leaks after 8-12 yr of storing non-heating wastes. In each case, the tanks' contents were pumped to another vessel. While radioactivity was detected in the ground surrounding the failed vessels, no radioactivity reached the ground water. A fifth tank was withdrawn from service when a distortion of the carbon steel liner was observed.

At Savannah River, carbon steel vessels are constructed within concrete vaults. Four of fourteen such tanks developed small cracks in the side walls as a result of stress corrosion in the weld-affected areas. The small volume of waste which seeped through the cracks was caught in the vault and returned to the vessels. The seepage has now stopped and the vessels are still in use.

At Idaho Falls, stainless steel tanks are constructed within concrete vaults. No operational problems or tank failures have been encountered.

While the current practice of storing radioactive solutions has been completely successful in preventing significant amounts of radioactivity from escaping to the environment, the feeling persists that a better way at reasonable cost should be found to assure the long-term containment of radioactive materials.
après stockage, pendant 8 à 12 ans, de déchets ne dégageant pas de chaleur. A chaque fois, on a pompé le contenu de réservoir pour le stocker dans un autre. On a constaté une radioactivité dans le terrain entourant les réservoirs défectueux, mais cette radioactivité n’a pas atteint l’eau outremer. Un cinquième réservoir a été mis hors service parce qu’on a constaté une déformation du revêtement d’acier.

A Savannah River, on a construit des citernes d’acier ordinaire dans des caves en béton. Quatre de ces citernes ont présenté de petites fissures latérales à la suite d’une corrosion dans les zones à soudières. La faible quantité de déchets qui avait suinté à travers les fissures a été récupérée dans la cave et remise dans les citernes. Le suintage a maintenant cessé et les réservoirs sont toujours en usage.

A Idaho Falls, ce sont des citernes d’acier inoxydable construites dans des caves en béton. Leur utilisation n’est heurtée à aucun problème et on n’a pas constaté de défaillance des récipients.

Ainsi, la méthode courante de stockage des solutions radioactives donne des résultats excellents puisqu’elle empêche que des quantités appréciables de radioactivité ne s’échappent dans le milieu ambiant; mais on continue à penser qu’on pourrait trouver un meilleur procédé d’un coût raisonnable pour assurer le stockage de longue durée des matières radioactives.

MÉTODOS CORRIENTES DE TRATAMIENTO Y EVACUACIÓN DE DESECHOS DE ELEVADA ACTIVIDAD APLICADOS EN LOS ESTADOS UNIDOS DE AMÉRICA. En un principio, se atendió a la necesidad de confinar en lugar seguro los productos de fisión y elementos transuránicos radioactivos construyendo grandes depósitos subterráneos. Este sencillo procedimiento sigue aplicándose en la actualidad, habiéndose acumulado más de 70 millones de galones de soluciones radioactivas en unos 200 depósitos subterráneos pertenecientes a la Comisión de Energía Atómica de los Estados Unidos.

Se utilizan depósitos de muy diferentes tipos. Esta variedad es consecuencia de la diversidad de las cantidades y composiciones de los desechos que han de almacenarse, de las condiciones ambientales de los diferentes lugares de almacenamiento y de los criterios técnicos aplicados. Los diversos tipos de depósito
representan en cada caso una solución equilibrada cuyos factores determinantes son la seguridad de funcionamiento, la duración y el costo.

Los gastos de inversión unitarios correspondientes a los dispositivos de almacenamiento de desechos actualmente utilizados oscilan entre 0,47 y 2,66 dólares/gal. También han de incluirse en el cálculo de los gastos a largo plazo los correspondientes a vigilancia, tratamiento o transvase de desechos e instalaciones de reemplazo. Los autores llegan a la conclusión de que los datos disponibles no permiten por ahora formular predicciones precisas.

En Hanford se utilizan depósitos de hormigón armado, con revestimiento de acero al carbono, para almacenar soluciones radiactivas. En cuatro de los 145 depósitos puestos en servicio desde 1945, se produjeron escapes después de contener durante períodos de 8 a 12 años desechos que no generan calor. En cada caso, el contenido de los depósitos se transvasó por medio de bombas a otro recipiente. Si bien se detectó radiactividad en el terreno circundante de los depósitos defectuosos, la radiactividad no pasó a las aguas subterráneas. Otro depósito fue retirado del servicio al observarse una deformación de su revestimiento de acero al carbono.

En Savannah River, se construyen recipientes de acero al carbono alojados en bóvedas de hormigón. En cuatro de estos depósitos, de un total de 14, se han formado pequeñas grietas en las paredes laterales a consecuencia de corrosión con tensión en las zonas afectadas por la soldadura. La pequeña cantidad de desechos que escapó por las grietas se recogió en la bóveda y se volvió a introducir en los depósitos. En la actualidad ha cesado el escape y los recipientes siguen utilizándose.

En Idaho Falls, se están construyendo depósitos de acero inoxidable alojados en bóveda de hormigón. No se han planteado problemas ni se han observado defectos en los depósitos.

Si bien los métodos actuales de almacenamiento de soluciones radiactivas son enteramente eficaces para impedir el escape de cantidades importantes de radiactividad al medio ambiente, persiste la creencia de que debería hallarse un procedimiento más adecuado para lograr a un costo razonable el confinamiento a largo plazo de los desechos radiactivos.

INTRODUCTION

Concurrent with the initiation of production-scale splitting of the atom in 1944, industrial management was faced with a new problem - the assured containment of radioactive fission products and transuranic elements. The need for containment has been reviewed extensively, and will not be reviewed in detail here. Perhaps a single example is sufficient to recall the crux of the problem. Consider only the strontium-90 contained in a ton of low enrichment uranium fuel used to produce 10 000 MWe of thermal power. About 1000 yr would be required for this material to decay to innocuous levels, or 80 cubic miles of water would be required to dilute this material to a concentration safe for human consumption.

The need for containment of process wastes was met initially by constructing large tanks several feet below ground. This simple approach is still being used today, with more than 70 million gallons of radioactive solutions and sludges being stored in nearly 200 underground tanks throughout the USAEAC complex.

The purpose of this paper is to review the pertinent features of current waste-storage practices, and to present this information in a form useful to management and engineering personnel.

CHARACTERISTICS OF WASTES

Of the many factors that influence the design and operation of facilities for high-level waste containment, the radiochemical and chemical composition of wastes are of primary importance. Radiochemical composition estab-
lishes the base for hazards control and heat-dissipation requirements. Chemical composition directly influences corrosion rates and imposes the principal limitation on the volume reductions that can safely be achieved.

For storage purposes, high-level wastes are segregated into two categories, depending on relative fission-product content. In the most active wastes, enough heat is generated by radioactive decay of fission products to heat the liquid to boiling and special provisions must be made to dissipate this heat safely. For purposes of this discussion, these wastes will be designated as "self-heating" wastes. The less active wastes, which nevertheless contain enough radioactive materials to require storage, will be designated "non-heating" wastes. The point of demarcation between "self-heating" and "non-heating" wastes in Hanford-type tanks is about 0.1 to 0.5 BTU/hr-gal of waste.

More than 99% of the fission products in the fuel being reprocessed are contained in the self-heating wastes. In a typical high-level waste the rate of heat generation will decrease by a factor of about ten as the waste ages from 0.5 to 10 yr from time of reactor discharge. At 10 yr, most of the heat comes from the decay of Sr\(^{90}\) and Cs\(^{137}\), which have half-lives of 28 and 30 yr, respectively. For estimating waste-storage requirements, therefore, the heat generation from the decay of Sr\(^{90}\) and Cs\(^{137}\) may be considered to be a practical terminal condition. Each of the isotopes contributes about half of the "terminal" heat-generation rate. In alkaline systems containing iron, the strontium is almost entirely in the insoluble fraction, while the caesium is concentrated in the supernatant solution. Because of these factors, the supernatant solutions from aged wastes are frequently "non-heating". Hanford routinely transfers aged Redox waste solutions to non-heating storages and Savannah River plans to treat aged Purex wastes similarly.

Significant characteristics of several high-level wastes produced at the major USAEC processing sites are listed in Table I. The wastes shown for Hanford (Richland, Washington) and Savannah River (Aiken, South Carolina) arise from the processing of aluminium clad, natural uranium fuels. The Idaho Chemical Processing Plant (Idaho Falls, Idaho) processes a variety of fuels; the principal wastes originating from the processing of fully-enriched uranium alloyed with aluminium or zirconium were selected as most typical for this plant.

Section A of Table I lists the approximate chemical composition of the various wastes under consideration. The major constituents of the self-heating wastes are the concentrated solvent extraction raffinates and head-end precipitates (Savannah River only). Self-heating waste at the Idaho Chemical Processing Plant is limited to the first-cycle raffinates. Decladding solution is the main constituent of non-heating wastes currently being generated at Savannah River and Hanford, although several other low-activity streams are also included at Savannah River. At Idaho Falls, raffinates from the second and third solvent extraction cycles are the main constituents of non-heating waste. Certain other process wastes are also included in this category; since these wastes are quite variable in volume and character, they have not been included in the listing.

Section B of Table I lists the volumes at which the various wastes are stored. As produced in the solvent extraction operations, most high-level
TABLE I

APPROXIMATE COMPOSITION
OF TYPICAL HIGH-LEVEL WASTES AS STORED

<table>
<thead>
<tr>
<th>Purex</th>
<th>SRP</th>
<th>ICPP</th>
<th>HAPO</th>
<th>SRP</th>
<th>ICPP</th>
<th>Decladding waste</th>
<th>&quot;Low-Level&quot; waste</th>
<th>2nd &amp; 3rd cycle</th>
</tr>
</thead>
</table>

A. Chemical components, moles per liter

<table>
<thead>
<tr>
<th>H</th>
<th>Na, K</th>
<th>Fe, Ni, Cr</th>
<th>Hg</th>
<th>NH₄⁺</th>
<th>Al</th>
<th>Mn</th>
<th>Zr</th>
<th>NO₃⁻, NO₂⁻</th>
<th>HSO₄</th>
<th>CO₃²⁻</th>
<th>OH⁻</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>8.0</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>3.7</td>
<td>1.0</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.9</td>
<td>10.3</td>
<td>0.2</td>
<td>0.9</td>
<td>-</td>
<td>1.8</td>
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<tr>
<td>(+0.2)</td>
<td>(+0.2)</td>
<td>-</td>
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<td>2.2</td>
<td>-</td>
<td>-</td>
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</table>

B. Volume in storage

<table>
<thead>
<tr>
<th>Gal/t U²³⁵</th>
<th>Gal/kg U²³⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>140</td>
</tr>
<tr>
<td>-</td>
<td>690</td>
</tr>
<tr>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>135</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>6</td>
</tr>
</tbody>
</table>

Wastes are too dilute for economic storage and are concentrated before removing from the process building. Condensates are discharged to the environment; re-evaporation of condensates is sometimes required to produce waste water suitable for ground disposal. Generally, the in-plant waste concentration limit is determined by the solubility of the bulk salts and the need to insure a free-flowing solution or slurry for material transfer and heat dissipation. At Hanford the self-heating wastes are also permitted to self-concentrate in storage.

STORAGE FACILITIES

A wide variety of tank designs has been used to contain radioactive wastes. This variety results from variations in volumes and compositions...
of wastes to be stored, in environmental conditions surrounding the storage sites and in engineering judgment factors. In each case, the particular tank design reflects a balanced judgment in which operational safety, long-term integrity and cost are the controlling factors. The choice between acid and alkaline storage systems is based on the volume increase from neutralization and the unit cost of storage space as determined by materials of construction and containment-features required by the environment.

Most of the tanks used for the storage of radioactive process wastes range in size from 300,000 to 1,330,000 gal capacity; they are 50 to 85 ft in diam., and have a useable depth ranging from 18 to 32.5 ft. In addition, about 20 tanks range from 30,000 to 50,000 gal in size. These smaller tanks have no unique features and will not be discussed further. The tanks are generally covered with 7 to 10 ft of earth which serves as a radiation shield. Since tanks were constructed at various times during the last seventeen years, the construction costs are not directly comparable. For convenience, all cost data have been adjusted to 1962 prices.

The type of tank used at Hanford for the storage of self-heating wastes is shown in Fig. 1. This is a reinforced concrete tank lined with carbon steel to above the liquid level. The dome is not lined. The tank has an inside diameter of 75 ft. With a liquid depth of 32.5 ft, it has a capacity of 1,000,000 gal. Agitation is provided by four airlift circulators, 24 in diam., and 10 to 14 ft tall. Vapours from the boiling liquid pass through a header to a shell-and-tube type surface condenser which is vented through a fibrous glass filter to the atmosphere. The condensate is collected in a pump tank and returned to the tank or discarded to the environment as a low-level waste. De-entrainment factors of about $10^6$ are realized as measured by the ratio of caesium concentration in the self-boiling wastes to that in the condensate. The construction cost for one of these tanks, excluding the vapour-handling system, is about $575,000. The condenser-condensate...
MANAGEMENT OF HIGH-LEVEL WASTES

handling system for a six-tank farm cost $950,000. Leak detection is provided by a series of vertical dry-wells in which radiation instruments can be used to detect the presence of radioactive materials in the soil. In addition, three horizontal laterals are being installed under each of these tanks, together with additional vertical wells. This system will add about $30,000 to the cost of each tank. The cost of each tank is then estimated at $765,000, including a proportionate share of the leak-detection and condenser-condensate handling systems.

The type of tank used for storing self-heating wastes at Savannah River is shown in Fig. 2. This is a completely enclosed, carbon steel tank. Each tank is contained within an individual concrete vault. The bottom portion of each vault is lined with carbon steel to provide a saucer beneath the primary tank. The saucer and annular space surrounding the tank provide a very sensitive means of leak detection and permit the retention and return of any liquid that escapes the tank. Heat is dissipated to cooling water circulated through independent vertical and horizontal cooling-pipe systems. A condenser is provided as a back-up for the cooling coils and the entire unit is vented through a fibrous glass filter. The tank has an inside diam. of 85 ft. With a liquid depth of 27 ft, it has a capacity of 1,070,000 gal. The construction cost of each of these tanks is about $1,500,000. Since these tanks were constructed, additional data, to be discussed later, indicates that subsequent steel tanks of this design should be heat-treated before use. Preliminary estimates indicate that heat treatment would increase the cost by about 20%, to about $1,800,000.

The type of tank used at Idaho Falls for the storage of self-heating wastes is shown in Fig. 3. This is a free-standing, completely enclosed, stainless-steel tank, contained in a concrete vault. Each vault may contain from one to four tanks, providing a very sensitive means of leak detection. Heat is dissipated to cooling water circulated through the horizontal and
vertical stainless-steel pipe systems. A back-up condenser and fibrous glass filter are also provided. This tank has an inside diam. of 50 ft. With a liquid depth of 21 ft, it has a capacity of 300,000 gal. The construction cost of one of these tanks is about $800,000.

A typical tank for the storage of non-heating waste at Hanford is shown in Fig. 4. This is a 75-ft diam. concrete tank with the bottom and sides lined with carbon steel. The dome is not lined. The tank is vented to the
atmosphere through an air-cooled reflux condenser. With a liquid depth of 18 ft it has a capacity of 533,000 gal. Tanks of this type have been in use at Hanford since 1945. The construction cost of a tank of this type is about $475,000. Tanks of a similar design are also used at Savannah River for the storage of concentrated non-heating wastes; these tanks are 85 ft in diam., hold about 1,330,000 gal, and cost about $630,000 each. At ICPP, Idaho Falls, non-heating wastes are stored in 300,000-gal stainless-steel tanks similar to the tanks described above (Fig. 3), but without cooling coils. These vessels cost about $600,000 each.

OPERATING TECHNIQUES AND EXPERIENCE

Throughout the years of operating experience, four areas of primary concern have received considerable attention. These areas are (1) the assurance of tank integrity, (2) the safe removal of heat, (3) the safe removal of radiolytic hydrogen, and (4) the long-term cost of waste containment and surveillance. These factors are discussed below.

A. Assurance of tank integrity

Of utmost importance to operating management is the knowledge that the high-level wastes are contained so that the radioactive materials do not enter the potable waters in the environment. Monthly measurements are made of the liquid level in inactive storage tanks more frequently or if transfers are made into or out of the vessel or if a leak is suspected. The current accuracy of measurement of liquid level by manual probe in a non-boiling vessel is about plus or minus one-half inch; this measurement is equivalent to about plus or minus 1,400 gal of liquid in a 75-ft diam. tank. A more precise electronic measurement device is being developed at Hanford, together with a centralized read-out facility for improved surveillance.

At Hanford, the second line of defense is the more than 200 ft of dry soil between the tank and the ground water. This soil is capable of retaining liquids to the extent of 7 to 10% of its volume by capillarity; up to 50,000 gal of liquid can be released at a point without drainage to the ground water. In addition, the soil has ion-exchange properties, so that the migration rate of the fission products is slower than that of the liquid. A grid of dry wells is used regularly to monitor the soil for radioactivity and thus to detect any leakage that might have escaped detection through liquid-level measurement. During the last few years, four of the 145 underground tanks at Hanford have leaked non-heating wastes to the ground. In each case, the leak was first detected by liquid-level measurement, with leak-rates of 100 to 700 gal/d being observed. Subsequently, radioactivity was detected in the dry-wells in the vicinity; in no case was radioactivity from a leaking tank found in the ground water. In each case, the contents of the leaking tank were transferred to another vessel.

For all tanks at Idaho Falls and the tanks for self-heating waste at Savannah River, the second line of defense is the vault which contains the storage tank. The absence of radioactivity solution in the vault attests the integrity of the storage vessels. The additional leak protection afforded by
the vaults compensates for the less favourable geological situation existing at Idaho Falls and Savannah River. To date, no leakage has been detected from any radioactive waste-storage tank at ICPP, while four tanks developed very small leaks at Savannah River. The small volume of leaked waste is being caught in the saucers and returned to the vessels.

B. Safe removal of heat

At Savannah River and Idaho Falls heat is removed from the self-heating waste via cooling coils. Since the acid wastes stored at Idaho Falls have a very small content of solid phase, the temperature of the stored wastes is relatively uniform and is held below 55°C. At Savannah River, a sludge layer of hydrous iron oxides and other chemicals forms in the bottom of the tanks and interferes with the transfer of heat to the cooling coils. While the supernatant solution is readily held below 40°C, the temperature in the sludge layer approaches, and on occasion has exceeded, the boiling temperature of the supernatant solution; the sludge temperature declines slowly as the stored waste ages. This condition creates no known hazard and causes no operating concern.

At Hanford, the wastes are permitted to self-concentrate to reduce the volume of the stored wastes to a practical minimum. This operation requires the imposition of operating procedures and limits unique to the Hanford operation. Some of these restrictions are discussed below:

Restriction 1

In preparing the store self-heating wastes, an underground tank is heated at a rate of about 1°C/d to avoid undue stress in the structure. This stress is created as a thermal gradient is imposed on the reinforced concrete wall; the inner rings of reinforcing steel are at a higher temperature than the outer rings, placing the inner rings in compression and the outer rings in tension. Calculations indicate that stress can be kept within reasonable limits if the temperature gradient through the concrete wall is held below 13°C/ft. Heating the tank within these limitations is accomplished by first placing a heel of water in the tank, then adding a quantity of radioactive waste calculated to raise the temperature of the tank and its contents by about 25°C during the next few weeks. Four weeks later, another increment of self-heating waste is added and so on until the tank is heated to the boiling temperature of the waste.

Restriction 2

The simmering liquid is kept agitated to avoid pressure surges from sudden increases in the boiling rate. Without agitation, the hydrostatic head on the liquid deep in the tank permits that liquid to attain a temperature higher than its atmospheric boiling point. The sensible heat thus accumulated is instantly available to evaporate water if, by some mechanism, the solution is elevated in the tank. The lifting mechanism is readily available in the form of rising bubbles of steam from the self-boiling action itself. The
gas-lift action permits more solution to rise and partially vaporize, thereby providing more gas to accelerate the self-boiling action. In the 75-ft tanks, peak rates of condensate accumulation of 40 gal/min were observed; the vapour space above the liquid would typically be pressurized to about 2lb/in² gauge, returning to normal in 30 to 45 min. Up to 1000 gal of condensate would be accumulated during this time. This sudden boiling, or "bumping" effect was completely eliminated by the installation and operation of the totally submerged air-lift circulators. Circulation rates of thousands of gallons per minute can be obtained by the introduction of air at rates of a few cubic feet per minute.

In an effort to understand the bumping action better, the phenomenon was studied in a 40 in diam. experimental tank using radioactive wastes under plant conditions of sludge deposit, depth of solution and self-concentration. The tank was insulated and heated in such a way that the only heat lost from the stored waste was by the boiling of water. The bumping observed in this vessel essentially duplicated the time/pressure characteristics of the larger vessels. In this tank it was observed that a fairly uniform temperature gradient would be gradually established during the period of "normal" boiling, with the solution temperature near the sludge layer rising to as much as 14°C above that at the surface. With the initiation of the more rapid boiling, the temperature of the solution about 5 ft below the surface would drop to that at the surface. During the time of rapid boiling the layer of uniform temperature would gradually expand toward the tank bottom until all of the stored liquid would attain the same temperature. At no time was the temperature of the sludge layer observed to change. Increasing the cross-section of the vapour line to the condenser by a factor of seven decreased the time required to return to the "normal" rate of boiling, but had little effect on the peak pressure or on the amount of water evaporated in a single bump.

Restriction 3

The supernatant solution is not permitted to concentrate beyond about eight molar sodium ion, additional concentration interfering with the removal of heat from the sludge. If permitted to over-concentrate without limit, the sludge layer would self-heat to the point of calcination; nitrogen oxides would be evolved and the concrete in the tank bottom might be weakened through dehydration. In the few instances of temporary over-concentration (nine to ten molar sodium) experienced, the sludge temperature rose from its normal 140°C to the range of 200 to 300°C. The sludge temperature was returned to normal by diluting to about seven molar sodium and agitating the supernatant solution.

The removal of heat from the sludge layer almost certainly requires the percolation of supernatant solution through it. Thermal conductivity alone cannot explain the heat-transfer rates obtained at the observed temperature gradients. It is postulated that, if the supernatant solution is nearly saturated, crystallization of soluble salts occurs within the sludge layer as some of the water is vaporized from the percolating solution. This crystallized salt is postulated to inhibit the percolation of the supernatant solu-
tion, decreasing the rate of heat removal and causing the observed temperature increase.

Restriction 4

During the period of self-boiling in a Redox or Purex waste tank, a load limit equivalent to 775,000 gal of concentrate is imposed. This load limit is based on calculations of the structural strength of the reinforced concrete tank walls, allowing for the reduction of strength due to a thermal gradient and for a potential pressurization of the tank from the sudden boiling or "bumping" effect.

C. Removal of radiolytic hydrogen

Water and other chemicals tend to be decomposed by the intensive irradiation they receive from the decaying fission products. From available information on "G values", it can be estimated that 40 ft$^3$ of hydrogen (STP) will be produced with each million BTU of heat. At Hanford this hydrogen is swept from the tank with the steam from self-concentration and hydrogen has not been detected in any tank at concentrations above one tenth the lower explosive limit. At Savannah River hydrogen is detected in the vapours above the self-heating wastes. The concentration of hydrogen is kept well below the lower explosive limit by periodically blowing air into the tank above the liquid, exhausting the gases to the atmosphere through the fibrous glass filter. At Idaho Falls hydrogen has never been detected in a waste-storage tank. It appears that the air changes from natural causes (convection, changes of atmospheric temperature and pressure) are sufficient to remove the hydrogen as rapidly as it is formed in systems containing relatively little radioactivity.

D. Long-term costs of waste containment

The total costs of storing radioactive wastes may be considered to include the capital cost of the initial storage facilities plus the present worth of the future capital and operating costs. Included in future costs are the operational costs of tank surveillance and concentration or movements of the waste and the construction costs of a new storage facility to replace the existing one at the end of its useful life. Some of these factors can be estimated fairly well, while other factors are rather poorly defined.

In Table II, the capital-cost data presented earlier are summarized on a unit cost basis. Each type of stored waste is associated with an existing tank type to provide a spectrum of unit costs related to storage requirements. It should be noted that heat generation again becomes a limiting factor when "non-heating" wastes are evaporated to a salt cake. In a salt cake, heat must be transferred to the surface by conduction, since convection is eliminated as a heat-transfer mechanism. The limiting dimension of the salt mass is determined by the permissible temperature, the thermal conductivity and the rate of heat generation in the crystallized mass.
TABLE II

APPROXIMATE UNIT COST OF STORAGE FACILITIES FOR RADIOACTIVE WASTES - ADJUSTED TO 1962 PRICES

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Capital cost per gal</th>
<th>Reference</th>
<th>Site</th>
<th>Volume, M-gal.</th>
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<tbody>
<tr>
<td>Alkaline - non-heating</td>
<td>$0.47</td>
<td>SRP</td>
<td>1330</td>
<td></td>
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<tr>
<td>As solution or salt cake</td>
<td>0.89</td>
<td>HAPO</td>
<td>533</td>
<td></td>
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<tr>
<td>Alkaline - self-heating</td>
<td>0.99(1)</td>
<td>HAPO</td>
<td>1000</td>
<td></td>
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<tr>
<td>Self-concentrating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooled</td>
<td>1.69</td>
<td>SRP</td>
<td>1070</td>
<td></td>
</tr>
<tr>
<td>Acid - non-heating</td>
<td>2.00</td>
<td>ICPP</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Acid - self-heating</td>
<td>2.66</td>
<td>ICPP</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

(1) Based on a storage volume of 775000 gal

The cost of tank surveillance and of subsequent waste processing is less easily allocated on a per-gallon basis, since the unit cost is highly dependent on the quantity of waste stored in a given complex, the type of waste stored and the processing activities in progress. Inspection of the available data indicates that the annual operating costs run about one-half to three percent of the capital cost of the storage facilities. If perpetual surveillance is indicated, the long-term costs may be estimated by assuming that a fund is created, the interest from which is to be used to cover the necessary expenses. In the subsequent discussion we assume that such a fund will earn four percent interest.

The proper provision for future replacement of the storage vessels is even more difficult to estimate since we do not yet have a valid basis for predicting the service life of waste-storage tanks. Data on tank service life are not yet sufficient to be meaningful. Corrosion data for carbon steel in an alkaline waste environment are erratic on both laboratory and field specimens. While the general corrosion rates are indicated to be low (around 0.02 mil/yr), pitting attack is noted in most specimens. The data indicate that the pitting penetrates in a few months to the extent of perhaps 5 mil; pitting then stops, or at least slows to a very low rate. Stress corrosion is also observed in alkaline nitrate systems under some conditions. These data indicate that a tank may last several decades; on the other hand, the tank’s life is determined by the most active corrosion attack and may well be limited to a much lower value. Corrosion data for stainless steels in acid media also indicate a long service life for these vessels, although some intergranular attack has been noted in laboratory tests.

Examination of the actual service life of the existing storage tanks in use is also inconclusive. Table III summarizes the available information. The two tanks suspected of failure through flexure of the tank liner should
TABLE III
SUMMARY OF PERFORMANCE
TANKS STORING RADIOACTIVE WASTES

<table>
<thead>
<tr>
<th>Location</th>
<th>Waste type</th>
<th>Number of tanks Failed</th>
<th>Tank use, yr</th>
<th>Probable failure mechanism</th>
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</thead>
<tbody>
<tr>
<td>HAPO</td>
<td>Non-heating - BiPO₄</td>
<td>4</td>
<td>9 - 17</td>
<td>Liner flexure - 1</td>
</tr>
<tr>
<td>HAPO</td>
<td>Non-heating - Redox and Purex</td>
<td>0</td>
<td>10 - 17</td>
<td>Pit corrosion - 3</td>
</tr>
<tr>
<td>HAPO</td>
<td>Self-heating - Redox</td>
<td>(1)</td>
<td>2 - 8</td>
<td>Liner flexure; no leakage indicated</td>
</tr>
<tr>
<td>HAPO</td>
<td>Self-heating - Purex</td>
<td>0</td>
<td>0 - 6</td>
<td>-</td>
</tr>
<tr>
<td>SR</td>
<td>Non-heating - Purex</td>
<td>0</td>
<td>0 - 6</td>
<td>-</td>
</tr>
<tr>
<td>SR</td>
<td>Self-heating - Purex</td>
<td>4</td>
<td>0 - 6</td>
<td>Stress corrosion</td>
</tr>
<tr>
<td>IDO</td>
<td>Non-heating - acid</td>
<td>0</td>
<td>0 - 11</td>
<td>-</td>
</tr>
<tr>
<td>IDO</td>
<td>Self-heating - acid</td>
<td>0</td>
<td>0 - 11</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) Some of these tanks were previously used to store BiPO₄ wastes.
(b) Some of these tanks are used to store wastes from the processing of enriched U-Al fuels. One of these tanks leaked.

be considered non-typical. In the case of the BiPO₄ tank, the vessel was filled and emptied repeatedly. The design of the liner is such that the weight of the side liner tends to be transmitted around the knuckle at the junction of the side and base plate in such a way that the bottom tends to buckle upward. The first indication of a non-standard condition was the inability to install a jet dip-leg of the proper length; investigation revealed that the bottom liner was elevated a few feet from its original position. Later the tank started leaking. The Redox tank was withdrawn from service when erratic liquid-level measurements indicated an abnormal condition. Subsequent investigation revealed that the steel bottom liner had buckled upward when self-heating Redox wastes were added to the tank. The liner slowly receded to its original position after the boiling wastes were pumped out. It is postulated that the heat vaporized some water from the concrete grout below the liner, building up sufficient steam pressure to lift the liner and the small amount of waste in the tank at the time. While all evidence indicates the tank did not leak, the tank has remained empty since that time.

The three tanks which are suspected of failing through pit corrosion were used to store a concentrated waste from the obsolete bismuth phosphate process. These wastes contain appreciably more sulphate and phosphate ions than current wastes and laboratory studies indicate that these wastes are much more corrosive than current Redox and Purex wastes. It is clear that
we can expect more failures of tanks storing these wastes, but it is not clear how these data apply to the estimation of life expectancy of waste storage tanks for current process wastes.

The four Savannah River tanks listed started seeping through the weld-affected areas of the side walls after several months of use. Investigation indicated that the seepage is the result of stress corrosion of the carbon steel by the alkaline nitrate system. The seepage slowed and stopped during the next several months; in only one tank is there now any restriction on the amount of liquid to be stored. A careful review of the records revealed that the materials and workmanship in these tanks are of the same high quality that went into the construction of the other storage tanks in use at Hanford and Savannah River. There is at present no explanation as to why these tanks should leak while so many other tanks are giving longer service life under very similar chemical and thermal conditions. Tests indicate that the stress corrosion can be avoided in future construction by heat-treating the tank in place before use.

In view of the available data, it would appear presumptuous to assign definite values to the total cost of long-term storage of radioactive wastes. We can, perhaps, approximate the costs for perpetual storage of three waste types to obtain a range of probable values.

Let us consider first a dejecting waste. Since for practical purposes, this material is non-heating, it would appear most practical to evaporate this material to essentially a salt cake and to store in a minimum cost vessel. Laboratory data indicate that these conditions can be met if the solution is concentrated by a factor of about three, the free hydroxide ion neutralized with carbon dioxide and the concentrate permitted to cool. Preliminary Hanford estimates indicate that the concentration could be effected for about seven cents per gallon of condensate, including amortization, operating labour, heat and chemicals. Once solidified, the salt cake should require minimum surveillance - perhaps one percent of the capital investment is a reasonable annual assessment. A fund equal to one-fourth the construction cost is therefore assumed to earn sufficient interest to defray surveillance costs (Table IV). Assuming the mass is stored in a permanently restricted access area, in an arid climate and well above the water table, no replacement tank should be necessary. The safety of the storage should be adequate even after the tank loses its integrity.

<table>
<thead>
<tr>
<th>TABLE IV</th>
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</thead>
<tbody>
<tr>
<td>ESTIMATED STORAGE COST</td>
</tr>
<tr>
<td>AS SALT CAKE DEJACKETING SOLUTION</td>
</tr>
<tr>
<td>FROM ONE TON OF HANFORD FUEL</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation - 7d x (180 - 60)</td>
<td>$8.40</td>
</tr>
<tr>
<td>Capital cost - 60 x $0. 47</td>
<td>28.20</td>
</tr>
<tr>
<td>Surveillance fund - ($28.20 x 1%)/(4%)</td>
<td>7.05</td>
</tr>
<tr>
<td>Total Cost</td>
<td>$43.65</td>
</tr>
</tbody>
</table>
For our second case, let us consider the self-heating Purex waste from a ton of Hanford fuel. Lacking a valid basis for estimating tank life, let us arbitrarily assign a life expectancy of ten years. From Fig. 5 we find that the present worth of the cost of providing 99¢/gal storage every 10 yr is $3.05. The stored liquid can be expected to self-boil for at least 50-100 yr. Since continual surveillance and periodic waste movement will be required, an annual assessment of four percent of capital is assumed (Table V).

The long-term cost of storage is very dependent on tank life. If the tank life were assumed to be 20 yr, the present worth of the capital costs would fall to 60 x $1.82 or $109.20 and the total cost to $169.00/t.

For our third case, let us consider the self-heating waste from the processing of a kilogram of fully enriched uranium as zirconium-alloyed fuel. Let us assume that the cooled stainless-steel vessel has a life expectancy of 50 yr and that the annual surveillance cost for the cooled tank will be one-
half percent of the capital cost. The replacement tank would probably not have to be cooled. The cost picture might then be as shown in Table VI.

**TABLE VI**

**ESTIMATED STORAGE COST AS LIQUID SELF-HEATING WASTE FROM ONE KILOGRAM U$^{235}$ AS U-Zr FUEL**

<table>
<thead>
<tr>
<th>Description</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital cost of initial tank</td>
<td>$1840</td>
</tr>
<tr>
<td>Surveillance fund (5%)/(4%)</td>
<td>230</td>
</tr>
<tr>
<td>Present worth of replacement tanks (2.33 - 2.00)</td>
<td>228</td>
</tr>
<tr>
<td><strong>Total cost</strong></td>
<td><strong>$2298</strong></td>
</tr>
</tbody>
</table>

These sample calculations are not intended to convey the impression that storage for radioactive wastes can be accurately projected. The calculations do, however, illustrate the fact that storage costs vary sharply with the volume and character of the waste, with the environmental conditions as they affect the degree of conservatism required in the facility design and with the degree of continued surveillance considered appropriate.

**OUTLOOK**

The current practices used in storing radioactive solutions have been completely successful in preventing significant amounts of these materials from escaping to the environment. The operations do, however, require continual surveillance and are dependent on prompt and proper operational response to any abnormal condition that may develop. These facts have been recognized by engineers throughout the industry and development programmes are well under way to find a better way to handle these radioactive materials. The feeling persists that, while storage in tanks is quite acceptable as an interim measure, a better way at reasonable cost should be found to assure the long-term containment of these radioactive materials.
BIBLIOGRAPHY


DISCUSSION

E. GLUECKAU (Chairman): Did the nitric acid evaporation carried out in the Purex waste mentioned in Table I precede neutralization? If so, what was the evaporation factor?

R. E. TOMLINSON: The Purex high-level waste was concentrated as an acid prior to neutralization, by a factor of about 25 - 30. Other wastes were then added to dilute this waste to the indicated volume.

N. E. BREZHNEVA: When the Savannah River tanks became defective, was the rate of seepage into the soil studied? If so how far did the radioactive elements penetrate?

R. E. TOMLINSON: All of the material which seeped from the Savannah River tanks was retained in the saucer in the annular space inside the concrete vault. At Hanford, radioactivity was detected in the soil up to 75 feet from the tank, but none was detected in the ground water.

P. DEJONGHE: Was the amount of leakage from Hanford tanks of the same order of magnitude as that normally admitted from other discharges? If not, did you try to remove the leaked active material?

R. E. TOMLINSON: The amount which leaked was of the same order of magnitude as is normally admitted to the ground and no attempt was made to remove it.

J. M. HOLMES: What is the source of the carbonate in the Hanford waste that you show in Table I?

R. E. TOMLINSON: The carbonate wastes arise from the washing of the solid in the Purex process.

D. W. CLELAND: How does the long-term reliability of the stainless-steel tanks used at Idaho compare with that of the mild steel tanks employed elsewhere?

R. E. TOMLINSON: I think there is no question that the stainless-steel vessels will have a longer service life than the mild steel vessels. The question as to which type of vessel will have the lowest long-term cost has not yet been answered.
II

CONCENTRATION AND STORAGE
CONCENTRATION ET STOCKAGE DES PRODUITS DE FISSION A L'USINE D'EXTRACTION DU PLUTONIUM DE MARCOULE

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Abstract — Résumé — Аннотация — Resumen

CONCENTRATION AND STORAGE OF FISSION PRODUCTS AT THE MARCOULE PLUTONIUM EXTRACTION PLANT. The very highly active effluents of the Marcoule plutonium extraction plant consist mainly of the raffinate obtained in the course of the first extraction, during which nitric acid is used as salting-out agent.

After washing with a diluent in a mixer-settler, the effluents are concentrated by evaporation at atmospheric pressure, the nitric acid being destroyed simultaneously by the formaldehyde.

Concentration is carried out in two stages. The nitric acidity of the boiling solutions in the evaporators and the concentrate for storage is 3N. The overall decontamination factors are of the order of $10^6$.

After final evaporation, the concentrated solution of fission products is led, by gravity, to storage installations near the plant, composed of stainless-steel tanks with a useful capacity of 60 m$^3$. Effluents are stored at the ordinary temperature and cooled by closed-circuit water-circulation in the pool in which each tank is immersed and within internal coils.

A permanent check is maintained on the volume and temperature of the stored liquids, on pressure in the storage tanks and on the activity of the cooling circuits.

Before discharge into the stack, the ventilation air of the buildings is filtered through glass wool and monitored for radioactivity. After de-entrainment, the ventilation air of the storage tanks is passed through paper filters before entering the waste circuit.

In the event of an incident, it is possible at any moment to effect emergency transfer of the contents of a given tank into a reserve tank. If necessary, contaminated cooling water can also be sent to the Centre's effluent treatment station.

The entire installation is divided into four quite distinct areas as regards radioactivity hazards.

Possible soil pollution is monitored by measuring the activity of water collecting in channels round the installation. A watch is maintained on the water table by means of four tubed probes placed in a semi-circle round the store.

CONCENTRATION ET STOCKAGE DES PRODUITS DE FISSION A L'USINE D'EXTRACTION DU PLUTONIUM DE MARCOULE. Les effluents de très haute activité de l'usine d'extraction du plutonium de Marcoule sont essentiellement constitués par le raffinat de la première extraction, dans laquelle on utilise l'acide nitrique comme relargant.

Ces effluents, après lavage au diluant dans un mélangeur-décanteur, sont concentrés par évaporation à la pression atmosphérique avec destruction simultanée de l'acide nitrique par l'aldéhyde formique.

Cette concentration est effectuée en deux stades.

L'acidité nitrique des solutions à ébullition dans les evaporateurs et du concentrat envoyé au stockage est de 3 N. Les facteurs globaux de décontamination y sont de l'ordre de $10^6$.

Après l'évaporation finale, la solution concentrée de produits de fission est transférée, par gravité, vers le stockage implanté au voisinage de l'usine. Ce stockage est constitué de cuves en acier inoxydable d'une capacité utile de 60 m$^3$. Les effluents sont stockés à la température ordinaire, le refroidissement étant assuré par circulation d'eau, en circuit fermé, dans la piscine où est immersée chaque cuve et dans des serpentinets intérieurs.

On contrôle en permanence le volume et la température des liquides stockés ainsi que la pression dans les cuves de stockage et l'activité des circuits de refroidissement.

L'air de ventilation du bâtiment est, avant rejet à la cheminée, filtré sur laine de verre et contrôlé au point de vue de l'activité. L'air de ventilation des cuves de stockage est, après dévésiculage, filtré sur papier avant d'être introduit dans le circuit de rejet.
En cas d'incident, le transfert d'urgence du contenu d'une cuve dans une cuve disponible est toujours possible. On peut également, si nécessaire, évacuer à la Station de traitement des effluents du Centre les eaux de refroidissement contaminées.

L'ensemble de l'installation est divisié en quatre zones nettement différenciées en fonction des risques radioactifs.

Le contrôle de la pollution éventuelle du sol est assuré par la mesure de l'activité de l'eau collectée par des drains placés autour de l'installation. La nappe phréatique est surveillée par quatre sondages tubés disposés en demi-cercle autour du stockage.

**CONCENTRACIÓN Y ALMACENAMIENTO DE LOS PRODUCTOS DE FISIÓN EN LA PLANTA DE EXTRACCIÓN DE PLUTÓNIO DE MARCOULE.**

Los efluentes de actividad muy elevada de la planta de extracción de plutonio de Marcoule están formados esencialmente por los desechos del refinado de la primera extracción, en la cual se utiliza, como agente salino coadyuvante, el ácido nítrico; dichos efluentes, una vez lavados con un diluyente en una mezcladora-decantadora, se concentran por evaporación a la presión atmosférica, destruyéndose simultáneamente el ácido nítrico por ataque con aldehida formaldehida.

Esta concentración se efectúa en dos etapas. La acidez nítrica de las soluciones de ebullición en los evaporadores y del concentrado que se envía al lugar de almacenamiento es de 3N. Los factores globales de descontaminación son del orden de 10⁶.

Después de la evaporación final, la solución concentrada de los productos de fisión se transporta, por gravedad, hasta el lugar de almacenamiento, situado en las cercanías de la planta. El almacenamiento se efectúa en cubas de acero inoxidable, de 60 m³ de capacidad útil. Los efluentes se almacenan a la temperatura ordinaria, asegurándose su enfriamiento por circulación de agua en circuito cerrado en la piscina en que está sumergida cada cuba y en los serpentines internos.

Se controlan constantemente el volumen y la temperatura de los líquidos almacenados, así como la presión en las cubas y la actividad en los circuitos de enfriamiento.
Antes de pasar por la chimenea el aire de ventilación del edificio, se filtra con lana de vidrio y se controla su actividad. El aire de ventilación de las cubas de almacenamiento, una vez eliminadas las vesículas, se filtra con papel antes de introducirlo en el circuito de evacuación.

En caso de accidente siempre es posible trasladar rápidamente el contenido de una cuba a otra cuba disponible. Si es necesario, se pueden también evacuar las aguas de enfriamiento contaminadas a la instalación de tratamiento de los efluentes del Centro.

La instalación está dividida en cuatro zonas netamente diferenciadas según los riesgos radiactivos. El control de la contaminación eventual del suelo se efectúa midiendo la actividad del agua recogida en los desagües situados en torno de la instalación. La capa freática se vigila por medio de cuatro sondas tubulares dispuestas en semicírculo alrededor del lugar de almacenamiento.

Le traitement de l'uranium naturel irradié à l'Usine d'extraction du plutonium du Centre de Marcoule s'effectue suivant un procédé classique dont les étapes sont représentées sur la figure 1.

Le solvant utilisé pour les trois cycles d'extractions est le tributylphosphate dilué avec du n-dodécane dans les proportions 30-70 en volume. Ceci permet, en ce qui concerne la première extraction, de séparer les produits de fission dans une solution aqueuse ne contenant pas de cations relargants.

Les effluents radioactifs liquides produits au cours du traitement peuvent se diviser en deux grandes catégories:

a) les effluents de très haute activité constitués par le raffinat de l'extraction I qui contient plus de 99,9% de l'activité γ du combustible,

b) l'ensemble des autres effluents: distillats de l'évaporation des produits de fission, raffinat de la décontamination uranium, solution de lavage des solvants etc. dont la radioactivité est 1 000 à 100 000 fois plus faible.

Ces effluents subissent à la Station de traitement des effluents du Centre des traitements différents suivant leur niveau d'activité.

Le problème des effluents radioactifs liquides est un des problèmes majeurs du traitement des combustibles irradiés, en particulier dans le cas des effluents de haute activité, à cause des difficultés posées par la concentration et le stockage. Nous allons étudier pour ces deux derniers points les solutions choisies par le Commissariat à l'Énergie atomique à Marcoule et les résultats d'exploitation des installations en service.

1. CONCENTRATION DES PRODUITS DE FISSION

1.1. Description du procédé

Le procédé adopté à Marcoule pour la concentration par évaporation (figure 2) des solutions aqueuses de produits de fission présente les caractéristiques suivantes:

a) concentration en deux stades,

b) évolutions effectuées à la pression atmosphérique,

c) acidité des solutions à concentrer maintenue constante pendant toute la durée des opérations en utilisant le formaldéhyde.

La solution aqueuse de produits de fission est, à sa sortie de l'extraction I, traitée dans un mélangeur-décanter par du n-dodécane pour en éliminer le solvant entraîné. Ce lavage permet de récupérer un volume
Figure 1
Schéma du procédé de traitement de l'uranium naturel irradié.
CONCENTRATION ET STOCKAGE DES PRODUITS DE FISSION

Figure 2
Schéma du procédé de concentration des produits de fission.

de tributylphosphate correspondant à un entraînement par la solution aqueuse de produits de fission de 1/2 000.

Après ce traitement la solution aqueuse est stockée avant évaporation. Bien que ce stockage permette un temps de repos minimum de 24 h il n'y a jamais séparation de solvant par décantation.

Dans le premier stade d' évaporation on concentre d'un facteur 10 à 15. L'évaporateur travaille d'abord à volume constant alimenté par un dispositif mesurant (figure 3). On effectue ensuite une réduction de volume par évaporation sans alimentation jusqu'à obtenir le facteur de concentration désiré. Pendant ces deux opérations, l'acétidité nitrique est maintenue constante (3 N), l'évaporateur étant alimenté en formaldéhyde de manière continue. Les distillats obtenus au cours de cette première évaporation sont envoyés à la Station de traitement des effluents du Centre après contrôle d'activité.

Après ce premier stade d'évaporation le concentrat obtenu est transféré dans un evaporateur de volume et de capacité d'évaporation plus faible. On poursuit alors la concentration jusqu'à obtenir un volume de concentrat correspondant à 50 l par tonne d'uranium naturel traité, soit pour les deux évaporations un facteur de concentration global de 70 environ. Pour cette opération, comme pendant le premier stade d'évaporation, l'acétidité nitrique est maintenue constante (3 N), l'évaporateur étant alimenté en continu en formaldéhyde. Les distillats peuvent être également envoyés à la Station de traitement des effluents du Centre après contrôle d'activité bien que dans le projet leur recyclage ait été prévu au premier stade d'évaporation.

Les vapeurs nitreuses produites par les groupes d'évaporation sont collectées et traitées dans une installation commune constituée par deux colonnes en série où s'effectuent l'oxydation par l'air et l'absorption par
Figure 3
Principe d'implantation de l'installation.
L'eau. L'effluent gazeux de ces colonnes après dévésiculage et filtration est rejeté à la cheminée. L'effluent liquide qui est une solution nitrique faiblement radioactive n'est pas récupéré mais envoyé à la Station de traitement des effluents du Centre.

1.2. Description de l'installation

1.2.1. Conception générale de l'installation

L'installation comporte essentiellement:

a) trois cuves de stockage du raffinat de l'extraction I avant concentration,
b) trois ensembles de mesureurs à relevage sous vide permettant d'alimenter chaque groupe d'évaporation à partir des trois cuves de stockage,
c) trois groupes d'évaporation avec pour chacun un évaporateur pour le premier stade de concentration et un évaporateur pour le deuxième stade,
d) deux colonnes d'oxydation et d'absorption des vapeurs nitreuses.

L'ensemble de l'installation a été implanté dans le bâtiment principal de l'usine. Dans la zone dite inactive se trouvent le pupitre de commande et les appareils annexes qui véhiculent des fluides inactifs. La zone dite semi-active renferme les appareils qui ne sont pas normalement contaminés ou, compte tenu du fait qu'ils ne véhiculent que des liquides faiblement radioactifs et des volumes réduits, sont munis de protections individuelles en plomb; c'est le cas des échangeurs de chauffage et refroidissement, des condenseurs, des vanne de commandes des siphonnages. La zone active renferme les cuves de stockage du raffinat de l'extraction I, les évaporateurs, les cuves de stockage du distillat, qui sont isolées dans des casemates assurant également la protection des circuits très actifs. Les trois zones, inactive, semi-active et active, sont ventilées indépendamment et de manière à assurer un gradient de dépression pour éviter toute contamination des locaux où peut être amené à circuler le personnel. Les différents appareils sont eux-mêmes en dépression par rapport à la zone active. La figure 3 donne le principe d'implantation de l'installation.

1.2.2. Technologie

En zone active tous les appareils sont réalisés en acier inoxydable dans une nuance à 18% Cr, 8% Ni, bas carbone (< 0,03%) pour ce qui concerne les gaz ou liquides froids et dans une nuance à 25% Cr, 20% Ni, bas carbone pour ce qui concerne les solutions nitriques chaudes. Les raccordements entre tuyauteries et entre tuyauteries et appareils sont tous réalisés par soudure. Il n'y a aucun organe mécanique (bride, vanne, pompe) sur ces circuits.

Les transferts de liquides actifs sont effectués par gravité et vide en utilisant soit des siphons à amorçage par vide, soit des circuits de relevage.
1.2.3. Les évaporateurs

On a choisi pour réaliser les opérations d'évaporation des appareils classiques constitués par un bouilleur cylindrique à axe vertical. Ils ont été réalisés de manière à disposer d'une surface assez importante pour limiter le taux d'évaporation au m² de surface libre et d'un volume mort important au-dessus du liquide pour faciliter le dévésiculage. Ils sont surmontés d'une colonne à garnissage d'anneaux Raschig en tête de laquelle s'effectue le reflux.

Le chauffage et le refroidissement sont assurés par circulation de liquide thermofluide dans des demi-serpentins soudés sur les parois externes. Cette solution permet d'avoir des échangeurs qui d'une part ne travaillent pas en pression et d'autre part ne sont pas soumis à la corrosion du liquide à l'ébullition.

Ces appareils sont munis de dispositifs de prise d'échantillons pour contrôle de l'acidité.

1.3. Résultats d'exploitation

Les caractéristiques essentielles à considérer dans le procédé de concentration des produits de fission par évaporation décrit précédemment sont:
- l'utilisation du formaldéhyde pour effectuer la concentration à acidité constante,
- le comportement des produits de fission et des autres éléments chimiques de la solution en cours de concentration et en particulier les risques de précipitation qui peuvent entraîner des difficultés,
- le facteur de décontamination des distillats qui conditionne leur facilité d'élimination,
- la réduction de volume obtenue qui conditionne l'importance et par conséquent la sécurité et le coût des installations de stockage.

Nous allons les examiner successivement.

1.3.1. Utilisation du formaldéhyde pour la concentration à acidité constante

L'utilisation du formaldéhyde pour la destruction continue de l'acide nitrique pendant la concentration permet d'effectuer cette opération à acidité constante et relativement faible, à la pression atmosphérique, avec reflux et sans augmenter la salinité de la solution à concentrer. Elle présente donc des avantages certains en ce qui concerne les risques de corrosion des évaporateurs et les risques de précipitation ou de cristallisation de sels dus à la forte acidité.

Dans le domaine d'acidité (trois normalités) où l'on opère, la réaction de l'acide nitrique avec le formaldéhyde devrait s'effectuer suivant la stoechiométrie.

\[
4 \text{NO}_3 \text{H} + 3 \text{HCHO} \rightarrow 4 \text{NO} + 3 \text{CO}_2 + 5 \text{H}_2 \text{O}
\]

en fait, dans l'ensemble évaporateur - colonne de dévésiculage se produisent simultanément plusieurs réactions [1]. A la réaction du formol et de l'acide
CONCENTRATION ET STOCKAGE DES PRODUITS DE FISSION

nitrique citée plus haut et qui peut s'effectuer en plusieurs stades suivant le processus

\[ 2 \text{NO}_3\text{H} + 3 \text{HCHO} \rightarrow 3 \text{HCOOH} + 2 \text{NO} + \text{H}_2\text{O} \]
\[ 2 \text{NO}_3\text{H} + 3 \text{HCOOH} \rightarrow 3 \text{CO}_2 + 2 \text{NO} + 4 \text{H}_2\text{O} \]

peuvent s'ajouter des réactions mettant en jeu les vapeurs nitreuses et l'acide nitreux du distillat refluxé.

La prévision de la cinétique et des mécanismes réactionnels de ces phénomènes serait évidemment difficile mais pratiquement pour des conditions de marche déterminées telles que acidité et débit de la solution à concentrer, acidité de la solution à l'ébullition, taux de reflux, on peut déterminer expérimentalement le coefficient k de la réaction globale

\[ \text{NO}_3\text{H} + k \text{HCHO} \]

(qui est de 0,45 avec nos conditions opératoires) cela permet d'ajuster avec une assez bonne précision le débit de solution de formaldéhyde. Pratiquement un contrôle d'acidité de la solution en ébullition toutes les huit heures permet de rectifier ce débit et de maintenir l'acidité constante à ± 0,3 normalités.

Le choix de l'acidité 3 N pour la solution à ébullition a résulté d'un compromis entre:

- la vitesse de réaction formol - acide nitrique qui croît avec l'acidité de la solution,
- le coefficient k qui décroît lorsque l'acidité croît,
- les risques de corrosion et de précipitation qui sont d'autant plus élevés que l'acidité est forte.

Le procédé de concentration par évaporation des solutions nitriques en présence de formaldéhyde a souvent été décrié à cause des risques qu'il pourrait présenter. L'exploitation industrielle de l'installation de Marcoule a permis de vérifier que:

- le démarrage de la réaction acide nitrique - formol se fait sans retard, à l'ébullition, en présence d'une faible quantité de nitrite de soude,
- le contrôle de démarrage de la réaction et le contrôle de sa continuité sont aisés par dosage de l'acidité du distillat qui est très faible en l'absence de réaction car elle se réduit à l'acidité nitrique à l'équilibre alors qu'en cours de réaction elle est importante sous forme d'acide nitreux,
- la vitesse de réaction étant importante à l'ébullition, l'accumulation de formaldéhyde ou d'acide formique dans l'évaporateur reste très faible. Une sécurité interdit toute alimentation d'évaporateur en formaldéhyde si la température est inférieure à 90°C.

L'expérience acquise dans ce procédé permet de penser que son application industrielle ne pose pas de problèmes insurmontables, en particulier au point de vue sécurité, et présente des avantages importants.
1.3.2. Comportement des produits de fission en cours de concentration

La précipitation des produits de fission ou d'autres constituants chimiques de la solution constitue le principal obstacle à la concentration des solutions de produits de fission. Dans les évaporateurs, ce phénomène peut entraîner une accumulation importante d'activité, provoquer un «entartrage» des surfaces de chauffe ou refroidissement, entraîner des difficultés pour les transferts de solutions. Dans les stockages il peut avoir pour conséquence l'accélération de corrosions locales et donner d'autre part naissance à des ébullitions brutales dues à l'accumulation de chaleur au sein des précipités.

Les études effectuées sur les solutions au cours de la concentration ont montré que pendant le premier stade d'évaporation 80% de l'activité due aux émetteurs zirconium-niobium disparaît de la solution. Au cours du deuxième stade d'évaporation 40 à 80% de l'activité restante disparaît également de la solution [2].

Cette disparition du zirconium et du niobium est due très probablement, comme on a pu le constater lors d'essais inactifs, à la précipitation de phosphates. L'ion phosphorique était soit présent dans le raffinat de l'extraction I, soit formé au cours de l'évaporation par dégradation du tributylphosphate.

Bien que cette précipitation de phosphates n'ait pas provoqué jusqu'ici de difficultés sérieuses dans l'exploitation de l'installation de concentration, elle constitue néanmoins un écueil du procédé qui ne semble pouvoir être surmonté, si la formation d'ion phosphorique se produit essentiellement dans l'évaporateur, que par un traitement avant concentration (entraînement à la vapeur) du raffinat de l'extraction I pour en éliminer aussi complètement que possible le tributylphosphate.

1.3.3. Facteur de décontamination des distillats

La contamination des distillats au cours des opérations d'évaporation de liquides radioactifs peut être provoquée par:
- la présence en solution de produits de fission volatils comme l'iode ou le ruthénium,
- les entraînements de particules solides, vecteurs d'activité, en suspension dans le liquide en ébullition,
- les entraînements de vésicules liquides qui peuvent présenter des formes très diverses.

Le problème de l'iode est aisément résolu par le «temps de refroidissement» du combustible avant traitement qui est en règle générale de 120 jours. La limitation de l'acidité nitrique du concentrat en ébullition à 3 N et le dégagement de vapeurs nitreuses au sein du liquide permettent de se placer dans des conditions favorables, bien que l'on travaille à la pression ordinaire, pour la non volatilisation du ruthénium [3]. Effectivement avec ces conditions opératoires on n'a jamais constaté de contamination sensible des distillats par l'iode ou le ruthénium.

Le rôle joué par les phénomènes d'entraînements de particules solides ou de vésicules liquides est assez difficile à prévoir à cause de l'influence de nombreux facteurs physiques et chimiques. Dans la conception de l'in-
Installation de nombreuses précautions avaient été prises pour réduire au mieux leur importance :

- taux d'évaporation au m$^2$ de surface libre du liquide à l'ébullition limité à 80 l/h-m$^2$ pour l'évaporation du premier stade et 20 l/h-m$^2$ pour l'évaporation du deuxième stade ;
- hauteur libre importante au-dessus du liquide à l'ébullition : 800 mm pour l'évaporation du premier stade, 700 mm pour l'évaporation du deuxième stade ;
- montage sur chaque évaporateur d'une colonne de dévésiculage garnie d'anneaux Raschig en inox de 1 pouce (hauteur 3 m pour les évaporateurs du premier stade et 2,5 m pour les évaporateurs du deuxième stade) ;
- conduite de l'évaporation avec reflux

\[
\frac{\text{volume liquide reflué}}{\text{volume liquide soutiré}} = 0,31
\]

- chauffage étudié pour assurer une ébullition aussi régulière que possible sans surchauffes locales.

Deux facteurs pouvaient être considérés comme défavorables, a priori :

- la présence possible de traces de tributylphosphate dans la solution aqueuse de produits de fission traitée,
- le dégagement de vapeurs nitreuses au sein du liquide, susceptibles de provoquer la formation de mousses comme nous l'avons montré certains essais.

Pratiquement l'exploitation industrielle de l'installation nous a montré que pour les conditions opératoires indiquées ci-dessus :

a) Le facteur global de décontamination $\gamma$ est de l'ordre de $5 \cdot 10^5$ pendant le premier stade d'évaporation et de $10^6$ pendant le deuxième stade.

Il varie peu en cours de concentration,

b) L'élément contaminant est essentiellement le cérium.

Ces facteurs de décontamination sont comparables à ceux que l'on trouve dans la littérature. Le choix d'un procédé de concentration en deux stades dont les buts étaient de séparer, pour recyclage, les distillats actifs de fin de concentration et d'éviter une contamination importante des circuits distillats, s'est révélé inutile.

1.3.4. Réduction du volume des solutions traitées

La réduction maximale du volume de concentrat à stocker est évidemment l'objectif le plus important de la concentration des produits de fission. Le traitement d'uranium non allié, l'utilisation comme solvant du tributylphosphate, qui permet d'effectuer l'opération d'extraction sans autre relargant que l'acide nitrique, donnent de grandes possibilités : le raffinat de l'extraction I à concentrer est en effet constitué par une solution ne contenant que quelques centaines de milligrammes par litre d'uranium, plutonium, produits de fission, fer apporté pour la corrosion, sous forme de nitrates.
La concentration a jusqu'ici été limitée à l'obtention d'un volume final minimum de concentrât de 40 l par tonne d'uranium traité, soit une réduction de volume du raffinat de l'extraction I d'un facteur 85 environ. Le concentrât se présente alors sous forme d'une solution légèrement colorée ayant les caractéristiques moyennes suivantes:

- densité ~ 1,20
- viscosité ~ 2 cP
- concentration uranium ~ 5 g/l
- concentration plutonium ~ 5 mg/l
- concentration fer ~ 5 g/l
- concentration sodium* ~ 10 g/l
- acitidé nitrique ~ 3 N.

La composition de cette solution et sa viscosité relativement faible permettent d'envisager un accroissement du facteur de concentration et ceci malgré deux éléments défavorables: la densité de la solution et la précipitation des phosphates au cours de la concentration. La densité de la solution concentrée paraît en effet anormalement élevée compte tenu des concentrations en sels et acide nitrique. La précipitation des phosphates semble peu influencée par le facteur de concentration puisqu'elle se produit essentiellement au début du premier stade d'évaporation. Elle peut être par contre d'autant plus gênante, en particulier pour les transferts, que le volume final est plus réduit. Seuls des essais très progressifs actuellement en cours peuvent permettre d'améliorer les résultats dans ce domaine.

2. STOCKAGE DES PRODUITS DE FISSION

2.1. Principe de l'installation

Pour l'installation de stockage des produits de fission dont la première tranche est actuellement en exploitation et la deuxième tranche en construction, le projet initial avait prévu un stockage à court terme constitué par deux cuves en acier inoxydable et un stockage à long terme, après neutralisation des solutions, dans un ensemble de cuves en acier ordinaire. Pour de très grands volumes d'effluents le stockage en milieu basique est pratiquement le seul utilisé. Pour des volumes plus réduits, comme à Marcoule où l'on a un facteur de concentration déjà important, le choix du milieu basique est beaucoup moins impératif. Finalement, le stockage liquide des produits de fission ne pouvant être considéré que comme une étape intermédiaire il a été décidé de garder pour la deuxième tranche de l'installation le principe du stockage en milieu acide pour éviter au maximum les précipitations et faciliter la reprise ultérieure des solutions en vue de leur conversion en déchets solides.

L'installation définitive comportera donc deux réservoirs de transit et stockage à court terme en acier inoxydable et en aval un ensemble de réservoirs également en acier inoxydable.

* Le sodium est apporté par l'opération d'amorçage de la réaction acide nitrique - formol par le nitrite de soude.
Signalons pour mémoire l'existence d'un réservoir utilisé lors du démarrage actif de l'usine qui est situé dans une installation indépendante mais est relié aux réservoirs de stockage à court terme.

Les dispositifs de refroidissement ont été conçus pour maintenir les solutions stockées à une température maximum de 60°C.

2.2. Description de l'installation

2.2.1. Conception générale de l'installation

L'installation de stockage des produits de fission est située à 100 m au sud du bâtiment usine. Elle comporte un bâtiment qui abrite les services généraux: pupitre de commande et appareils de contrôle, production de vide et air comprimé, groupe électrogène de secours, ventilation, pompes de circulation d'eau de refroidissement. Dans une zone active en sous-sol sont rassemblés: condenseurs, dévésiculeurs, cuves de réception de distillat, mesureurs de relevage.

Enfin, toujours en sous-sol du bâtiment, deux casemates formant piscines abritent les deux réservoirs de stockage à court terme.

A l'extérieur du bâtiment, dans un cuvelage en béton enterré, seront implantés les réservoirs constituant la deuxième tranche de l'installation.

Cette installation a été conçue suivant les principes généraux dont nous avons parlé aux paragraphes 1.2.1. et 1.2.2., en particulier en ce qui concerne la ventilation du bâtiment et la réalisation des liaisons de tuyauteries et d'appareils.

Pour les transferts de solutions actives on utilise également des dispositifs de siphonnage et de relevage par mesureur sous vide. Cependant, pour certains transferts exceptionnels nécessitant un débit relativement important ou une grande hauteur de relevage, on a installé des pompes multicellulaires.

Tous les appareils essentiels sont munis de dispositifs de prises d'échantillons.

2.2.2. Les cuves de stockage

Les cuves de stockage à court terme sont des cuves cylindriques, à axe horizontal, de capacité utile de 60 m³. Elles sont réalisées en acier inoxydable 18/8 bas carbone. Chaque cuve est équipée: d'un précondenseur, de serpentin de refroidissement, de rampes perforées pour agitation à l'air comprimé, d'une alimentation en air pour le renouvellement de l'atmosphère à la surface du liquide.

Le refroidissement est assuré par deux installations indépendantes, fonctionnant en circuit fermé. On dispose d'une circulation d'eau à 8°C, dont le refroidissement est réalisé par une installation frigorifique, dans des serpentinssimmersgés dans la cuve. Ces serpentinss au nombre de trois peuvent être alimentés ensemble ou séparément. Une circulation d'eau de refroidissement dans la piscine peut également être mise en service. Pour ces refroidissements, afin de limiter les risques de corrosion des serpentinss ou de la cuve, on utilise une eau déminéralisée ajustée à pH = 9 avec du phosphate trisodique et de la soude.
La mise en dépression des cuves est assurée par une ventilation indépendante dont l'aspiration se fait à travers le condenseur, le dévésiculeur et une filtration sur filtre papier avant reprise par la ventilation générale pour rejet à la cheminée.

Pour les nouvelles cuves en projet qui seront de forme cylindrique à axe vertical et également de capacité voisine de 60 m³, le refroidissement sera uniquement assuré par serpentin immergés dans la cuve.

La figure 4 donne le principe d'installation d'une cuve de stockage.

2.2.3. Installations annexes

Elles comprennent essentiellement les circuits de distillat et les différents circuits de transferts internes.

Les deux cuves de stockage à court terme sont reliées à un condenseur commun. Le distillat peut être recueilli dans un bac de réception où l'on peut prélever des échantillons et d'où l'on peut, par pompe, soit le recycler vers une cuve de stockage, soit le diriger vers la Station de traitement des effluents du Centre. Le même principe sera adopté pour les nouvelles cuves installées.
Les moyens de transfert de solutions actives installés permettent ou permettront d'assurer les liaisons normales entre les cuves de stockage à court terme et les cuves de stockage à long terme, les liaisons entre les cuves de stockage à court terme et entre les cuves de stockage à long terme pour cas de fuite ou d'incident (voir figure 5). On pourra également reprendre les solutions stockées dans les différents réservoirs pour traitements complémentaires, conversion des solutions en déchets solides, séparation des radioisotopes intéressants.

2.3. Conditions d'exploitation du stockage

Bien qu'aucune opération physique ou chimique n'y soit effectuée et que les transferts de solutions actives soient peu fréquents, l'exploitation de l'installation de stockage entraîne une surveillance sévère. On contrôle en permanence :
- le niveau de toutes les cuves de l'installation afin d'y déceler toute fluctuation anormale,
- les débits d'eau de refroidissement des cuves et les débits d'eau de refroidissement des condenseurs et précondenseurs alimentés en permanence,
- les températures à l'intérieur des cuves de stockage à la fois dans le liquide et à proximité des parois pour déceler la présence éventuelle de dépôts,
- le débit d'air de ventilation des cuves ayant pour but d'éliminer les gaz de radiolyse,
- les dépressions entre les appareils et les différentes zones de bâtiment,
- l'activité des effluents gazeux et des différents circuits d'eau de refroidissement.
2.4. Sécurité et contrôle dans le stockage des effluents de très haute activité

Les effluents stockés ont une activité spécifique très élevée. Il était donc impératif que l'on s'attache d'une part à avoir une installation présentant le maximum de sécurité contre les fuites possibles, et, d'autre part, un contrôle efficace pouvant déceler rapidement toute fuite de produits radioactifs.

2.4.1. Sécurité de l'installation

Les produits de fission stockés peuvent s'échapper vers l'extérieur soit à l'état liquide, soit à l'état d'aérosols. Dans le premier cas, ils tendront à polluer la nappe phréatique et dans le deuxième, l'atmosphère. La conception de l'installation permet de fixer chaque fois un certain nombre de barrières au cheminement de la contamination.

A. Dispersion des aérosols

Les aérosols sont dus principalement aux gaz de radiolyse et aux entrainements vésiculaires de solution très active. Ils doivent être éliminés de l'air de ventilation des cuves avant le rejet dans l'atmosphère.

Le dévésiculeur et le réfrigérant en permettant la condensation des vapeurs débarrassent l'air de l'humidité dont il peut être chargé. Il est à signaler que depuis le début de l'exploitation, aucun liquide actif de condensation n'a été recueilli. Une filtration sur filtre papier à haut rendement permet l'élimination de ces aérosols (voir 2.2.2.). Le filtre papier est changé fréquemment avant que sa contamination ne rende la manipulation difficile.

Des aérosols peuvent aussi être créés dans les zones de travail de l'installation par l'évaporation de liquides en provenance de fuites de solutions contaminées à la suite d'un incident de fonctionnement. Pour limiter leur dispersion et leur inhalation par le personnel, l'ensemble de l'installation est divisé en quatre zones de travail:

a) La zone de travail normal, dans laquelle le danger est limité à une irradiation externe inférieure à la limite maximale admissible. Elle comprend la salle de commande, la salle des compresseurs et des pompes, la salle des filtres et le local des vannes.

b) La zone à risque permanent de contamination dans laquelle le danger est surtout lié à la présence de sources non scellées de produits de fission. C'est la salle des bancs de prises d'échantillons.

c) La zone de séjour occasionnel dans laquelle existe un risque potentiel de contamination et d'irradiation compatible avec les normes d'exposition concertées. Il s'agit de la salle dans laquelle se trouvent les vannes pneumatiques commandant les transferts par siphons.

d) La zone interdite qui est constituée par les piscines dans lesquelles sont immergées les cuves de stockage et où se trouvent les bidons de transferts, les précondenseurs, les siphons et les tuyauteries véhiculant les solutions de produits de fission.
CONCENTRATION ET STOCKAGE DES PRODUITS DE FISSION 59

Toutes ces zones sont fortement ventilées. Le taux horaire de renouvellement de l'air est égal à 10 dans les zones les plus dangereuses. L'air aspiré à l'extérieur est dépoussiéré à l'entrée de l'installation.

Une dépression croissante avec les risques radioactifs l'oblige à circuler de la zone de travail normal vers la zone interdite. Il est rejeté à l'extérieur à travers un filtre en laine de verre.

B. Dispersion des liquides

La dispersion des produits de fission peut se produire dans le cas d'une corrosion des parois de la cuve ou des serpentins de refroidissement. Elle peut aussi avoir pour origine une fissuration produite par une montée en température ou liée à l'explosion des gaz de radiolyse.

La réfrigération des cuves est réalisée par deux procédés indépendants l'un de l'autre: extérieurement par les eaux de la piscine et internièrement par les serpentins. Un brassage à l'air comprimé peut être mis en service pour éviter si nécessaire la formation d'un dépôt dans le fond de la cuve et par suite la création de points chauds. Le fonctionnement du groupe frigorifique, des ventilateurs, et la circulation de l'eau de refroidissement dans la piscine et les serpentins sont assurés de façon continue. En cas de défaillance du réseau de distribution électrique, la continuité dans l'alimentation des moteurs est obtenue grâce à un groupe diesel électrogène. La température de la solution est suivie par des appareils enregistreurs munis d'alarme.

La sécurité contre l'explosion des gaz de radiolyse est assurée par la ventilation de la cuve qui entraîne les gaz au fur et à mesure de leur formation.

La corrosion des parois de la cuve et du serpentins de refroidissement est un risque moins brutal mais plus insidieux. Il est limité par le choix de l'acier inoxydable comme matériau de construction et par le type de la solution radioactive qui est une solution nitrique 3 N. Par ailleurs, l'eau des piscines et celle qui circule dans les serpentins sont en surpression par rapport à la solution des produits de fission. S'il y a fissure, il y aura donc passage des eaux de refroidissement dans la solution et non l'inverse. Le contrôle continu du niveau du liquide dans la cuve constitue une indication sur l'importance de la fuite.

Les mesures de sécurité qui viennent d'être énumérées sont du type préventif; elles doivent permettre d'éviter la dispersion des produits de fission dans le milieu environnant. Elles sont complétées par des précautions destinées à maintenir dans tous les cas une bonne sécurité d'exploitation et à fixer des limites à un cheminement éventuel des produits de fission vers l'extérieur.

Ainsi, en cas d'incident, est prévue la possibilité de transférer la solution dans une cuve de secours identique à la cuve de stockage.

Dans le cas d'une fuite accidentelle de la cuve en remplissage, ce transfert permet en particulier de limiter la radioactivité susceptible de s'échapper. Il rend plus efficace le rôle de barrière que jouent les circuits fermés de refroidissement.

La pollution des eaux de la piscine est contrôlée en continu dans le puisard de pompage, à l'aide d'un détecteur à cristal de NaI-Tl pouvant
déclencher une alarme. Si une contamination est observée, les eaux peuvent être dirigées avec une dilution convenable vers la Station de traitement des effluents. Cette évacuation limite le risque d’infiltration d’eau contaminée à travers le béton du puisard et, par suite, évite la pollution de la nappe phréatique.

Les piscines plongent partiellement dans une formation de marne bleue dont l’épaisseur est partout importante (plusieurs dizaines de mètres) mais dont le relief est relativement accidenté et ne correspond pas exactement au relief topographique. La compacité, l’imperméabilité et la forte capacité d’échange d’ions de cette marne sont des caractères favorables de la géologie du terrain; ils contribueraient à atténuer les conséquences de l’accident maximum prévisible.

2.4.2. Contrôle de l’installation

Effluents gazeux: Ils sont constitués par l’air de ventilation des zones de travail et de balayage des cuves. Ils sont donc une conséquence normale de l’exploitation de l’installation de stockage des produits de fission.

L’efficacité de la filtration qu’ils subissent avant leur rejet dans l’atmosphère est contrôlée de façon continue par un enregistreur d’aérosols radioactifs. Cet appareil permet une mesure instantanée et une mesure différée de l’activité des poussières collectées sur une bande filtrante mobile.

Effluents liquides: Ils ne peuvent être que la conséquence d’un incident de fonctionnement qui a permis le passage de la solution de produits de fission dans les eaux de refroidissement et éventuellement à l’extérieur de l’installation dans la nappe phréatique. La contamination des eaux de la piscine est, comme nous l’avons vu, contrôlée de façon continue par un détecteur à cristal de NaI-Tl. Elle est, de plus, mesurée sur des prélèvements périodiques.

Dans l’éventualité où, malgré toutes les précautions prises, la solution active arriverait à migrer hors de l’installation, un contrôle de la contamination de la nappe phréatique a été en place. Un réseau de drains installés sous le bâtiment collecte les eaux d’infiltration et les dirige vers un puisard. On peut alors effectuer des prélèvements et mesurer leur radio-activité. Les eaux du puisard sont, dans les conditions normales, rejetées par des pompes dans des égouts inactifs. Si, à la suite d’un accident, elles étaient polluées, elles seraient dirigées vers la Station de traitement des effluents.

Quatre forages tubés de 10 mètres de profondeur sont disposés autour du bâtiment. Ils complètent les possibilités de surveillance de la pollution du terraiï et permettraient, dans l’éventualité de l’accident maximum, d’évaluer la progression de la contamination de la nappe phréatique.

3. CONCLUSION

Le traitement des effluents de haute activité, obtenus au cours du recyclage de l’uranium naturel irradié, peut se résumer pour l’Usine d’extraction du plutonium de Marcoule aux deux étapes:

a) concentration par évaporation à acidité constante (3 normalités),

b) stockage en milieu acide (3 normalités).
Le stockage en milieu acide n'est considéré que comme une étape intermédiaire qui doit être suivie ultérieurement de traitements complémentaires permettant de fixer les produits de fission en milieu solide avec probablement élimination préalable des éléments les plus dangereux comme le césium et le strontium.

RÉFÉRENCES


DISCUSSION

E. GLUECKAUF (Chairman): It is stated in the paper that in the formaldehyde destruction of nitric acid 1 HNO₃ reacts with 0.45 CH₂O. This is clearly too little formaldehyde to convert all the nitric acid into NO. Does this imply that a fairly large amount (40%) of the nitric acid is in fact distilled off undecomposed during the treatment?

C. LEFÈVRE (On behalf of M. CHAMBON and J. RODIER): A very small amount of nitric acid is distilled off. Nitrous oxide is also formed in a reaction between 0.25 molecule of CH₂O and 1 molecule of nitric acid.

W. C. BELTER: With regard to the two evaporation steps described in the paper it was mentioned that the very low-activity distillate was transferred to an effluent processing plant for further handling. Would you care to explain briefly what this effluent processing plant consists of?

C. LEFÈVRE: Since I am not a member of that particular section, all I can say is that I believe some of the supernatants are thrown back into the Rhône and other effluents are returned to underground tank storage.

E. GLUECKAUF (Chairman): In his oral presentation M. Lefèvre mentioned that the major contaminant of the condensate from the evaporation of the HNO₃ consists of cerium. Does this mean that the activity is mainly due to carry-over of spray and cerium provides the main activity of the treated fission-product solution?

C. LEFÈVRE: The cerium contaminating the distillate is carried over during evaporation.
CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES FROM THE FIRST STAGES OF THE UNITED KINGDOM CIVIL NUCLEAR POWER PROGRAMME

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Abstract — Résumé — Аннотация — Resumen

CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES FROM THE FIRST STAGES OF THE UNITED KINGDOM CIVIL NUCLEAR POWER PROGRAMME. The general problems of highly-active waste disposal are discussed and in particular the United Kingdom system of concentrating and storing highly-active waste as an acidic liquid concentrate is described. A speculative estimate is made of the amount of highly-active waste which will arise from reprocessing during the first two decades of the United Kingdom Civil Nuclear Power Programme and engineering design and technical problems associated with the safe and economic confinement of this material are examined.

1. INTRODUCTION

Processing of irradiated fuel from nuclear reactors has been carried out at the Windscale factory of the UKAEA since 1952 when the First Chemical Separation Plant was commissioned to separate plutonium from fuel
irradiated in the two air-cooled Windscale reactors. This plant was later modified to increase its capacity and it has since dealt with the progressively increasing load of irradiated fuel from the four gas-cooled reactors at Calder Hall (completed 1956-58) and four reactors at Chapelcross (completed in 1959-60).

To deal with future fuel arisings from the expanding civil nuclear power programme a Second Chemical Separation Plant is now under construction at the Windscale factory and this is expected to be operational in 1963.

The process used in the First Chemical Separation Plant and present methods of dealing with highly active waste arisings have already been described in a number of papers [1-5]. The present paper is confined to technical and engineering problems associated with the concentration and storage of future highly active liquid wastes. Present plant design philosophies and technical information are applied to the disposal of highly active wastes arising in the period 1962-80 and it is shown that the present basic system of concentration and storage of highly active waste liquors can be successfully and economically extended to support the UK civil nuclear power programme over this period.

Two forms of highly radioactive waste arise during the processing of irradiated fuel. The first is a solid waste, produced during the removal of the can from the fuel before aqueous processing. This consists of the can material and associated particles of the highly active fuel. This waste, which is stored in concrete silos and presents no undue technical problems, is not discussed further in this paper.

After removing the can the irradiated fuel is dissolved in nitric acid and the uranium, plutonium and fission products are separated from each other in a series of liquid/liquid extraction operations. In the first of these extraction operations a very high degree of separation of fission products from uranium and plutonium is achieved. The aqueous raffinate from this primary separation contains over 99.95% of the fission products and constitutes the main highly active liquid waste.

This paper deals with the concentration and storage of this acidic liquid waste, together with some subsidiary streams which arise from other parts of the process.

The paper examines the results of applying to future processing programmes a system of concentration and storage similar to that which has been in use at Windscale for a number of years, and discusses the technical and economic performance which might be expected. The results may serve as a basis for comparison when alternative systems, for example the fixation of fission products in glass, are being considered.

2. GENERAL

Since the amounts of radioactivity associated with the highly active wastes from a nuclear power programme are too large to allow disposal to the environment, containment of these materials is required. In addition, biological protection from penetrating radiation and means of removing heat from fission-product decay must be provided.
As well as ensuring safe containment and satisfactory cooling and shielding the overall cost of a disposal system for highly active wastes must be economic in relation to the cost of the product from the overall system. For example if waste is arising from processes, the aims of which are to recover plutonium or say enriched uranium, then the storage costs should be related back to these products. Alternatively if generation of electricity is the main objective then storage costs should be related to electrical units generated. Costs of storage expressed as cost per gallon or per square meter are not comparable unless they can be related back to the same main product and true economic comparisons can only be obtained by comparing the costs of alternative methods of dealing with the same storage problem.

The UK system for dealing with highly active liquid wastes is firstly; a concentration of the acid liquors by evaporation to a small bulk, followed by storage in stainless-steel tanks which are housed in thick-walled concrete cells. The cell walls are lined with stainless steel to form a secondary containment and means of stock checking and tank-leak detection are provided. The removal of fission-product decay heat is achieved by circulating water through cooling coils built into the storage tanks. Means of transferring the liquors are provided and spare capacity is always available to guard against possible failures.

3. FUTURE HIGHLY-ACTIVE WASTE ARISING

Nuclear power generation

The scale of future highly-active waste arisings depends mainly upon the amount of electrical power which is generated by nuclear means and the types of reactor systems employed. It has been estimated [6] that the electrical power consumption in the United Kingdom will double between 1960 and 1970 and that it may double again by 1980-85. This rate of growth would result in a total installed capacity of about 60 000 MWe in 1970 and over 100 000 MWe by 1980-85. This is approximately 7%/yr increase and the demand has been rising at this rate since about 1925.

The fraction of the total electrical demand which will in future be met by nuclear stations is dependent on a large number of factors, none of which can be resolved at present and many of which are interdependent, e.g. the future costs of power from nuclear, coal, and oil stations, the extent to which oil may be used for power generation and the future coal production capacity in the United Kingdom.

The present Government White Paper Programme [7] provides for an installed nuclear capacity of 5000 MWe by 1968. Beyond this date it is possible that further installation may be continued at the rate of about 1000 MW/yr to give a total of 12 000 MWe in 1975 and about 19 000 MWe in 1980. Beyond 1970 these assumptions become increasingly speculative and are regarded only for the purposes of the present paper as a guide to future levels of highly-active waste arisings.

Up to 1980 nuclear installations will probably be mainly of the gas-cooled type with fast reactors coming into operation in the later years.
Irradiated fuel arisings

An estimate of future rates of irradiated fuel arisings from such a civil reactor programme is shown in Fig. 1. This is used later as a basis for examining various design concepts in relation to alternative schemes for dealing with future highly-active waste arisings. The estimate excludes Fast-Reactor fuel which may arise in later years and also excludes the base load of irradiated fuel from the eight reactors at the Calder Hall and Chapel-cross power stations, which has been processed at Windscale since 1956. This programme is necessarily speculative and, in years to come, will be subject to many fluctuations and changes. However, its use here is only intended to serve as a broad basis for design considerations, which are dealt with in the following section.

The volume and composition of highly-active liquid waste

A new re-processing plant is now under construction at the UKAEA Windscale Factory in which the irradiated fuel from the civil nuclear reactor programme will be processed. After discharge from the reactors the irradiated fuel will be delayed for a total of about 150 d in pond storage, partly at the reactor site to allow some decay of heat before transporting, and partly at the processing site to allow decay of I$^{131}$ before feeding to the primary separation process. The highly active section of the separation process, to be operated in this new plant, will now be outlined to define the source and composition of the highly-active waste arisings.

The fuel is mechanically decanned and transferred, by the use of specially designed magazines, to the Separation Plant where it is charged into
a dissolver. Here the irradiated uranium rods are continuously dissolved by addition of 6N HNO₃ to produce a solution containing about 300 g/l uranium and about 3N in HNO₃. An oxygen feed is admitted to the atmosphere in the dissolver to aid the recovery of nitric acid from the off-gases in a super-imposed absorber and condensing system. The rod solution from the dissolver is continuously adjusted as required to 3N in HNO₃ and cooled to 20°C in a conditioning vessel following the dissolver. The solution is then fed to the first liquid/liquid extractor. Here the uranium and plutonium are almost completely extracted into 20% TBP/OK solvent and the loaded solvent scrubbed with 2.4N HNO₃ to improve fission product decontamination. The volume and composition of the aqueous raffinate from the first extractor is shown in Table I. This stream contains over 99.9% of the total activity fed to the process and is the main active liquor stream for concentration and storage. The phosphate content of the raffinate, shown as H₃PO₄ equivalent, arises from a number of sources, as impurity in the metal feed, in the recovered acid used for dissolving and stripping, in water used for acid make-up and to a small extent from radiolysis of solvent in the first extractor.

The aluminium and iron arise mainly as minor additions to the fuel for metallurgical reasons and the silica originates from impurities in the metal.

The raffinate from the first extractor is preheated to 80°C and passed through a steam-stripping column where a counter-current flow of steam

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<th>TABLE I</th>
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<td>COMPOSITION OF THE PRIMARY SEPARATION AQUEOUS RAFFINATE</td>
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<td>(per tonne uranium processed)</td>
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| Volume | 6 m³ |
| HNO₃   | 2.54 N |
| U      | < 80'g |
| Pu     | > 1 g |

Solvent

TPB ~ 2 kg
OK ~ 4 kg

Phosphate content = 35 g H₃PO₄

Total fission products ~ 0.6 × 10⁶ c (3600 MWd/t, 3.98 MW/t feed to separation plant)

Al      | 500 - 1200 g |
Fe      | ~ 200 g |
SiO₂    | 35 g |
Total insolubles | < 50 g |
removes almost all the contained solvent. The small amount remaining then raises the total phosphate content, shown in Table I, to about 56 g equivalent of $H_3PO_4$ per tonne of uranium processed. This highly active liquor stream after steam stripping constitutes the main feed to the Highly Active Waste Plant. Its volume is increased during steam stripping to about 6.5 m$^3$/t uranium processed.

The loaded solvent from the first extractor passes into a backwashing contactor where the uranium and plutonium are transferred into a dilute nitric acid solution. The acidity of this aqueous solution is then raised to 3N $HNO_3$, by the addition of strong acid and it is then fed to a second extraction operation similar to the first. The solvent extract, carrying the further purified uranium and plutonium from the second extraction operation, then passes to a "splitting" operation and the uranium and plutonium purification sections of the plant.

The second extraction operation before "splitting" improves the decontamination of uranium and plutonium from fission products and produces a salt-free aqueous raffinate. This increases the fraction of the total activity fed to the process, which can be economically concentrated and permanently stored on the site. This scheme is sometimes referred to as a "late split". The aqueous raffinate (22 m$^3$/t U) from the second extraction is fed to a Medium Active Evaporation and Nitric Acid Recovery Plant along with the following medium active salt-free streams:

1. Steam condensate (3 m$^3$/t U) from the steam-stripping operation on the first extraction raffinate;
2. An acid liquor (1.7 m$^3$/t U) used to wash the solvent from the first extraction cycle;
3. Condensate (6.2 m$^3$/t U) from the evaporation of highly active wastes;
4. Steam condensates (2 m$^3$/t U) from vacuum ejectors used in the Highly Active Waste Plant.

These combined streams are concentrated to a small volume by evaporation and the nitric acid vapour fed to a distillation column which produces 12 N nitric acid for recycle to selected points in the main separation process. The medium-active evaporator concentrate (about 0.2 m$^3$/t U), the composition of which is shown in Table II, is fed to the Highly Active Waste Plant.

**TABLE II**

THE COMPOSITION OF MEDIUM ACTIVE EVAPORATOR CONCENTRATE

(per tonne uranium processed)

<table>
<thead>
<tr>
<th>Volume</th>
<th>0.2 m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HNO_3$</td>
<td>11.5 N</td>
</tr>
<tr>
<td>U</td>
<td>~ 30 g</td>
</tr>
<tr>
<td>Pu</td>
<td>~ 1 g</td>
</tr>
<tr>
<td>Phosphate content ~ 15 g $H_3PO_4$</td>
<td></td>
</tr>
<tr>
<td>Fission products ~ 160 c (3000 MWD/t, 3.98 MW/t feed to separation plant)</td>
<td></td>
</tr>
</tbody>
</table>
along with the steam-stripped first-extraction raffinate. The combined volume of these two streams fed to the Highly Active Waste Plant, allowing a 5% dilution for transfer by steam ejectors will be about 7 m^3/tU processed.

On this basis, the rate of highly-active waste arising for concentration and storage has been inserted as a right-hand ordinate in Fig. 1, and it will be seen that this rises over the period 1962-80 from about 5 to 55 m^3/d.

**Fission-product heat associated with highly-active waste liquors**

Providing for fission-product heat removal in highly-active waste concentration processes and in storage systems is one of the main technical problems in the design of waste facilities. An estimate of the fission-product heat associated with the irradiated fuel-processing programme of Fig. 1 has been made from fission-product yield and decay data and is shown in Fig. 2. This has assumed a gradual build-up in the irradiation levels achieved in the expanding civil nuclear power programme and also an increase in the ratings of reactors introduced in the later years. The cumulative rate of heat output is given in both millions of BTU/hr and in tens of millions of cMeV and it will be seen that the rate of heat output rises to about $23 \times 10^6$ BTU/hr over the 18-yr period. It is generally expected in storage systems that the cumulative rate of heat output will increase fairly rapidly at first and then level off when the rate of activity decay in the system equals the
rate at which the activity is being added to it. However, in this case with an expanding programme, increasing reactor ratings and rising fuel-irradiation levels, the overall effect is a fairly linear increase in the rate of heat output in the period up to 1980.

Seven decay curves have been constructed in Fig. 2 representing the decay of the cumulative activity starting at various points in the programme. The times have been chosen so that the curves will indicate the rate of heat output over the period of the programme, in each of a series of 150-m³ storage tanks filled with highly-active waste concentrate. It is assumed that the liquid waste is concentrated (by evaporation) by a factor of 150:1, giving a final volume of concentrate for storage of 40 l/t U processed. The rate of heat output in any 150-m³ tank at any time is given by the height of the ordinate of its decay curve above the decay curve for material in the previous tank. Although the feed to the Highly Active Waste Plant contains the medium-active concentrate as well as the first-extractor raffinate, and some dilution takes place during the transfer of these streams, it is a convention here that evaporation factors quoted are always based upon the volume of the untreated and undiluted raffinate from the primary separation extractor.

4. FUTURE PROCESSING OF HIGHLY-ACTIVE LIQUID WASTE

In this section, the process which will be used for dealing with future highly-active waste arisings is described and various technical aspects of the processes are discussed. The process, which is shown diagrammatically in Fig. 3, consists of reducing the volume of the acid liquid wastes by evaporation. This ensures that the final storage facilities are as small and there-
CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES

fore as economic as possible. The highly active concentrate is transferred to storage tanks and the nitric acid condensate from the process is fed to a medium-active evaporation and nitric acid recovery plant. The reasons for the choice of the main chemical and physical parameters can be brought out by an examination of the following technical aspects of the process and it is proposed to discuss these separately below.

Maximum concentration factor

The reprocessing system is designed so that the liquors, which contain almost all the fission products from the irradiated fuel, will be free from dissolved salts with the exception of the small amounts of impurities present in the fuel. This allows the largest practical concentration factor to be achieved before the crystallization of the concentrate becomes a problem. The maximum concentration which can be obtained is limited by the crystallization of iron and aluminium nitrate. The aluminium originates solely as a metallurgical addition to the fuel and the iron arises partly from the same source and partly from plant corrosion. The crystallization point is affected by the nitric acid concentration, higher evaporation factors being possible at lower acidities. The presence of phosphoric acid and fission products has only a second-order effect on the crystallization point, but results in the deposition, at fairly low evaporation factors, of finely divided precipitates. The amount and importance of these are discussed under a following heading. The evaporation factors which result in the formation of crystals of iron and aluminium nitrates in highly-active waste concentrate are shown in Fig. 4 for various nitric acid concentrations. It will be seen that for concentrate with an acidity of 5N in nitric acid, an evaporation factor of 250:1 results in a solution which deposits crystals at 20°C. It should be made clear that this graph does not represent the conditions under which the solution completely solidifies due to crystallization but indicates conditions at which the first crystals start to appear. Complete solidification is known to result from an evaporation factor of about 500:1 at 30°C and an acidity of about 3N.

In the evaporation plant it is necessary to cool the concentrate before transferring it from the evaporator to the storage tanks and so, allowing a margin for operating variations, a factor of 150:1 could safely be achieved in the evaporator. This could probably be increased to 200:1 (30 l/t U) in the storage tanks where the concentrate will be maintained at a temperature of about 60°C by fission-product heating and this is a point in favour of having some facilities to allow a concentration factor to be achieved during storage.

The evaporator is operated semi-continuously, having a continuous feed of waste liquor for a period of some months when it is kept at constant level with no take-off. During this time the acidity of the contents follows the curve shown in Fig. 5 rising in the early stages to 8 - 9N and eventually falling and levelling out at about 5N in nitric acid. A curve is also included in the Figure showing how the acidity would vary under similar operating conditions if the feed was pure 2.35N nitric acid. In this case, the acidity rises to 9 - 10N when the vapour in equilibrium with the concentrated acid has the same normality as the feed acid. With the waste solution, the acidity
Evaporation factors resulting in crystallization at 20°C in highly-active waste concentrate at various nitric acid concentrations. (Data from work by P. G. M. Brown, W. T. Fullwood and P. M. Naylor, Chemical Plant Development Group, UKAEA, Windscale).

Acid profiles during the concentration of highly-active waste liquor. (Data from work by P. G. M. Brown, W. T. Fullwood and P. M. Naylor, Chemical Plant Development Group, UKAEA, Windscale).
rises initially in a similar manner to the pure acid, but as the salt content increases and affects the nitric acid vapour/liquid equilibrium the acidity of the concentrate falls and levels out about 5N.

By reference to both Figs. 4 and 5 it can be seen that the high initial acidity during the evaporation cycle does not result in any increased danger of crystals being formed, since at the points where the acid profile is high the concentration factor, and therefore the salt concentration is low.

At the end of an evaporation run, when the contents of the evaporator have reached the desired degree of concentration, water is substituted for the active feed for a period of about two days and the evaporation continued at constant level. In this way the acidity of the final concentrate is reduced to about 4N. It is then cooled and transferred to storage.

Precipitation of finely divided solids in the highly-active waste concentrate

Precipitation of finely divided solids commences at evaporation factors about 3:1 and 10:1 in wastes arising from the processing of fuels having had irradiations of 3000 and 300 MWd/t respectively. At these evaporation factors only traces of solids separate and the amount increases with further concentration. The amount of precipitate produced depends mainly upon the concentration of fission products, particularly Mo and Zr, the phosphate concentration, the acidity and the evaporation factor employed. The quantities of precipitated solids expected in concentrates for various fuel irradiations are shown in Fig. 6 for the anticipated phosphate concentration (approximately \(7.5 \times 10^{-5} \text{ M}\)). The detailed chemistry of the precipitation process is not completely understood but the first material to precipitate is believed to be zirconium phosphate and this is followed by hydrated molybdc oxides and phosphomolydbdate. There is some evidence that at one point the phosphomolydbdic acid \(H_3\text{PO}_4\cdot 12(\text{MoO}_3\cdot x\text{H}_2\text{O})\) is a major product and that later lower phosphomolydbic acids are formed. Molybdenum, zirconium and phosphate are major constituents of the precipitates which also contain to a lesser extent aluminium, caesium, iron, uranium and silicon. The precipitated solids in Fig. 6 are shown as vol./vol. solids, this being the settled volume of the precipitate after standing about 15 hr. The physical characteristics of the precipitates vary according to the precipitation conditions but the corresponding weight/vol. % of dried (110°C) solids is generally about one tenth of the vol./vol. % value, and the solids content of the settled precipitate layer varies between 0.125 and 0.34 g solids/ml.

The problems associated with the presence of these solids in the system are the possibility of blockages of pipe lines in the plant and that of enhanced corrosion where solids accumulate on equipment surfaces. The latter problem of corrosion will be discussed separately in a section below.

Considerable attention has been given to the possibility of modifying the chemical conditions to minimize solids formation in the evaporation plant since it is thought that here, rather than in the storage system, it is more important to keep the solids content as low as possible to minimize any possibility of blockages occurring.

It has been found that the acid peak which occurs during the early stages of the evaporation cycle is partly responsible for the early precipitation of solids, especially fission-product molybdenum, and methods of modifying
The effect of the evaporation factor on the quantities of precipitated solids expected in the highly-active evaporation process for various fuel irradiations and with a phosphate concentration in the highly-active feed of $7.5 \times 10^{-5}$ m. (Data from work by P. G. M. Brown, W. T. Fullwood and P. M. Naylor, Chemical Plant Development Group, UKAEA, Windscale).

The acid profile during concentration have been considered as a means of reducing the amount of solids. The addition of formaldehyde during the evaporation cycle to maintain a constant acidity of about 6N has been tested to an evaporation factor of 150:1 and, under these conditions, the volume of settled solids was reduced to a tenth of its previous level. The solids precipitated, however, were much more dense and the total weight of solids precipitated was only reduced by about 35%. The higher density of the precipitate which would make it more difficult to move in the plant is an unattractive feature of this scheme and formaldehyde does not react smoothly at the temperature of operation (60°C) desired for corrosion reasons.

The addition of an added soluble nitrate, Zn(NO$_3$)$_2$ to reduce the peak acidity conditions has also been considered but this showed an improvement only at lower evaporation factors and it was recognized that this would be a retrograde step with regard to eventual overall volume reduction.

It is considered that the best method of reducing the solids in the evaporation plant is to restrict the evaporation factor there to about 50:1 or
75:1 and to obtain a further 3:1 or 2:1 reduction in the storage tanks. In this way the solids content of liquors in the evaporation plant can be kept below 10% vol./vol. and there is considerable experience, over many years, of operating highly-active evaporation equipment at Windscale with concentrates containing about this level of solids.

In addition, extensive inactive proving trials have been carried out with simulated fission-product precipitates in mock-up plant assemblies and these have shown that this level of solids can be successfully handled.

Corrosion

The need for exceptional equipment reliability in these processes makes the study of the corrosion of stainless steel an important part of technical appraisals leading to the choice of process conditions. It is only possible here, however, to review briefly a few results from the large amount of information which is available on this subject and to summarize the conclusions which are immediately relevant to the highly active waste process.

In highly active plants where maintenance is either entirely precluded or extremely difficult it is the practice to have all plant fabricated of 18/13/Nb stainless steel because of its superior corrosion resistance. This is also used in less active plants for vessels containing strong acid at elevated temperatures. In the case of Highly Active Waste Plants all equipment inside the shielding is of 18/13/Nb. The corrosive attack on this material by nitric acid and highly-active waste concentrates is illustrated by the results of corrosion trials shown in Table III. The penetration rate is affected by temperature, acidity, irradiation of the fuel from which the waste solutions are derived, and the evaporation factor applied to the waste liquors. Increases in temperature have the greatest effect upon the penetration rate, which is unacceptable in strong acid at ordinary boiling temperatures. At 60°C or below the rate of attack is low under all conditions, but between 60°C and 90°C there is a significant increase in the corrosion rate and although the rate is not then at an unacceptable level, wherever possible (for example in storage tanks) 60°C is regarded as an upper limiting figure which should result in the vessels having a very long life.

In the evaporation process it is not practicable to keep all temperatures at this low level but these are reduced as far as possible by vacuum operation at 70 mm Hg pressure. The surface temperature of the boiling concentrate is 60 - 65°C at this pressure, depending upon the degree of concentration attained, and the highest temperature of the metal-heating surface inside the vessel and in contact with the liquor will be about 90°C with a steam pressure of 30-lb/in² gauge. The steam temperature is limited to 135°C in order to ensure that violent solvent/nitric acid reactions are not initiated. This is, in fact, a double safety precaution since a previous steam-stripping process is intended to ensure almost complete removal of solvent from the liquors before feeding to the evaporation stage.

The metal-surface temperature of 90°C which is the worst corrosive condition anticipated in evaporator operation, with a vessel-wall thickness of 1.25 in should give the vessel a life of at least 10 yr with a reasonable safety factor. The possibility has been considered of enhanced corrosion
<table>
<thead>
<tr>
<th>Solution</th>
<th>Acidity</th>
<th>Evaporation factor</th>
<th>Fuel irradiation MWD/t</th>
<th>Temperature</th>
<th>Test period (hr)</th>
<th>Penetration rate (mm/yr)</th>
<th>Parameter investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HNO₃</td>
<td>6 - 12N</td>
<td>-</td>
<td>-</td>
<td>70°C</td>
<td>155</td>
<td>0.2 - 0.8</td>
<td>Acidity</td>
</tr>
<tr>
<td></td>
<td>3 - 6N</td>
<td>-</td>
<td>-</td>
<td>70°C</td>
<td>815</td>
<td>0.0003 - 0.002</td>
<td></td>
</tr>
<tr>
<td>Mock highly-active waste</td>
<td>3 - 9N</td>
<td>150:1</td>
<td>330</td>
<td>80°C</td>
<td>837</td>
<td>0.0005 - 0.005</td>
<td>Effect of acidity</td>
</tr>
<tr>
<td>concentrate</td>
<td>5N</td>
<td>30:1</td>
<td>330 - 3000</td>
<td>60°C</td>
<td>2700</td>
<td>0.0013 - 0.0025</td>
<td>Effect of irradiation</td>
</tr>
<tr>
<td></td>
<td>5N</td>
<td>30:1</td>
<td>330 - 3000</td>
<td>Boil</td>
<td>1000</td>
<td>0.4 - 0.55</td>
<td>Effect of irradiation at boil</td>
</tr>
<tr>
<td></td>
<td>5N</td>
<td>0 - 150:1</td>
<td>3000</td>
<td>60°C</td>
<td>2700</td>
<td>0.002 - 0.006</td>
<td>Effect of evaporation factor at 60°C.</td>
</tr>
<tr>
<td></td>
<td>5N</td>
<td>0 - 150:1</td>
<td>3000</td>
<td>Boil</td>
<td>1000</td>
<td>0.3 - 3.5</td>
<td>Effect of evaporation factor at boil</td>
</tr>
</tbody>
</table>

* Data from the work of W. T. Edward and J. F. Gerrard, UKAEA Reactor materials Laboratory, Culcheth.
arising from deposition of fission-product precipitates on the inside surfaces of the evaporator since it can be postulated that such deposits might increase the metal-skin temperature in localized areas. Extensive inactive trials with mock fission-product precipitates have been carried out to examine the possible build-up of these solids. It has been found that, under boiling conditions, the vigorous liquor movement prevents deposition and solids remaining at the end of an evaporation cycle are easily removed by a simple water wash. Lengthy trials have shown that no significant scale formation occurs and it is considered that the presence of these solids will not make any significant contribution to corrosive attack in the evaporator.

5. FUTURE HIGHLY-ACTIVE LIQUOR EVAPORATION PLANT

To deal with the future arisings of highly-active waste liquors, details of which have been discussed in previous sections, extensions to the Highly Active Evaporation Plant at Windscale are now under construction. Two new evaporation units are being built to carry out the evaporation process described in the previous section of this paper and it is now proposed to discuss the engineering aspects of the design of this new plant.

Design philosophy

The extreme hazards of ionizing radiation and the highly toxic materials involved in the process largely dictate the general design philosophy of the plant. These hazards make it necessary to have remote operation of the plant, heavy shielding to protect the operators from radiation and ventilation provisions which prevent escape of toxic vapours.

Since the decontamination of such highly-active plant is an expensive and lengthy procedure a general direct maintenance system is impracticable. The philosophy adopted is to provide, for the main plant items, simple equipment of high reliability which should require no maintenance. The highly active section of the plant is duplicated to provide a standby unit. This is preferred to introducing the additional complications and expense associated with remote maintenance techniques. Experience of the reliability of previous plants has demonstrated that plant can be fabricated to a high enough standard to allow this philosophy to be applied. Provision is made for direct maintenance of certain selected minor pieces of equipment which are segregated from the main plant and housed in shielded "bulges" situated round the main cell. For example ejectors and sampling equipment are contained in "bulges" and provisions are made for the decontamination of these, followed by direct maintenance which can be carried out without personnel being exposed to radiation from the main plant items. No valves or pumps are used inside the main active cell and a very high standard of fabrication is employed for all equipment in the no-maintenance section of the plant. All vessels and pipelines inside the main cell are manufactured from 18/13/Nb stainless steel and all welds are fully radiographed.

The adoption of a no-maintenance philosophy requires the use of a simple type of evaporator (jacketted kettle) which has a lower performance than
more advanced calandria types. The latter at present require the adoption of remote maintenance techniques involving provisions for replacement of the calandria. The remote maintenance system results in high service and canyon costs and low equipment costs whereas the bias of costs is reversed with a no-maintenance system. Ideally, the combination of a high performance design with high reliability would result in the cheapest system and methods of designing calandria evaporators of improved reliability are now being studied.

Plant description

A flow diagram showing the main items of equipment in the new Evaporation Plant is given in Fig. 7.

The highly-active waste liquor flows along duplicated lines from the Separation and Medium-Active evaporation plants to the feed distributor in the Highly Active Evaporation Plant. This distributor is located at a height to command the cell in use, its duplicate and two lines for future extensions. The liquor then flows through a feed cooler into a 20-m³ stock tank. The cooler extracts the heat which has arisen from the use of force-lift steam ejectors to transport the liquor. The stock tank is also equipped with cooling coils to remove fission-product decay heat if storage becomes necessary for a short period. Force-lift ejectors are used to lift the liquor batch-wise from the stock tank via a break vessel to the constant volume feeder. The ejectors, which are housed in shielded "bulges" on the main cell wall, are equipped with maintainable nozzles and installed spares are provided. The constant volume feeder is a rotating bucket device mechanically driven through the shield wall, the liquor feed-rate being determined by the speed of rotation.

The constant volume feeder is vented to atmosphere through the vessel vent system and the operating pressure in the evaporator is 70 mm Hg. The pressure differential conveys the liquor from the feeder through the in-line cooler into the evaporator. The in-line cooler removes the heat arising from the use of steam ejectors and prevents vaporization in the vacuum leg carrying the feed to the evaporator. The evaporator is heated by a steam jacket and the nitric acid vapour passes through a disentrainment column to the evaporator condenser. The distillate is transferred to the Medium Active Evaporation Plant for concentration and nitric acid recovery. The reduced pressure (70 mm Hg) in the evaporator is maintained by double-stage steam ejectors connected to the evaporator condenser.

The liquor feed to the evaporator is continued until the required evaporation factor is obtained. The active feed is then stopped and replaced by a water feed until the acidity in the concentrate has been reduced to about 4N in nitric acid. On completion of acid reduction the steam supply to the evaporator is stopped, the pressure is allowed to rise to atmospheric and cooling water is applied to reduce the temperature of the concentrate before its removal to storage tanks. Duplicate transfer routes are installed, and in each the concentrate can be removed either by starting a syphon in the outlet leg or by pressurizing the evaporator. The concentrate passes to storage via a distributor which commands all tanks in the storage system.
A simplified flow diagram of the highly-active evaporation plant.
Design criteria

The main design considerations in the plant are those relating to the evaporator where the primary objectives are to achieve the maximum throughput consistent with the high degree of reliability required. The factors affecting these aspects of the design are discussed below.

Corrosion data has shown the need to limit the temperature of operation as far as possible and vacuum operation at 70 mm Hg has been chosen. Recent design studies indicate that a lower pressure may be possible, down to about 50 mm Hg.

To obtain a plant life of at least 10 yr, with a reasonable safety factor, under these vacuum conditions, plate thicknesses of 1.125 in for the evaporator shell and 1.25 in for the bottom are required. The largest diameter petalled dished end which could be fabricated at the time of design, at this metal thickness, was 10 ft. It is now considered that could be possibly increased for later designs.

Experience with existing evaporators of this type has shown that a satisfactorily low carry-over of activity in the distillate results when low boil-up rates of about 25 lb/ft²/hr are employed in conjunction with a simple disentrainment column. The throughput of the evaporator at this low boil-up rate would be about 18 m³/d of waste liquor, but in this design the performance of the disentrainment column has been improved and higher boil-up rates should be possible while still maintaining a low level of activity in the distillate.

The distillate from the existing evaporators is routed to an effluent treatment plant before sea disposal and this limits the amount of activity which can be tolerated in this stream. In the Second Separation Plant, however, a Medium Active Liquor Evaporation Plant will be available to handle the distillate and higher amounts of activity in this stream can be allowed. For this reason it is also expected that the boil-up rate and therefore the throughput of the evaporator may be substantially increased, and the design of ancillary equipment in the cell has taken this into account.

At the end of the evaporation cycle it is necessary to cool the highly active concentrate to avoid vaporization in pipelines during vacuum transfer to storage. It is also necessary to remove fission-product decay heat from the concentrate. Cooling-coils have therefore been installed in the evaporator to supplement the cooling obtained by using cooling water in the steam jacket at the end of the evaporation cycle. Provision has also been made to allow the use of steam in the cooling coils during the evaporation cycle to obtain higher throughputs.

6. FUTURE STORAGE PLANT FOR HIGHLY-ACTIVE LIQUOR CONCENTRATE

Up to the present time highly-active liquid wastes from reprocessing operations at Windscale have been successfully concentrated by a factor of 150:1 in the evaporation plant before storage in 70-m³ stainless-steel tanks which are housed in underground concrete cells. Future highly active
CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES

Waste concentrate will be of higher specific activity and will contain precipitated compounds of fission products of greatly increased activity.

In the period 1962-80 it is estimated that about 28 000 t (metric) of irradiated uranium will arise for reprocessing from the civil nuclear reactor programme.

Assuming that an evaporation factor of 150:1 is applied to this waste the total volume of highly active concentrate for storage during this period will be about 1127 m$^3$. This is equivalent to a concentrate volume of 40 l/t of uranium processed and it is anticipated that the overall concentration will be achieved by obtaining an evaporation factor of 50:1 or 75:1 in the evaporation plant and a further 3:1 or 2:1 in the storage tanks.

Future storage facilities will differ from existing ones in the following respects. The size of tanks will be increased in proportion to the rising scale of reprocessing programmes and the cooling coil density will be increased to deal with the decay heat from concentrates of higher specific activity. A means of agitation will be provided in each tank, so that if required, precipitated solids can be maintained in suspension and provision will be made for a limited amount of evaporation to be carried out in the tanks.

The design of the first new tank for storage of this more highly active waste has now been completed and incorporates the above features. It is expected that this tank will be operational by about the end of 1964. It is now proposed to describe the design features of this new tank and then to discuss the requirements for further storage facilities which will be required up to 1980.

First new storage tank

The new tank will have a liquor capacity of 150 m$^3$ being an upright cylinder 20 ft diam. and 20 ft high with a flat bottom and top. It will be fabricated from 18/13/Nb stainless-steel plate and a multi-pass cooling water jacket of 18/8/1 will cover the bottom of the tank and the lower 3-ft section on the shell.

The water-cooling coils will consist of about 4000 ft of 4-in normal bore (N.B.) 18/13/Nb stainless-steel pipe in the form of hairpin pancake coils. The method of arranging these can be seen from Fig. 8 which shows a scale model of the storage tank with its coil assembly separate.

The coils, five airlift circulators (one large and four small units), and the top of the tank will be assembled separately and attached to a portal framework. When this is complete the coils and circulators will be lowered into the tank and the portal framework, resting on a prepared pin base outside the tank, will support the weight of this assembly.

With a liquor temperature of 50°C and an overall heat-transfer coefficient of 40 BTU/ft$^2$/°F/hr the cooling capacity of the tank will be about $6 \times 10^6$ BTU/hr.

Six jet sparge units, shown in Fig. 8, are built on to the inside wall of the tank. These have nozzles at the lower end and compressed air connections at the top. When in operation the liquor contained in the cylinder will be expelled rapidly through the nozzle by the air pressure and the jet will sweep
the bottom of the tank. The cylinder will then be allowed to refill with liquid for a second purge and the operation will be repeated. The jet sparges can be operated in series to provide an initial dispersal of solids from the bottom of the tank and the airlifts will then maintain this dispersion for some considerable time. It may only be necessary to operate the jet sparges a few times each day.

The tank will be contained in a concrete cell, the walls and roof of which will be about 5 ft thick. The cell will be lined with 18/8/1 stainless-steel sheet up to a level which would contain the complete contents of the tank.

A diagram of the storage cell and ancillary equipment is shown in Fig. 9. Three high-duty ejectors will be installed inside the tank and above the top liquor level for emergency transfer of liquor to a spare storage tank should this be required. The ejectors will raise the liquor to a break vessel and it will then flow by gravity to a distributor which will command all the other tanks in the storage system.

The purpose of the other ancillary equipment associated with the tank is to provide for some evaporation of the tank contents. Filtered air will be pumped through a heater to raise its temperature to 60°C and then supplied to the airlift circulators. The air will be withdrawn from the top of the tank by ventilation fans at the end of the air circuit. On leaving the tank, the air will first pass through a packed disentrainment column (which will drain back into the tank) and then enter a dehumidification tower where it will be cooled and scrubbed by a counter-current flow of cold water. It will then pass to a Peabody scrubber for final decontamination before discharge through a high stack to atmosphere. The water used in the dehumidifier will be recycled through a cooler and returned to the Highly Active Evaporation Plant as necessary.

Technical and economic aspects of future storage tank extensions

In this section it is proposed to discuss the basic principles which will lead to the most economic storage scheme and to examine the importance
Fig. 9
Simplified flow diagram of new storage tank and associated equipment
of various factors in relation to the anticipated waste arisings in the period up to 1980.

The total volume of concentrate arising for storage in this period is 1127 m$^3$ and, after allowing for a small volume which (see Fig. 2) will be stored in existing tanks, the remaining volume requiring new storage has been rounded to 1050 m$^3$. This is a convenient figure for accommodating in the tank schemes considered, which all commence with the 150-m$^3$ tank now under design followed by 150-m$^3$, 300-m$^3$ and 450-m$^3$ tanks.

The overall cost of a storage scheme is affected by the degree of concentration achieved, the tank size chosen and the cooling and shielding requirements. The effects of these factors on the overall cost are discussed separately below.

Evaporation factor

The overall evaporation factor which can be achieved on the highly active waste liquors is of prime importance in determining the scale of highly active concentrate storage facilities and achievement of higher evaporation factors can lead to major economic savings. For example it is shown below that if the 1050 m$^3$ of concentrate which arises over the period 1964-80, with an evaporation factor of 150:1, could be reduced to 750 m$^3$ (200:1) the overall cost of an otherwise optimized storage scheme could be reduced by about 20%. It is important therefore that investigational work to increase evaporation factors be continued and it seems likely on recent evidence that an improvement to about 200:1 can be achieved.

Tank size

Estimates of the capital costs of tanks of various sizes are shown in Fig. 10 and since larger tanks have a lower cost per unit volume it would seem desirable to use the maximum practicable tank size. However, other considerations make it inadvisable to follow this premise to its conclusion. Firstly, the order of tank size must bear a reasonable relationship to the volume rate of concentrate arisings. Also it is undesirable to commit a large capital sum on a storage scheme based on present technical knowledge when substantial improvements in technique (e.g. higher evaporation factors) may be developed before the scheme is fully utilized. It should be the aim therefore to determine an optimum tank size, within a range which is suitable to the size of programme, which will allow advantage to be taken of the future development of new techniques and which is not so small that a heavy financial penalty results from high cost per unit volume. A decision on the best tank size for a future programme can be made by reference to a diagram of the type shown in Fig. 11 which gives estimates of capital costs for a number of tanks of various sizes shown against the total volume of highly active concentrate which they will accommodate. Each horizontal line indicates the capital cost (on the Y axis) of a number of tanks of specific size. Each line is drawn in such a position that it indicates (on the X axis) the total size of waste programme which that number and size of tank could accommodate. For example, a waste programme resulting
CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES

**Capital Costs of Storage Tanks**

COSTS INCLUDE: BUILDING AND CIVIL WORK, PLANT AND EQUIPMENT

COSTS EXCLUDE: COIL COSTS, DEHUMIDIFICATION EQUIPMENT, AND COOLING-TOWER COSTS

**Fig. 10**

Capital costs of tanks of various sizes

**Fig. 11**

Capital costs of various tank schemes for different volumes of highly-active waste concentrate
in a final volume of 1000 m$^3$ of concentrate could be dealt with by providing, 3 $\times$ 600-m$^3$ tanks (1 spare), 4 $\times$ 450-m$^3$ tanks (1 spare), 6 $\times$ 200-m$^3$ tanks (1 spare), or 5 $\times$ 250-m$^3$ tanks (1 spare) etc., and reading the diagram in another manner 5 $\times$ 200-m$^3$ tanks (1 spare) might be built for a programme which would result in a final concentrate volume between 600 and 800-m$^3$. One spare tank has been allowed in each case when the number of full tanks is five or less. Where six or more tanks are to be filled two spare tanks are allowed. This is an arbitrary allowance and present information indicates this may be over-generous since we have not had a storage-tank failure.

By reference to this type of diagram the capital cost of tanks for any programme can be ascertained for a variety of tank sizes. Since evaporation factors might be improved over a period of time, and therefore reduce the final volume for storage, it is necessary to select a tank size which has good cost characteristics over the anticipated volume range of arisings. For example, if it was decided to build 600-m$^3$ tanks in the expectation of a final waste volume of 1200 m$^3$ and later it was found possible to reduce the volume to 500 m$^3$ by increasing the evaporation factor, the initial cost advantage of the 600-m$^3$ tank scheme would then be lost. It would have been cheaper to have used 200-m$^3$ or 300-m$^3$ tanks and only very marginally more expensive to have used 150-m$^3$ or even 450-m$^3$ tanks. In these circumstances the additional engineering difficulties of building such large tanks and the larger amounts of capital required each time of building, would have been no avail in improving the overall cost of the project. On this basis and assuming that the most likely volume range for the UK programme in the period up to 1980 is from 500-1200 m$^3$ the use of 300-m$^3$ tanks would be favoured for new extensions since this is the smallest size which has good cost characteristics over the range.

Cooling requirements

The cost of inactive cooling towers to provide cooling water for the heat-removal system can be regarded as a fixed cost for any scheme and depends upon the anticipated total fission-product heat output.

The cost of cooling coils in the tanks is, however, subject to variation for the same overall heat load depending upon the following factors: - the temperature of liquor in storage, the overall heat-transfer coefficient, the pipe diameter used for the coils and the method of filling the tanks.

It is known that a very low corrosion rate results when a maximum liquor temperature of 60°C is employed and recent designs have been based on an operating temperature of 50°C. This approach to the temperature limitation is probably conservative and temperature increases could result in economy in cooling-coil area, e.g. an increase in the liquor-storage temperature of 10°C could result in a saving of about 5% of the overall capital cost of an otherwise optimized storage scheme.

The heat-transfer coefficient used in recent designs of cooling coils is 40 BTU/hr/ft$^2$°F/hr. This figure is based on measured heat transfer in existing tanks which have no agitation devices fitted and the only circulation is due to convective effects. For future tanks with agitation it will be possible to increase this figure and effect a saving in coils e.g. if this is in-
creased from 40 to 60 BTU/ft²°F/hr. it would result in a saving of about 5% of the overall capital cost of an otherwise optimized storage scheme.

Generally the use of a smaller diameter pipe (2 in or 3 in N. B. as compared with 4 in or 6 in N. B.) for cooling coils would result in a cost saving, but there are a number of engineering considerations which, in certain cases, prevent the use of the smaller diameter pipe. This can for example lead to an inordinately large number of separate cooling circuits and, to give the required cooling area, sometimes leads to a very complex and dense coil system with associated fabrication difficulties. In this respect each tank has to be considered separately to ascertain if a cost saving can be achieved.

The method of filling the tanks influences the overall capital cost of any storage scheme because of its effect on the total coil investment. The simplest filling programme is the consecutive addition of concentrate batches to a single tank until it is full, and then passing on to new tanks and filling them one by one in the same way. This is referred to as series filling.

An alternative method is to use a few tanks which are referred to as "hot" tanks and to series fill these. When the last "hot" tank is full the contents of the first is transferred to a "cool" tank and the filling of the first "hot" tank is recommenced. Similarly, when this is full the contents of the second "hot" tank are transferred to "cool" storage and so on. This is referred to as a hot and cool-tank system.

A third method is to fill a number of tanks simultaneously by adding successive concentrate batches to each of a series of tanks in turn. This is referred to as parallel filling.

Series filling results in high peak cooling loads on individual tanks during the filling programme and later, after a decay period, the installed cooling coils are under-utilized. It also results in a requirement for high cooling capacity in spare tanks.

Parallel filling evens out the heat loading and allows the coil investment to be efficiently utilized and reduces the cooling capacity in spare tanks to a minimum.

The hot and cool system falls between the two in its overall effect on coil utilization, and requires, like series filling, high cooling capacity in spare tanks.

The effect of the choice of filling method upon the total coil investment required for the future waste programme is shown in Table IV. This shows the total cooling capacities and coil investments required in six alternative storage schemes each based on a different tank size or filling system.

The total volume available for liquor storage is the same (1050 m³) in each scheme, and schemes 1-4 have the same (300 m³) spare volume capacity. In schemes 5 and 6 the spare capacity has to be increased to 450 m³ because of the larger tank size employed. At the foot of Table IV the total cooling capacities required to operate the various schemes are shown and it will be seen that the use of a parallel filling method results in substantial reductions in the total cooling capacities required. The total cooling capacity theoretically required in 1980 is shown under all schemes and the cooling capacity required in spare tanks for each scheme is also shown. By adding these two amounts and deducting the sum from the total cooling capacity required to operate each scheme, figures are obtained which represent the cooling capacity wasted in each scheme.
TABLE IV
TOTAL COOLING CAPACITIES AND THE VALUES OF COOLING-COIL INVESTMENTS
IN SIX ALTERNATIVE STORAGE SCHEMES WITH VARIOUS TANK SIZES AND FILLING METHODS

<table>
<thead>
<tr>
<th>Operational date for each tank</th>
<th>Scheme 1</th>
<th>Scheme 2</th>
<th>Scheme 3</th>
<th>Scheme 4</th>
<th>Scheme 5</th>
<th>Scheme 6</th>
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</thead>
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<td>Parallel filling</td>
<td>Series filling</td>
<td>Parallel filling</td>
<td>Series filling</td>
<td>Parallel filling</td>
</tr>
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<td></td>
<td>Tanksize (m$^3$)</td>
<td>Rating ($\times 10^6$ BTU/hr)</td>
<td>Tanksize (m$^3$)</td>
<td>Rating ($\times 10^6$ BTU/hr)</td>
<td>Tanksize (m$^3$)</td>
<td>Rating ($\times 10^6$ BTU/hr)</td>
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<td>150</td>
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<td>150</td>
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<td>72</td>
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<td>8.8</td>
<td>150</td>
<td>3.4</td>
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<td>16.7</td>
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<tr>
<td>74</td>
<td>150</td>
<td>9.6</td>
<td>150</td>
<td>3.3</td>
<td>300</td>
<td>18.7</td>
</tr>
<tr>
<td>76</td>
<td>150</td>
<td>12.0</td>
<td>150</td>
<td>3.2</td>
<td>300</td>
<td>18.7</td>
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<tr>
<td>78</td>
<td>150</td>
<td>13.0</td>
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<tr>
<td>Spare Tanks</td>
<td>64</td>
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<td>150</td>
<td>5.0</td>
<td>300</td>
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<td></td>
<td>150</td>
<td>12.0</td>
<td>150</td>
<td>3.2</td>
<td>300</td>
<td>18.7</td>
</tr>
</tbody>
</table>

(A) Total cooling capacity required to operate schemes

(B) Total theoretical cooling capacity required

(C) Cooling capacity in spare tanks

(D) Cooling capacity wasted (D) = (A) - (B) - (C)

(E) Estimated cost * of coils for total cooling capacity required to operate schemes

(F) Value of cooling coils wasted

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*Note: Cost based on 4-in NB 18/3/Nb stainless-steel coils at £10 000 per million BTU/hr., liquor temperature 50°C and overall H. T. C. = 40 BTU/ft$^2$/°F/hr. If the liquor temperature is raised by 10°C the above coil costs can be divided by 1.4. If the overall heat-transfer coefficient is raised to 60 BTU/ft$^2$/°F/hr the costs can be divided by 1.5. With both effects together the factor is 2.1.
The total cooling capacity required for each scheme and the cooling capacity wasted have been converted to monetary values in the bottom two lines of the Table. It is assumed that 4-in N.B. 18/13/Nb stainless-steel coils would be installed to provide the cooling capacities, that the liquor temperature would be 50°C and the overall heat-transfer coefficient would be 40 BTU/ft²/°F/hr.

The figures show that substantial savings can be obtained by adopting a parallel filling technique. In fact the total investment in coils in the parallel filling schemes is less than the value of the coils wasted in one of the series filled schemes. The parallel filling method approaches the theoretical cooling requirement and results in a minimum of wasted cooling capacity. In a previous section on tank costs the 300-m³ tank size has been shown to have the best cost characteristics for the programme considered and again, in terms of coil investment, the 300-m³ tank with a parallel filling technique is the cheapest scheme. It might have been expected that the 450-m³ tanks would have better coil utilization than the 300-m³ size, but the advantages of the larger tank in this respect are more than offset by the higher spare cooling capacity required.

Overall costs of future highly-active waste storage

From the costs already given in Figs. 10 and 11 and in Table IV some examples of the overall capital costs of various schemes have been prepared and are given in Table V.

The total capital costs in all schemes include a fixed charge of £100,000 for cooling water towers and dehumidification plant, and variable charges for tank and coil costs. Each scheme provides for storage of a total volume of 1050 m³ of highly-active waste concentrate at an evaporation factor of 150:1 or a correspondingly lower volume at a higher evaporation factor.

It is known at present that the conditions (evaporation factor, temperature and heat-transfer coefficient) associated with schemes 1-6 in Table V can be technically achieved, while the use of higher temperatures, heat-transfer coefficients and evaporation factors in schemes 7-18 will depend upon the results of future technical development. The costs of these latter schemes show the extent to which further economic improvement is thought to be possible.

The costs of schemes 1-6 show that substantial savings can be achieved by adopting a parallel filling technique and increasing the tank size from 150 m³ to 300 m³, but that a further increase to 450 m³ results only in a marginal saving. Since it is desirable to build the smallest tanks which have good cost characteristics scheme 4 would be the preferred system.

The overall capital costs in each case have been converted to a unit charge on electricity generated from the future power programme. These are shown in parenthesis in Table V as pence/kilowatt hour. The costs derived in this way represent the capital cost component attributable to highly-active liquor storage. The cost of scheme 4 on this basis is about 0.001 pence/kWh and this might be reduced to about 0.00076 pence/kWh by further technical development.

Overall it is concluded that the concentration and storage of highly-active waste liquors can be successfully and economically extended using the
### TABLE V

ESTIMATES OF THE OVERALL CAPITAL COSTS OF VARIOUS METHODS OF EXTENDING THE STORAGE FACILITIES FOR HIGHLY-ACTIVE WASTE CONCENTRATE IN THE PERIOD 1962-80

<table>
<thead>
<tr>
<th>Method of filling</th>
<th>Tank size used after first tank which is 150 m³ in all schemes</th>
<th>150 m³</th>
<th>150 m³</th>
<th>300 m³</th>
<th>300 m³</th>
<th>450 m³</th>
<th>450 m³</th>
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<td>Parallel</td>
<td>Series</td>
<td>Parallel</td>
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<td></td>
<td>Scheme 1</td>
<td>£3,520,000</td>
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<td>£2,660,000</td>
<td>£2,330,000</td>
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<td></td>
<td></td>
<td></td>
<td>(0.00153)</td>
<td>(0.00130)</td>
<td>(0.00115)</td>
<td>(0.00101)</td>
<td>(0.00111)</td>
</tr>
<tr>
<td></td>
<td>Liquor temp. 50°C</td>
<td>Scheme 2</td>
<td>£3,000,000</td>
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<td>£2,330,000</td>
<td>£2,550,000</td>
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<tr>
<td>Overall heat-transfer coefficient = 40 BTU/ft²/°F/hr</td>
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<td></td>
<td>(0.00130)</td>
<td>(0.00115)</td>
<td>(0.00101)</td>
<td>(0.00111)</td>
<td>(0.00101)</td>
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<td>Scheme 3</td>
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<td>(0.00101)</td>
<td>(0.00111)</td>
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<tr>
<td>Overall heat-transfer coefficient = 60 BTU/ft²/°F/hr</td>
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<td>(0.00078)</td>
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</table>

Notes:  
1. Fixed charges on all schemes are New Cooling Towers and Dehumidification Plant £100,000.  
2. Variable charges are tank and coil costs.  
3. Figures in parenthesis are the average capital costs of storage schemes in pence per kilowatt hour of electricity generated.  

* These schemes use 1 x 150 m³ tank and 3 x 450 m³ tanks. At the end of the programme considered there would still remain a volume of 300 m³ available for further liquor storage in these systems. Allowances for this have been made to bring the figures to a comparable basis with the other capital costs in the Table.
CONCENTRATION AND STORAGE OF HIGHLY-ACTIVE WASTES

present plant design philosophy and this system can satisfactorily support the UK civil nuclear power programme during its first twenty years.

ACKNOWLEDGEMENTS

This paper draws extensively on the results of technical and engineering work by a large number of UKAEA staff. Grateful acknowledgement is made to Mr. B. F. Warner, Mr. W. W. Marshall and the staff of the Chemical Plant Development Group at Windscale for contributing technical information, and to Mr. L. P. Shortis and Mr. W. Higginson, Windscale Plants Design Office, for the engineering aspects of the plants described. The assistance of Mr. H. M. Gauld during the preparation of this paper is also gratefully acknowledged.

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HANFORD HIGH-LEVEL WASTE MANAGEMENT

R. E. TOMLINSON
HANFORD LABORATORIES, GENERAL ELECTRIC CO., RICHLAND, WASH.

Abstract — Résumé — Аннотация — Resumen

HANFORD HIGH-LEVEL WASTE MANAGEMENT. During the 17-year history of Hanford operations, a high degree of safety has been provided at reasonable cost by storing high-level radiochemical wastes as alkaline slurries in underground tanks. Since this operation has been regarded as an interim measure only, a programme is being developed to decrease the mobility of the stored materials in order to achieve an increased assurance of continued containment of the stored materials.

As currently visualized the large volumes of essentially non-heating dejacketing wastes will be evaporated to salt cakes in existing underground tanks. Laboratory studies and prototype operation in a 5000-gal tank indicate that the passage of heated air through the solution can remove enough water that, with controlled carbonation to convert free caustic to sodium carbonate, a non-hygroscopic salt cake can be formed. The self-heating wastes will be fractionized to permit the separate storage of the long-lived heat emitters in small volume, high-integrity containers. These materials could be made available for beneficial use on request. After 5 to 10 years decay of the short-lived heat emitters, the residual salt wastes will be combined with current dejacketing wastes and evaporated to salt cakes.

Assuming the concurrence of the United States Atomic Energy Commission an obsolete canyon-type building will be reactivated and revised to conduct the chemical processing operations required. Solvent extraction (D2EHPA) will probably be used to isolate strontium and cerium from acid waste. A choice has not yet been made between solvent extraction, ion exchange and precipitation for caesium isolation. The integrated operation is anticipated to be in operation about 1966.

GESTION DES DÉCHETS DE HAUTE ACTIVITÉ À HANFORD. Pendant les dix-sept années de fonctionnement des installations de Hanford, on a obtenu un degré de sécurité élevé à un coût raisonnable en stockant les déchets radiochimiques de haute activité, sous forme de boues alcalines, dans des réservoirs souterrains. Comme on considère cette opération comme une mesure provisoire, on s'occupe activement de mettre au point une méthode permettant de réduire la mobilité des matières stockées, afin d'être plus certain de leur confinement à long terme.

Dans les réservoirs souterrains existants, on fera évaporer, jusqu'à obtention de tourteaux de sel, les volumes importants de déchets et de gainage, qui, par nature, sont peu susceptibles d'auto-échauffement. Les études en laboratoire et les premiers essais effectués avec un réservoir de 5000 gallons montrent que le passage d'un courant d'air chaud à travers la solution, associé à une carbonatation contrôlée pour transformer l'hydroxyde de sodium libre en carbonate de sodium, permet d'éliminer suffisamment d'eau pour former un tourteau de sel non hygroscopique. Les déchets susceptibles d'auto-échauffement seront fractionnés pour permettre d'entreposer séparément les émetteurs de chaleur à longue période dans de petits récipients très résistants. Étant donné que ces matières peuvent être utilisées avec profit, on pourrait en obtenir sur demande. Après 5 à 10 ans de désintégration des émetteurs de chaleur à courte période, les déchets salins résiduels seront combinis avec les déchets courants de dégaineage pour évaporation comme il est dit plus haut.

Pour pouvoir mener à bien le traitement chimique nécessaire, on aménage un ancien bâtiment à cellules isolées. On recouvre probablement à l'extraction par solvant (D2EHPA) pour séparer le strontium et le céurium des déchets acides, mais on n'a pas encore décidé si la séparation du céurium se fera au moyen de l'extraction par solvant, par échanges d'ions ou par précipitation. On prévoit que l'ensemble de l'opération pourra être réalisé aux environs de 1966.

ОБРАБОТКА ВЫСОКОРАДИОАКТИВНЫХ ОТХОДОВ В ХЭНФОРДЕ. За 17 лет в Хэнфорде достигнута высокая степень безопасности хранения высокорадиоактивных отходов в виде целочных шламов в подземных баках при сравнительно невысокой стоимостью. В настоящее время осуществляется программа ощерения подвижности хранимых материалов для достижения большей уверенности в надежности их длительного хранения.
Большие объемы практически не нагревающихся отходов, полученных в результате снятия оболочек с тепловыделяющих элементов, будут упариваться в существующих подземных баках до получения соленых брикетов. Лабораторные исследования и пробная операция в баке емкостью в 18 900 л показывают, что путем пропускания нагретого воздуха через раствор можно удалить достаточное количество воды и что регулируемое насыщение угольной кислотой для превращения свободного щелочного натрия в карбонат дает возможность получать негигроскопичные соляные брикеты. Самопроизвольно нагревающиеся отходы будут фракционизироваться для того, чтобы долгоживущие излучатели тепла можно было хранить раздельно в прочных контейнерах малого объема. В случае необходимости эти материалы могут быть использованы для различных целей. Через 5 или 10 лет после распада короткоживущих излучателей тепла, оставшиеся солянные отходы будут смещиваться с отходами, полученными в результате удаления оболочек, упариваться и брикетироваться.

Для проведения необходимых работ по химической переработке в настоящее время восстанавливаются и реконструируются старое здание с каньонами. Для выделения стронция и церия из кислотных отходов, вероятно, будет использован метод экстракции растворителем (D2EHPA). Для выделения церия еще не сделан окончательный выбор между экстракцией, ионным обменом и методом осаждения. Предполагается, что процессы выделения отдельных изотопов будут внесены примерно в 1966 году.

1. INTRODUCTION

In 1944, the Hanford plant was activated to produce plutonium; the plant facilities are still in operation for this and other purposes. At the present time, the Hanford Atomic Products Operation (HAPO) is operated by the General Electric Company for the United States Atomic Energy Commission.

At Hanford, plutonium is produced by irradiating aluminium-jacketed, natural or slightly enriched uranium in graphite-moderated reactors. In the Chemical Processing Department, the irradiated fuel is processed for the recovery of useful products, including limited quantities of caesium-137 and strontium-90 on a custom-order basis. The residual fission products are concentrated in chemical process wastes, are made alkaline, and are stored in underground tanks.

During the past few years, research and development efforts at Hanford have been concentrated on developing ways to increase the certainty of con-
fining these highly radioactive materials for long periods of time. A definite programme for the immobilization of existing and future Hanford wastes has now been evolved. This programme has been proposed to the Atomic Energy Commission, but no decision has yet been reached as to when or how it will be implemented. This programme is specifically designed for Hanford's wastes, and it is designed to make optimum use of the existing facilities and of the favourable geology and climate of the area. The purpose of this paper is to describe the Hanford waste-management programme as currently visualized, noting those factors that influenced the particular choice of programme features.

The technologies embraced by this programme have been developed during the past several years by engineers and scientists at many locations in the USA and Europe. The more promising processes and techniques are currently undergoing intensive development in the Hanford Laboratories.

2. PROGRAMME OBJECTIVES AND PREMISES

The objectives of Hanford's programme for managing high-level wastes are to provide the technology and facilities required to:

1. Control and minimize the hazards, both short-term and long-term, associated with the high-level radiochemical wastes from the separations processes;

2. Recover by-products as requested by the Atomic Energy Commission; and

3. Reduce the cost of waste management to a minimum, consistent with meeting objectives (1) and (2).

After the required technology becomes available, the measurable cost of waste management includes two elements, viz.,

1. The capital and operating costs of processing the wastes to a form suitable for long-term storage; and

2. Future costs for surveillance, for the replacement of storage facilities, and for the transfer of waste or other processing as required.

Certain intangible cost factors should also be assessed. For example, there exists a potential liability arising from the inadvertent release of fission products by some unforeseen mechanism and some loss of public confidence could result from such a release. Since little basis exists for estimating either the magnitude or the timing of such cost factors, no attempt will be made here to evaluate these latter elements of cost.

3. THE SITUATION

The development of an optimum programme for managing high-level wastes at Hanford requires the consideration of many factors unique to the Hanford situation. Of primary importance are the characteristics of the environment, the magnitude and characteristics of existing and future radioactive wastes, the availability and potential usefulness of existing facilities not in current use, and the increasing interest in recovering specific fission products for beneficial use. These factors are discussed below.
A. Environmental factors

The Hanford plant is located in the south-eastern portion of the state of Washington. The terrain in this part of the state is typical of arid countries with an average rainfall of about 20 cm/yr. The site of the separations plants is on a plateau of dry sandy soil, about 60 to 70 m above the level of the underground waters. This soil is capable of retaining liquids to the extent of 7 to 10% of its volume by capillarity; lateral flow increases this retention capability such that at least 200,000 l of liquid can be released at a point without drainage to the underground water. In addition, the soil has ion-exchange properties so that the migration rate of fission products is slower than that of the liquid.

B. Radiochemical wastes

For purposes of this discussion, the high-level radiochemical wastes from Hanford separations processes are classified as "self-heating" or "non-heating", depending on the concentration of decaying fission products present. In the more concentrated wastes, enough heat is generated to self-heat the wastes to a boiling temperature in the Hanford tanks, while the less active wastes remain at some temperature below the boiling point. In the Hanford facilities, the point of demarcation between "self-heating" and "non-heating" wastes is about 20 to 50 W/m³ of waste.

1. Self-heating wastes

Since 1952 and 1956, respectively, the Redox and Purex solvent extraction processes have been used for the simultaneous recovery of uranium and plutonium from irradiated fuels. In each process, nearly all of the radioactive wastes are accumulated in a relatively small volume of solution of process chemicals. These waste solutions are made alkaline and are routed to underground tanks where they are permitted to self-concentrate as much as practical.

The volumes and approximate chemical compositions of these wastes, as currently stored in the concentrated condition, are tabulated in Table I. Plans are being implemented to remove some of the nitrate ion from the Purex wastes by reaction with formaldehyde before neutralization; the anticipated characteristics of this future Purex waste are also indicated. Scouting investigations are also in progress to develop changes in the Redox process so that a waste of lower salt content can be produced.

Earlier operation of the Redox and Purex processes gave rise to salt-waste effluents of essentially the same chemical composition as current wastes, but having significantly larger volumes per unit of production.

The stored self-heating wastes have separated into two phases - a supernatant liquid containing most of the caesium, and a sludge layer containing more than 99% of the strontium and rare earths. Preliminary data indicate that at least two-thirds of the sludge, which now occupies up to 15% of the total volume, can be dissolved in hot water. The dissolved material is com-
### TABLE I

HANFORD SELF-HEATING WASTES

<table>
<thead>
<tr>
<th>Chemical composition, in moles/l</th>
<th>Current, alkaline Purex</th>
<th>Future, acid Purex</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>NaNO₃, NaNO₂</td>
<td>3.1</td>
<td>7.0</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.8</td>
<td>0.05</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe(NO₃)₅</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Range in stored volume, in hundreds of liters per tonne of uranium

<table>
<thead>
<tr>
<th></th>
<th>Present</th>
<th>Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>3 - 5</td>
<td>15 - 20</td>
</tr>
<tr>
<td>Future</td>
<td>-</td>
<td>1.5 - 3</td>
</tr>
</tbody>
</table>

posed primarily of sodium nitrate, sodium nitrite and sodium carbonate; it contains some caesium but virtually no strontium or rare earths.

Tens of millions of liters of these self-heating radiochemical wastes are currently in existence. These wastes are being stored in the "A" and "SX" tanks described in a later section. The salt content of these wastes is such that, if water were removed, the resultant salt cake would occupy a volume about half that currently occupied by the wastes.

2. Non-heating wastes

Non-heating wastes have been generated from three sources, viz., the chemical dissolution of aluminium jackets, the processing of irradiated fuels by the now-obsolete bismuth phosphate precipitation process and the aging of the more dilute (in fission products) supernatant solutions in the Redox wastes. The approximate chemical compositions of the non-heating wastes are noted in Table II. The bismuth phosphate wastes in storage are the residue from several waste processing operations conducted in past years. The BiPO₄ process did not recover uranium, but routed it with the bulk of the fission products to underground storage. The uranium-containing
TABLE II

HANFORD NON-HEATING WASTES

<table>
<thead>
<tr>
<th></th>
<th>Aluminium Decladding waste</th>
<th>Bismuth phosphate, U-recovery waste</th>
<th>Aged Redox supernate</th>
<th>Zirflex waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in mole/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>NaNO₃, NaNO₂</td>
<td>2.0</td>
<td>6.0</td>
<td>3.7</td>
<td>0.06</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaAlO₂</td>
<td>1.9</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Na₂ZrF₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Range in stored volume,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in hundreds of liters</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>per tonne of uranium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>7 - 10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Future</td>
<td>7 - 10</td>
<td>-</td>
<td>-</td>
<td>20 - 40</td>
</tr>
</tbody>
</table>

Wastes were subsequently removed from the tanks by sluice-mining techniques and acidified; the uranium was recovered by solvent extraction and the residual wastes were again made alkaline. Caesium was concentrated in the insoluble fraction by scavenging with nickel ferrocyanide, and some of the residual supernatant solutions were routed to the soil where they were retained by capillarity. Some of the other BiPO₄ process wastes were concentrated in an external evaporator.

The decladding wastes are stored as produced. In the future, fuels irradiated in the new production reactor (NPR) currently under construction will be clad in zirconium. This material is to be removed by dissolution in ammonium fluoride and will be contained in the "Zirflex" wastes.

Many tens of millions of liters of non-heating wastes are currently in existence. These wastes are being stored in all of the tank farms (except A and SX) described in a later section. The salt contents of these wastes are such that, if all of the water were removed, the resultant salt cake would occupy a volume one-third to one-fourth that currently occupied by the wastes.

C. Existing facilities

During the past 18 years of plant operation, many facilities were constructed for specific purposes. Some of these facilities have fulfilled their
purposes and are no longer in use. Other facilities are in use, but their functions could be changed to meet new demands.

1. Waste-storage tanks

The complex of waste-storage tanks at Hanford includes 145 tanks, ranging in capacity from 200 000 to 3 785 000 l. These tanks are grouped in eleven tank farms; five of the farms are in the east operating area, while six are in the west area. The farms are within about a 2-km range within each area, and the areas are about 7 km apart. Some general information about these tanks is tabulated in Table III.

**TABLE III**

WASTE STORAGE TANKS AT HANFORD

<table>
<thead>
<tr>
<th>Location, tank farm</th>
<th>Year constructed</th>
<th>Number of tanks</th>
<th>Volume, thousands of liters per tank</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>B, C, T, U</td>
<td>1943-44</td>
<td>16</td>
<td>200</td>
<td>3 200</td>
</tr>
<tr>
<td>B, BX, C, T, U</td>
<td>1943-47</td>
<td>60</td>
<td>2000</td>
<td>120 000</td>
</tr>
<tr>
<td>B, Y, S, TX, TY</td>
<td>1947-52</td>
<td>48</td>
<td>2875</td>
<td>138 000</td>
</tr>
<tr>
<td>A, SX</td>
<td>1953-55</td>
<td>21</td>
<td>3785</td>
<td>79 500</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td><strong>145</strong></td>
<td></td>
<td><strong>340 700</strong></td>
</tr>
</tbody>
</table>

The vessels in the B, BX; C, T, and U farms are of the type described in Fig. 1. These vessels are constructed of reinforced concrete with a mild steel liner on the bottom and side walls. The vessels are placed with the top of the dome about 2 m below the ground surface. The earth serves both as shielding and as a sink for the dissipation of the heat from radioactive decay. The inside diameter of the 2 000 000-l vessels is 23 m, with a working depth of 5.5 m. These vessels are vented to the atmosphere through air-cooled reflux condensers.

Monthly measurements are made of the liquid level in all of these storage tanks; more frequent measurements are made if transfers are made into or out of the vessel or if a leak is suspected. The current accuracy of measurement of liquid level by manual probe is about plus or minus 1 cm; this measurement is equivalent to about plus or minus 4000 l of liquid in a 23-m-diam. tank. A more precise electronic measurement device is being developed at Hanford, together with a centralized read-out facility for improved surveillance. A grid of dry wells in the tank farms is used regularly to monitor the soil for radioactivity, thus serving as a secondary leak-detection system.

The vessels in the A and SX farms are of the type described in Fig. 2. These vessels are also constructed of reinforced concrete with carbon steel
liners on bottom and side wall. The diameter of this type vessel is also 23 m; with a working height of nearly 10 m, the tank will hold 3,785,000 l. These vessels are designed to permit self-concentration, the vapours being routed through headers to water-cooled surface condensers which are vented to the atmosphere through fibrous glass filters. Condensate is collected in a tank and is discarded or returned to the tank to avoid over-concentration. Agitation of the tank’s contents is provided by the operation of one or more of four air-lift circulators, each about 60 cm in diam, and 3 to 4 m tall. Since inventory measurements are not precise in the dynamic system, each tank is closely encompassed by a complex of vertical and horizontal dry
wells so that any leaks may be detected by monitoring for radioactivity in the soil surrounding the tank.

The vessels in the BY, S, TX, and TY farms are of the same diameter and are structurally similar to those in the A and SX farms. They are similar to the smaller tanks, however, in that they are not equipped with air-lift circulators or water-cooled condensers; leak detection is by periodic liquid-level measurement, with a grid of vertical dry wells providing a secondary leak-detection method.

Four of the older tanks developed leaks after 8 to 12 yr of storing non-heating wastes. The leaks were first detected by observing a slowly declining inventory (400 to 2500 l/d); the leaks were subsequently verified by detecting radioactivity in the soil. In each case, the tank's contents were pumped to another tank and the leaking tank was withdrawn from service. In no case was any radioactivity from a leaking tank found in the underground water. A fifth tank was withdrawn from service when the steel liner was observed to buckle soon after self-heating wastes were added to a nearly empty tank. While all evidence indicates that no leak actually developed, it was considered prudent to remove the radioactive wastes from the vessel.

2. Waste-transfer system

In 1952, a network of underground lines and transfer stations was installed to connect many of the underground tanks with the building used to recover uranium from the stored wastes from the bismuth phosphate process. These lines are constructed of stainless-steel tubing about 9 cm in diam, and are contained in concrete trenches. Multiple lines interconnect the older tank farms in each area with a pumping station, and the two pumping stations are interconnected by multiple inter-area transfer lines.

3. The 221-B canyon building

The 221-B Canyon Building was constructed in 1943 to recover plutonium using the bismuth phosphate precipitation process. The building was subsequently deactivated and is thus available for a new processing assignment.

The structure includes a heavily-shielded process area, together with service areas for chemical make-up, process control, administration, etc. See Fig. 3. The process area comprises a line of process cells which are covered with removable concrete blocks to form the canyon deck. The canyon contains 35 of these cells equipped for process functions, plus five cells equipped for service functions such as sump drainage, railroad access, and storage. Each process cell has a floor area 4 by 5.5 m, with a usable height of 6 m. Pipe and electrical outlets are located near the top on three sides of each cell. These outlets are connected, by piping through the concrete walls, with the operating area on the one side, and with a pipe trench for inter-cell transfer on the other. Equipment in the cells may be connected with these outlets through the use of jumpers, or short sections of pipe, with remotely-operable connecting heads. Cell equipment and jumpers can be installed or removed by a remotely-operated, travelling bridge crane; peri-
scopes enable the operator to see into the process cell and thereby manipulate hoods and wrenches suspended from the crane.

4. North area storage basin

During initial Hanford operations, irradiated fuel from the reactors was stored for decay, before chemical processing, in three storage basins located about 3 km north of the separations area. These facilities comprise the 200 north area. The use of these facilities was later discontinued, and the north storage basins are available for other use. Each basin covers an area of 9.5 by 18 m and has a water depth of 6.5 m. See Fig. 4. Material
Fig. 4
200-North storage basin.
handling facilities include an unloading station and an overhead monorail system for positioning storage containers in the basin.

5: The Purex head-end

As initially designed and operated, the Purex process included the centrifuging of dissolved fuel to minimize the quantity of extraneous solids carried into the solvent extraction equipment. The pulse columns were subsequently modified to tolerate these solids, and the clarification equipment was bypassed. This bypassed equipment consists of two solid-bowl centrifuges, 150 cm in diam, and associated tankage. This equipment is currently being used to recover strontium on a custom-order basis and to pilot the recovery of other fission products as well.

D. Fission-product recovery

Many of the fission products that create the problems of waste management have potential value as by-products. For example, the use of strontium-90 and caesium-137 is being developed as a source of power for specialized applications, and promethium-147 may prove valuable in this way as well. Caesium-137 is also of value for teletherapy and radiography. Technetium-99 is not found in nature and radioactive wastes constitute its only source of supply.

While the current demand for separated fission products is small, the optimists foresee a growing demand for these materials. Under these conditions, one is not justified in committing capital expenditures for the recovery of large quantities of isolated fission products. On the other hand, it would appear prudent to shape any new programme for waste management so that the recovery of fission products is compatible with the waste-processing operations, provided the compatibility can be achieved at little or no additional cost.

IV. THE PROGRAMME

Assuming the concurrence of the Atomic Energy Commission, the non-heating wastes are to be immobilized by the evaporation of water, permitting the residual salts to solidify in the existing underground tanks. Self-heating wastes would be processed for the removal of the long-lived heat producers (caesium and strontium), stored as required to permit the decay of the short-lived heat producers, and the residual salt solutions immobilized with the non-heating wastes. The separated caesium and strontium would be adsorbed on a zeolite and stored in stainless steel containers under controlled conditions. A diagram indicating the proposed sequence of processing operations is presented in Fig. 5. The process steps involved are described in more detail below.
A. Immobilization of non-heating wastes

Non-heating wastes would be immobilized by evaporation, passing heated air through the solution in the tank to remove the water. See Fig. 6. Air, pumped through a 1500-kW electric heater at about 140,000 l/min, would be heated to about 800°C. The passage of heated air was chosen as the concentration method because most of the required equipment can be located above ground; the major equipment would not be grossly contaminated while in use and would be readily moved from tank to tank. Electricity was chosen as the source of power because hydroelectric power is relatively inexpensive in the Hanford area ($17.50/kW-yr), and because the waste-evaporation unit can then be designed to be fail-safe so that constant operator attendance would not be required. The heated air would be introduced well below the surface of the liquid within a shroud tube. Introducing the heated air in this way accomplishes three things. First, the heated air is brought into intimate contact with the liquid, thereby assuring efficient use of the heat. Second, the air rising in the shroud tube creates liquid-circulation rates up to tens of thousands of liters per minute, thereby assuring uniform concentration of the tank's contents. Third, some heat is transferred from the incoming air to the liquid through the finned air-introduction tube, thereby reducing the air temperature at the time of initial air/liquid contact. Experimental work has shown that, in units of this type, entrainment in the effluent gases is minimized by keeping the temperature of the air relatively low (say, 400°
-500°C) at the time of initial air/liquid contact. The effluent gases would be passed through de-entraining devices, a condenser and a fibrous glass filter. The filtered air would be released to the atmosphere; if contamination of the environs becomes a problem, the air can be recycled. The condensate would be discarded to the ground where the trace fission products would be adsorbed and retained in the soil as the water percolates through the ground water.

Laboratory studies and small-scale pilot experiments indicate that water can be removed from the non-heating wastes in this way to such an extent that, upon cooling, the residual salts will crystallize to a massive salt cake. During concentration, the temperature of the liquid waste would rise from about 70°C to the range of 95° to 100°C. Some carbon dioxide would be added to neutralize excess sodium hydroxide, thereby reducing the affinity of the salts for water. After the external source of heat is removed, the partially crystallized mass would cool at a rate determined by the rate of heat loss to the environment, and by the rate of heat generation from the decay of contained fission products. Calculations indicate that self-generated heat can be dissipated at rates up to 5 W/m³ at temperatures that will permit the formation of a salt cake up to 5 m thick. It is predicted that, under operating conditions, a thick layer of salt cake would form on all sides within a few months, but that the centre may remain liquid for a few years.

After the salt cakes have formed, no operational control would be required and concern about structural failure would be minimal. The isolation
and immobility of the stored material are such that no postulated combination of equipment failure and natural phenomena characteristic of the Hanford area could expose the material to life cycles. Rainfall is so slight in the Hanford area that surface waters are evaporated and no percolation to the underground waters occurs. The level of the underground waters would have to rise more than 50 m before contact could be made with the stored material.

B. Fractionization of acid Purex wastes

The radiochemical wastes produced by the processing of irradiated fuels contain a variety of heat-producing fission products. Most of the heat emitters have half-lives measured in days or months, but a small fraction of the heat generation comes from the longer-lived isotopes. Of specific concern are 30-yr caesium-137, 28-yr strontium-90, 2.5-yr promethium-147, and 285-d cerium-144. The removal of some or all of these isotopes would permit the residual wastes to be treated as a non-heating waste after a few years storage. As illustrated in Fig. 7, the salt wastes from one year's processing at 10 t(m)/d uranium, after irradiation at 5 MW/t to 1000 MWd/t and a 90-d cooling, would generate heat at rates up to 3000 kW. If the accumulated wastes were then permitted to cool, the rate of heat generation would fall to a value about 5% of the peak rate during the first five years.

![Diagram of heat generation in hypothetical waste-storage tank.](image)

**Fig. 7**
Heat generation in hypothetical waste-storage tank.

- **Basis:** Enrichment - 1.2%
- Power level - 5 MW/t
- Irradiation time - 200 d
- Decay before separation - 90 d
- Fill rate - 10 t/d uranium

Fractionization:
1. None
2. Cs, Sr removed
3. Cs, Sr, Ce, RE removed
and would fall very slowly beyond that time. Using Fig. 7 and other data as a basis, the rates of heat generation and heat dissipation in postulated systems can be compared. In Table IV, a variety of processing conditions is assumed, and the decay times required before certain conditions could be met are tabulated.

Under the conditions assumed in Table IV, decades would be required before untreated stored wastes would stop boiling, and more than a century of storage would be required before such wastes could be safely evaporated to a massive salt cake. If all of the caesium and strontium were removed, however, it should be possible to evaporate the waste to a massive salt cake after less than 10 yr of decay. Any process inefficiency resulting in small amounts of caesium or strontium remaining with the salt waste would, of course, have a significant effect on the required decay time. In this case, up to 5% residual caesium/strontium might be tolerated if the amount of inert salts is doubled as by blending the salt wastes with the coating wastes before forming the salt cake. If an incentive were present to minimize the volume

**TABLE IV**

**OPERATING CHARACTERISTICS OF A HYPOTHETICAL WASTE STORAGE TANK**

<table>
<thead>
<tr>
<th>Assumptions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Uranium irradiated at 5 MW/t to 1000 MWd/t.</td>
</tr>
<tr>
<td>2. Fuel processed after 90 d cooling, at 10 t/d.</td>
</tr>
<tr>
<td>3. Salt waste occupies 500 l/t as liquid, 250 l/t as salt cake.</td>
</tr>
<tr>
<td>4. Coating waste occupies 1000 l/t as liquid, 250 l/t as salt cake.</td>
</tr>
<tr>
<td>5. Nominal 1800 000-1 tank used for storage.</td>
</tr>
<tr>
<td>6. Heat generation as a function of time as in Fig. 6.</td>
</tr>
<tr>
<td>7. Storage condition - Liquid Salt cake Salt cake</td>
</tr>
<tr>
<td>8. Waste contained - Salt Salt Salt + coating</td>
</tr>
<tr>
<td>9. Capacity, tonne-equiv. - 3650 7300 3650</td>
</tr>
<tr>
<td>10. Heat lost to ground, kW - 50 9 9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated decay requirements:</th>
<th>Years decay required before</th>
<th>Self-boiling stops</th>
<th>Salt cake can form</th>
<th>Salt + Coat cake can form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractionized Assumption</td>
<td>None</td>
<td>43</td>
<td>145</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Cs-Sr Removed</td>
<td>4.0</td>
<td>7.9</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>Cs-Sr-RE Removed</td>
<td>1.9</td>
<td>5.4</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>95% Cs-Sr Removed</td>
<td>4.2</td>
<td>20</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>95% Cs-Sr-RE Removed</td>
<td>2.3</td>
<td>20</td>
<td>6.2</td>
</tr>
</tbody>
</table>
of self-heating liquid waste in tank storage at any given time, about two
years storage time could be saved by removing rare earths with the stronti­
um and caesium. The separated rare-earth fraction could be packaged for
separate long-term storage, or held in process for the two years and re­
blended with the acid wastes after caesium/strontium rare-earth removal.

The fractionization of acid Purex wastes with separate treatment of
the long- and short-lived heat generators is an integral part of the proposed
Hanford programme for high-level waste management. Caesium and stronti­
um would be packaged for long-term storage while the inert salts would be
evaporated to a salt cake after decay of the short-lived fission products.
Rare earths would be separated and held in solution about two years before
recombining with the salt wastes and short lived fission products. The process
steps likely to be involved are outlined on Fig. 5 and discussed below.

1. Removal of extraneous solids.

As produced, the acid wastes from Purex solvent extraction contain
some solid materials, consisting primarily of siliceous materials and pre­
cipitates of iron and solvent degradation products. These solids carry ap­
preciable quantities of radioactive materials, notably zirconium-niobium,
rare earths and strontium. The acid wastes would be centrifuged in the Purex
head-end equipment to separate the solids before processing the liquids
for specific nuclide removal. The solids would be washed to reduce caesium
and strontium losses to a few percent and to remove the major fraction of
adsorbed rare earths. The solids would then be routed to interim storage
for decay before combining with non-heating wastes for reduction to a salt
cake.

2. Removal of caesium

The removal of caesium from acid wastes may be effected by precipi­
tation using phosphomolybdic acid or phosphotungstic acid, by solvent ex­
traction using a nitrobenzene solution of dipicryl amine as the solvent, or
by adsorption on a zeolite. While precipitation-centrifugation equipment
exists in the 221-B facility, its use is not preferred due to the colloidal
nature of the caesium precipitates; appreciable mechanical losses would
be likely to occur during centrifuging unless processing rates were se­
verely restricted. Since the non-heating wastes currently in storage already
contain some heat-producing caesium and strontium, it is pertinent to re­
move as much caesium from the self-heating wastes as is practical so that
the concentrated salt wastes can cool and solidify. Either solvent extraction
or zeolite adsorption is capable of removing caesium efficiently at reason­
able operating rates. While a final decision has not yet been made, the
currently favoured process for caesium extraction is adsorption on
clinoptilolite, as outlined in Fig. 8. Clinoptilolite is a naturally occurring
zeolite with a silicon-to-aluminium ratio of about 5:1. This material is
capable of selectively adsorbing caesium from solutions concentrated in
competing ions, although some of the competing ions adsorb with the caesium.
Of particular concern is sodium because of its high concentration and chemi-
Fig. 8

Caesium extraction from acid and alkaline wastes
cal similarity to caesium, and zirconium-niobium because of its heat-generating properties. Most of the competing ions can be preferentially eluted from clinoptilolite with dilute oxalic acid; a very small fraction of the absorbed caesium is removed during this step.

Caesium is readily eluted from clinoptilolite by ammonium carbonate solution at 55°C. The resulting eluate can be distilled, leaving a concentrated solution of relatively pure caesium carbonate. The distilled ammonia and carbon dioxide can be recovered and reused.

3. Removal of strontium and rare earths

Strontium and rare earths would be removed by solvent extraction, using di(2-ethyl-hexyl) phosphoric acid in a hydrocarbon dilutant as the solvent. The operation would be conducted in 221-B, using the flowsheet depicted in Fig. 9. In this process, citric acid is used as an aqueous complexing agent for iron; it also serves as a buffer to maintain a pH favourable for strontium/rare-earth extraction. Strontium and rare earths are extracted in the first column, strontium is stripped in the second column and the rare earths are stripped in the third. Experimental data indicate that adequate strontium/rare-earth removal can be effected with this flowsheet and that relatively small-volume strontium and rare-earth fractions can be obtained.

4. Disposal of residual wastes

The residual wastes containing the short-lived fission products and non-radioactive salts would be made alkaline and be routed to underground tanks for interim storage, initially under self-boiling conditions. After perhaps six to eight years decay, the wastes would be combined with other non-heating wastes for evaporation to a salt cake. Since new tanks must be constructed for the interim storage of self-heating wastes, and since the operating plan calls for these tanks to be filled and emptied repeatedly, a new tank design is proposed for the new AX farm. See Fig. 10. This design has the advantages of more positive temperature control (since the precipitated salts can be kept in suspension by the air-lift circulators), of simplified removal of tanks' contents and of simple detection and recovery of any leakage. An existing condenser, pump tank, and vent system would be used with these new tanks.

C. Treatment of stored self-heating wastes

The stored self-heating wastes would be removed from the tanks, treated to remove long-lived isotopes and the residual salts combined with non-heating wastes for in-tank solidification.

1. Treatment of supernatant solutions

Caesium removal from the supernatant solutions would probably be accomplished in 221-B by adsorption on a zeolite such as clinoptilolite. See Fig. 8. This flowsheet is essentially the same as that used for caesium
Fig. 9

Strontium/rare-earth extraction from acid wastes
removal from acid wastes, with adjustments being made for the higher concentration of competing ions and lower concentration of heat producing fission products. About 15 column volumes could be processed per batch, using clinoptilolite, with caesium losses of around 1%. Recent work indicates that up to 30 column volumes might be processed per batch, using a synthetic zeolite. The choice of zeolite would be based on overall economics. Consideration is also being given to recovering technetium by adsorption on a strong anion exchange resin.

2. Treatment of residual sludges

After removal of most of the supernatant solution, the sludge layer would be dissolved to the extent possible by successively diluting and removing the heel of supernatant solution. The heat generated in the sludge layer would warm the water, thereby assisting the dissolution operation by the creation of convection currents through the sludge. Sluice-mining techniques might also be used to improve liquid/solid contact. By controlling the pH of the leaching solution in the low alkaline range, it appears possible to remove a large fraction of the transuranic elements with the caesium and soluble salts. This leach solution would be treated for caesium removal as above. Flowsheets are also being developed for the recovery of the transuranic elements, plutonium, neptunium and americium, from the dissolved
Experiments are also in progress to determine the feasibility of removing strontium from the insoluble fraction by reducing the pH of the leaching solution to the range of perhaps 5 to 7. It is hoped that a set of conditions can be found that can either dissolve the hydrous iron oxide sludges and strontium salts or solubilize the strontium salts alone without attacking the carbon steel liner of the tank. If selective leaching or controlled pH dissolution does not prove to be practicable, the sludge would be slurried out of the vessel into a stainless-steel tank, acidified, and transferred to 221-B for further processing. After dissolution, the strontium would be removed from the salt solution by solvent extraction, using a flowsheet similar to that presented in Fig. 9.

3. Disposition of separated fractions

The separated strontium and caesium would be packaged for long-term storage. The residual salt solutions would be combined with non-heating wastes for in-tank solidification.

D. Storage of caesium and strontium

The caesium and strontium fractions would be adsorbed on a crystalline zeolite, dehydrated and stored in sealed stainless-steel containers. A crystalline zeolite is preferred for this use because it can be dehydrated without affecting its ion-exchange properties. While amorphous zeolites lose their exchange properties at temperatures slightly above 100°C, the crystalline forms can be heated to 700°C without essential change. When loaded from relatively pure solutions, some zeolites can adsorb up to 4 meq/g of caesium or strontium. Loadings up to 3 meq/g are anticipated under operating conditions. Under anticipated operating conditions, strontium-90 would constitute about 17% and caesium-137 about 35% by weight of the dehydrated material. It is anticipated that the dried material can be stored in sealed containers without pressure build-up; experimentation is in progress to assess this characteristic. If the zeolite were inadvertently exposed to environmental waters, the caesium or strontium could be leached very slowly. If, however, the elution of the isotopes were desired for any reason, the radionuclides could be readily eluted with solutions of mineral acids or ammonium salts.

In operation, the zeolite would first be placed in the container (see Fig. 11); the unit would then be placed in the operating cell and connected with the process equipment. The desired radionuclide would be loaded by passing a relatively pure caesium or strontium solution through the canister, the radionuclide adsorbing directly on the zeolite. The unit would then be dried at 500° to 600°C by passing dry heated air through the bed; the unit would then be cooled, capped, and welded closed. After leak testing, the canister would be transferred to the 200 North storage basin. A cooling tower would be added to the basin to increase its capability to dissipate heat.
E. Programme costs and timing

As outlined here, the programme is estimated to require a capital expenditure of about $12,000,000 (including that already authorized) and an annual operating cost of about $4,250,000 from 1966 to 1973. Of this total, about $1,000,000 capital and $350,000 annual operating cost is associated with the solidification of non-heating wastes. The balance is associated with the fractionization of the existing and future self-heating wastes. Assuming authorization is received to construct the facilities as rapidly as the required technology is developed, the entire complex could be activated by the end of calendar year 1966. The programme is designed to fractionize all existing and future Purex self-heating wastes, to reduce all non-heating wastes to salt cakes and to encapsulate the separated caesium and strontium by 1973. The processing of stored Redox self-heating wastes would continue for a few years beyond that time.

V. ALTERNATIVES

Two broad alternatives to the proposed programme include the storage of liquid wastes in tanks or selected geological formations, and the conversion of the radiochemical wastes to a thermally- and radiolytically-stable solid state for storage in selected locations. These alternatives should be considered separately as they might apply to the non-heating and to the self-heating wastes.
A. Non-heating wastes

The proposed programme of in-tank solidification is believed to offer long-term safe confinement of non-heating wastes at a lower cost than is possible by any known alternative.

The current practice is to store the non-heating wastes in underground tanks ranging in age up to 18 yr. Four of these tanks have already leaked and a finite life must be ascribed to the tanks remaining in service. Assuming no more tanks are withdrawn from service, new tanks of this type will be needed by 1967 if production schedules remain unchanged. Since the proposed programme for solidifying non-heating wastes involves a total expenditure of about $4,000,000 over the next ten years, it is highly probable that the cost of immobilization would be less than the cost of building new tanks as the need develops for new and replacement storage facilities. Minimal incremental costs would be incurred for long-term surveillance of solidified wastes, since surveillance will be required at the Hanford site in any event.

The calcination of non-heating wastes to a thermally-stable form is judged to be a relatively large and unwarranted expense. Similarly, the considerable expense of transporting the thousands of tonnes of radioactive materials to another site for injection into a salt dome or shale formation would also appear to be unwarranted.

B. Self-heating wastes

Logical alternatives to the proposed fractionization of self-heating wastes include the continued storage of liquid wastes in underground tanks and the calcination of the contaminated salts to a thermally- and radiolytically-stable form. From the viewpoint of assured confinement, the fractionization and calcination approaches appear equally desirable and superior to continued liquid storage. From the viewpoint of cost, however, the relative merits of the three alternatives are not so evident.

In order to compare the economic aspects of the three alternatives, the equipment additions and facility revisions required for implementing each of the three programmes at Hanford were estimated. To simplify the study, only Purex self-heating wastes were considered and it was assumed that processing activities would continue at current rates until 1973 when they would cease. The limited recovery of fission products for beneficial use was also included as a variable. The capital and operating costs through 1973 were then estimated for each case, together with the cost of continued surveillance and replacement facilities beyond that time. Only the incremental costs attributable to each alternative were considered. The total estimated costs for each alternative were then compared on the basis of present worth 1962 dollars, using an interest rate of 4%. The studies are summarized in Table V.

This comparison indicates that the continued storage of liquid wastes in underground tanks is the cheapest approach to the management of self-heating wastes at Hanford, provided one ascribes no value to the isolation of caesium and strontium in a useful form, or to the decreased mobility of
the biologically hazardous nuclides. If immobilization of fission products is to be effected, waste fractionization is cheaper than calcination regardless of whether or not fission products are recovered. This relationship results from the existing inventory of self-heating wastes which contain large quantities of inert salts to be processed; it is less costly to remove the long-lived heat producers for separate high-integrity storage than to process the large quantities of inert salts for storage with the hazardous materials in high-integrity containers.

VI. CONCLUSIONS

After considering the magnitude and characteristics of Hanford wastes, the unique geology and climate of the area, the potential usefulness of selected fission products and the relative costs of the various alternatives available, it is concluded that the combination of waste fractionization and in-tank solidification is the best approach to high-level waste management at Hanford. In-tank solidification offers a relatively cheap and efficient method of safely immobilizing the large inventories of contaminated salts. Although continued tank storage is the cheapest alternative for self-heating wastes, the added cost of fractionization is considered to be fully justified by the increased certainty of long-term confinement of the hazardous nuclides, and by the increased capability for fission-product recovery. Research and development efforts are therefore being directed toward the acquisition of the necessary technology and the programme is being recommended for implementation.
It should be re-emphasized that these conclusions are unique to Hanford because of the environmental characteristics, the availability of existing facilities and the existence of large inventories of radiochemical wastes. No attempts should be made to apply these conclusions to another site without individual study and evaluation of that site’s situation.

DISCUSSION

N. E. BREZHNEVA: What are the possibilities of using the fission products, particularly caesium and strontium? What part could be used and could this lead to a reduction in the cost of processing radioactive waste?

R. E. TOMLINSON: We think that perhaps 95% of the available caesium and strontium could be recovered in useable form. We certainly hope that there is a sale for this product, since it would reduce the net cost of our waste processing, but at the present time we have no assurance that a market will develop.

E. GLUECKAUFL (Chairman): I should like to make a comment myself on the same point. Mr. Tomlinson said very clearly in his paper that all the calculations applied to a situation at Hanford and that under conditions which were not quite so favourable - namely if there were less unused equipment and tank storage available - there might be less hope of using caesium and strontium to influence processing costs. Mr. Clelland has shown that in the UKAEA the concentration of solution is very high indeed and only little tank space has been required for storing it. Under these conditions, the removal of strontium and caesium and transformation of the material into a salt-cake or something else would not offer any economic advantage, though one might very well do it for reasons other than those of economy.

W. HARDWICK: Would Mr. Tomlinson still consider using the TBP process for primary separation if caesium and strontium became economically attractive to separate?

R. E. TOMLINSON: I would rather not comment on that point, as I have not yet thought about it.

B. KOLYCHEV: Do you place any limitation on the initial activity when using the tank solidification method?

R. E. TOMLINSON: Yes. We place an upper limit on the activity such that the solidified cake should contain the equivalent of not more than 5 W (thermal)/m³ of fission product.
THE PROBLEM OF STORING FISSION PRODUCTS ARISING FROM THE PROCESSING OF IRRADIATED URANIUM-MOLYBDENUM ALLOYS. Uranium-molybdenum alloys are of value thanks to their in-pile behaviour, but serious disadvantages arise in connection with the storing of fission products resulting from the processing of these alloys.

Because of the insolubility of molybdenum it is impossible to concentrate a solution of fission products by evaporation, and for this reason we have directed our efforts towards the solubilization of molybdenum through the addition of reagents such as iron or phosphoric ions. In this way one can obtain final solutions of

\[
\begin{align*}
60 \text{ g/l Mo} & \text{ with Fe} \\
100 \text{ g/l Mo} & \text{ with } \text{PO}_4\text{H}_3
\end{align*}
\]

The volumes to be stored are still considerable (especially with Fe) and the possibility of nitrate calcination in a fluidized bed was considered. The reaction takes place at about 400°C. The behaviour of the ruthenium and the friability of the calcined solid (formation of considerable amounts of fine material) have led us to abandon this process in favour of the preparation of phosphate glasses.

Les alliages U-Mo sont intéressants par leur tenue en pile, mais ils présentent des inconvénients sérieux quant au stockage des produits de fission resultant de leur traitement.

L'insolubilité du molybdenum interdit toute concentration par évaporation de la solution de produits de fission. C'est pourquoi les auteurs ont orienté leurs études vers la solubilisation du molybdenum par addition de réactifs tels que le fer ou les ions phosphoriques. Ainsi, on peut obtenir les solutions finales à

\[
\begin{align*}
60 \text{ g/l Mo} & \text{ avec Fe,} \\
100 \text{ g/l Mo} & \text{ avec } \text{PO}_4\text{H}_3
\end{align*}
\]

Les volumes à stocker sont encore importants (surtout avec Fe) et la calcination des nitrates dans un lit fluidisé a été étudiée. La réaction a lieu vers 400°C. Le comportement du ruthénium et la friabilité du solide calciné (formation importante de fines) a conduit à abandonner ce procédé au profit de la confection de verres phosphatés.

PROBLÈME DU STOCKAGE DES PRODUITS DE FISSION EN PROVENANCE DU TRAITEMENT DES ALLIAGES URANIUM-MOLYBDÈNE IRRADIÉS. Les alliages U-Mo sont intéressants par leur tenue en pile, mais ils présentent des inconvénients sérieux quant au stockage des produits de fission résultant de leur traitement.

Les volumes à stocker sont encore importants (surtout avec Fe) et la calcination des nitrates dans un lit fluidisé a été étudiée. La réaction a lieu vers 400°C. Le comportement du ruthénium et la friabilité du solide calciné (formation importante de fines) a conduit à abandonner ce procédé au profit de la confection de verres phosphatés.

ПРОБЛЕМА ХРАНЕНИЯ ОТХОДОВ ПОСЛЕ ПЕРЕРАБОТКИ ОБЛУЧЕНОГО СПЛАВА УРАН-МОЛИБДЕН. Поведение сплавов уран-молибден в реакторе представляет практический интерес. Однако возникает проблема хранения продуктов деления, которые получается в результате их переработки.

В этом случае, когда молибден находится в нерастворенном состоянии, любое концентрирование продуктов деления путем испарения раствора практически невозможно. Вот почему мы ориентировались на изучение растворения молибдена прибавлением таких реагентов, как железо или фосфат-ионы. Можно получить раствор состава: 60 г/л Mo с Fe или 100 г/л Mo с PO₄H₃.

В этом случае объемы, предназначенные для хранения, увеличиваются (особенно при добавлении Fe). Было изучено прокаливание нитратов в движущемся слое. Реакция проходит при температуре около 400°C. Летучесть рутения и хрупкость твердого прокаленного вещества (вследствие образования значительного количества угля) заставляют нас отказаться от этого процесса и перейти к изготовлению фосфатных стекол.
EL PROBLEMA DEL ALMACENAMIENTO DE LOS PRODUCTOS DE FISIÓN PROCEDENTES DEL TRATAMIENTO DE LAS ALEACIONES URANIO-MOLIBDENO IRRADIADAS. Las aleaciones U-Mo son interesantes por la forma en que se comportan en el reactor, pero presentan serios inconvenientes en lo que respecta al almacenamiento de los productos de fisión resultantes de su tratamiento.

La insolubilidad del molibdeno impide concentrar por evaporación las soluciones de los productos de fisión. Por tal motivo, los autores han estudiado la posibilidad de solubilizar el molibdeno agregándole reactivos tales como el hierro o los íones fosfóricos. De este modo, es posible obtener soluciones finales de

- 60 g/l Mo con hierro,
- 100 g/l Mo con PO₄H₃.

Los volúmenes que es preciso almacenar siguen siendo importantes (sobre todo con el hierro) y por eso se ha estudiado la calcinación de los nitratos en un lecho fluidizado. La reacción tiene lugar a los 400°C aproximadamente. El comportamiento del rutenio y la friabilidad del sólido calcinado (importante formación de partículas menudas) ha inducido a los autores a reemplazar este procedimiento por el de preparación de vidrios fosfátados.

I. INTRODUCTION

Actuellement, le stockage des produits de fission en provenance du traitement de l'uranium naturel irradié s'effectue sous forme de solution acide dans des récipients en acier inoxydable.

Afin de réduire le volume à stocker, on effectue une concentration par évaporation des solutions, avec destruction de l'acide nitrique par le formol pour obtenir une solution finale ayant une acidité libre de 2N HNO₃. On arrive ainsi à obtenir 30 à 50 litres de solution par tonne d'uranium naturel irradié.

Le programme français prévoyant l'utilisation de l'alliage UMo à 1% de Mo comme combustible, nous avons envisagé l'étude du stockage des produits de fission résultant de leur traitement.

Les essais préliminaires nous ont montré que la limite de précipitation de l'anhydride molybdique se situe vers quelques grammes de Mo par litre de solution de produits de fission, pour une acidité nitrique libre de 2N.

Nous avons alors cherché à réduire le volume de stockage des produits de fission. Les recherches se sont orientées dans les directions suivantes:
- utilisation de complexants pour augmenter la solubilité de l'anhydride molybdique en milieu acide,
- concentration des produits de fission sous forme solide.

II. UTILISATION DE COMPLEXANTS POUR AUGMENTER LA SOLUBILITÉ DE L'ANHYDRIDE MOLYBDIQUE EN MILIEU ACIDE NITRIQUE DILUÉ

Nos études ont porté sur les deux complexants bien connus de l'anhydride molybdique: le fer et l'acide phosphorique.

1. Utilisation du fer comme complexant

Les essais préliminaires nous ont montré que la concentration des produits de fission par évaporation, en détruisant l'acide nitrique en excès par
le formol, ne permettait pas une concentration supérieure au facteur 3 pour des solutions de produits de fission synthétiques ayant la composition suivante :
- produits de fission inactifs correspondant aux taux d'irradiation considérés,
- $U < 50 \text{ mg/l}$,
- Mo de l'alliage $1,25 \text{ g/l}$,
- $\text{HNO}_3 \sim 2 \text{ N}$.

L'addition de nitrate ferrique à des solutions nitriques d'uranium et de molybdène permet d'augmenter la solubilité de l'anhydride molybdique dans ces solutions [1, 2, 3].

Dans l'optique du stockage liquide acide (de 1 à 2N en $\text{HNO}_3$ libre) des produits de fission, nous avons cherché pour ce cas le maximum de concentration possible par addition de nitrate ferrique.

La redissolution d'un précipité d'anhydride molybdique par une solution de nitrate ferrique étant très difficile et souvent impossible, cette désolution dépendant fortement de l'histoire du précipité (âge, température de traitement, etc.), nous avons préféré ajouter le fer dans la solution à concentrer avant l'évaporation.

Le nitrate ferrique étant un sel relativement peu soluble en milieu acide nitrique dilué, nous avons cherché la quantité minimum de fer à utiliser pour obtenir le plus grand facteur de concentration possible.

Un deuxième paramètre très important pour la solubilité de l'anhydride molybdique dans ce milieu est l'acidité libre de la solution, une augmentation de celle-ci peut diminuer la solubilité de $\text{MoO}_3$.

La destruction de l'acide nitrique par le formol, selon les conditions opératoires (concentration en acide nitrique, température, temps de séjour moyen des produits dans l'évaporateur, présence de catalyseur, etc.), peut s'effectuer avec des rendements stoïchiométriques très différents [4].

D'après les conditions opératoires, le formol peut donner de l'acide formique ou de l'anhydride carbonique, tandis que l'acide nitrique donnera toute une série de produits de décomposition.

Les concentrations des produits de fission provenant du retraitement des barreaux d'uranium non alliés donnent une consommation de formol, dans nos conditions opératoires, telle que l'équation stoïchiométrique théorique

$$3 \text{HCHO} + 4 \text{HNO}_3 \rightarrow 4 \text{NO} + 5 \text{H}_2\text{O} + 3 \text{CO}_2$$

semble être satisfaite.

En ajoutant du nitrate ferrique à nos solutions de produits de fission à concentrer, pour une même concentration et une même acidité libre finale, la teneur en ions nitriques augmente, d'où un rendement plus élevé de l'utilisation du formol. En effet, l'acide nitrique ou les nitrates concentrés ont tendance, au moment de leur réduction, à dégager du NO₂ au lieu du NO pour les solutions plus diluées. Ainsi, dans une solution de plus en plus concentrée en nitrates, la réaction stoïchiométrique théorique

$$\text{HCHO} + 4 \text{HNO}_3 \rightarrow 4 \text{NO}_2 + 3 \text{H}_2\text{O} + \text{CO}_2$$

devient de plus en plus prépondérante.
Dans nos recherches, nous avions donc deux paramètres interdépendants à étudier simultanément:

a) la quantité de formol à utiliser, pour maintenir l'acidité libre de la solution entre 1 et 2N pendant la concentration, et

b) la concentration de la solution en nitrate ferrique pour maintenir l'anhydride molybdique en solution.

Dans un évaporateur de laboratoire, nous avons introduit en continu:
- la solution de produits de fission additionnée de nitrate ferrique,
- une solution de formol. En distillant, nous avons maintenu constante la concentration de l'acide correspondant à la solution finale recherchée.

Toute une série d'essais effectués dans ce but nous a permis de déterminer:

1° qu'il est nécessaire d'ajouter environ 2 Fe par Mo pour maintenir l'anhydride molybdique en solution pour une acidité libre d'environ 2N HNO₃ et pour une concentration de plusieurs dizaines de gramme de Mo/l, le facteur de concentration étant limité par la solubilité du nitrate ferrique;

2° que le rapport formol/acide nitrique doit être de 1/2 pour avoir un fonctionnement sûr, assurant une acidité nitrique libre aux environs de 2N. En effet, une destruction très poussée de l'acidité libre fait apparaître un précipité d'hydroxyde de fer; par contre, une acidité trop forte favorise la précipitation de l'anhydride molybdique. (Il faut signaler ici que le rendement de la réaction formol-acide nitrique dépend également de la géométrie de l'appareillage utilisé, et pour chaque nouvel évaporateur le rapport formol/acide nitrique doit être légèrement ajusté.)

Les caractéristiques du concentrat final obtenu par cette méthode de concentration sont reproduites au tableau 1.

Les densités et les viscosités des concentrats sont données sur les figures 1 et 2. Par cette méthode de concentration, nous pouvons donc prévoir, pour les solutions de produits de fission industrielles, un facteur de concentration de l'ordre de 50.

**TABLEAU I**

**CARACTÉRISTIQUES DU CONCENTRAT FINAL**

<table>
<thead>
<tr>
<th>Facteur de concentration</th>
<th>Teneur en Mo (g/l)</th>
<th>Teneur en Fe (g/l)</th>
<th>Densité (g/cm³)</th>
<th>Viscosité (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>20</td>
<td>28</td>
<td>1,17</td>
<td>0,014</td>
</tr>
<tr>
<td>32</td>
<td>40</td>
<td>56</td>
<td>1,28</td>
<td>0,022</td>
</tr>
<tr>
<td>48</td>
<td>60</td>
<td>84</td>
<td>1,33</td>
<td>0,028</td>
</tr>
</tbody>
</table>
DENSITÉ DU CONCÉNTRAT

Fe = 3M

Figure 1
Densité du concentrat

VISCOITÉ DU CONCÉNTRAT
(EN POISES)

Fe = 3M

Figure 2
Viscosité du concentrat (en poises)
2. Utilisation de l'acide phosphorique comme complexant

Les composés de l'acide phosphomolybdique sont connus depuis le début du 19e siècle (Berzélius, Gmelin). C'est en chimie analytique que les études de ces composés ont été entreprises.

La forte solubilité de l'acide phosphomolybdique nous a orienté vers la recherche de la solubilisation de l'anhydride molybrique par addition d'acide phosphorique dans les solutions à concentrer[5] . Les solutions de produits de fission contiennent déjà un peu d'acide phosphorique provenant de l'hydrolyse et de la radiolyse du tributylphosphate. La quantité d'acide phosphorique ainsi produite peut varier d'environ 10 à 40 mg/l exprimés en phosphore. En supposant la formation de l'acide $\text{H}_3(\text{MoO}_3)_{12}\text{PO}_4$ on aurait besoin d'un atome de phosphore pour douze atomes de molybdène pour former l'acide soluble.

L'acide phosphorique provenant de l'hydrolyse et de la radiolyse du tributylphosphate ne présentant pas obligatoirement une concentration constante dans les solutions à concentrer, nous avons préféré ajouter l'acide phosphorique nécessaire à la complexation au moment de la concentration. La présence des éléments donnant un phosphate insoluble (comme le zirconium) consomme également une quantité d'acide phosphorique variable.

Nos solutions à concentrer contiennent 1,25 g de Mo par litre, qui nécessitent environ 34 mg de phosphore par litre sous forme d'acide phosphorique pour former l'acide phosphomolybdique. En tenant compte des éléments ayant des phosphates insolubles, nous avons effectué des concentrations en présence de 40, 80, 120 et 160 mg de phosphore par litre.

Comme il existe des sels de l'acide phosphomolybdique insolubles en milieu faiblement nitrique, il faut compter qu'il se produira, dans cette méthode, un précipité de ces composés. Parmi les produits de fission c'est surtout le césium qui est susceptible de précipiter. Bien que cette précipitation soit gênante pour le stockage des produits de fission, elle peut être exploitée pour récupérer le $^{137}\text{Cs}$ après une séparation solide-liquide à la sortie du concentrateur.

Dans nos expériences, nous avons donc toujours tenu compte d'un précipité constitué essentiellement de phosphomolybdate de césium, de phosphate de zirconium et d'anhydride molybdique.

Les essais effectués avec 40, 80, 120 et 160 mg de phosphore par litre de solution à concentrer ont montré que la quantité stoechiométrique de phosphore (40 mg/l) est suffisante pour maintenir l'anhydride molybdique en solution jusqu'à une concentration de 100 g de Mo/l. Dans ce cas, l'opération est assez délicate, en effet, la moindre erreur sur la quantité d'acide phosphorique peut amener une précipitation intempestive de l'anhydride molybdique. Pour un fonctionnement plus sûr, nous avons préféré doubler la quantité d'acide phosphorique ajoutée (80 mg de P/l) les expériences ayant montré que l'addition de 120 ou de 160 mg de P/l n'améliorait pas le procédé.

En utilisant cette méthode de concentration, nous pouvons donc obtenir une solution finale contenant 100 g de Mo/l de solution et un précipité jaune.

* Ce procédé, proposé par M. RAGGENBASS, permet à la fois la concentration du molybdène dans la solution, et la récupération du césium par la précipitation du phosphomolybdate.
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d’or de phosphomolybdate de césium, la quantité de précipité dépendant du taux d’irradiation (concentration des produits de fission en césium). Le précipité peut représenter quelques kilogrammes par tonne d’uranium traité. La solution obtenue a une densité de 1,1 et une viscosité de 0,013 P.

Dans le cas où l’on désirerait supprimer la précipitation du phosphomolybdate de césium, on peut ajouter un très grand excès d’acide phosphorique, égal à 120 fois la quantité stoéchiométrique de phosphore correspondant à la formule $H_3(MoO_3)_{12} \cdot PO_4$. Avec cet excès d’acide, il n’y a pas de précipitation de césium dans la solution. La forte concentration en acide phosphorique présente un certain nombre d’inconvénients pour le stockage: corrosion, densité élevée (1,7), forte viscosité (0,300 P), etc.

Il faut encore noter que le précipité de phosphomolybdate de césium est très soluble dans la soude, ce qui permet une dissolution facile du précipité séparé.

III. CONCENTRATION DES PRODUITS DE FISSION SOUS FORME SOLIDE

Dans ce paragraphe nous décrivons le mode d’obtention d’une poudre par séchage dans un lit fluidisé. Le séchage complet des solutions de produits de fission permet d’obtenir un plus grand facteur de concentration. Le séchage d’une solution peut être fait de diverses manières. Comme, dans notre cas, les solides envisagés sont très radioactifs, nous avons choisi un procédé qui ne nécessite pas d’appareillage dont certaines parties sont en mouvement. Nous avons donc étudié la possibilité de concentrer les produits de fission par lits fluidisés.

Au début, nous nous sommes inspirés des études faites par l’Argonne National Laboratory et la Philipps Petroleum Company, pour la concentration des solutions de produits de fission provenant du retraitement des combustibles type MTR, contenant environ 2 M de nitrate d’aluminium.

1. Appareillage utilisé

Les premiers essais ont été effectués dans un appareil de laboratoire dont le schéma est celui de la figure 3.

Le réacteur (80 mm de diamètre intérieur, 400 mm de longueur) en acier inoxydable est chauffé par un enroulement de résistance électrique.

L’air de pulvérisation traverse un rotamètre et un préchauffeur, puis est admis dans le réacteur à travers un distributeur en acier inoxydable fritté, de 50 à 60 μ de porosité. Au centre de ce fritté, nous avons aménagé une sortie pour particules lourdes afin d’en soutirer la production.

Au tiers de sa partie inférieure, le réacteur comporte un pulvérisateur à air comprimé. Le réacteur est surmonté d’une enceinte de détente contenant des bougies filtrantes en acier inoxydable fritté, de 1 à 2 μ de porosité. Les bougies filtrantes sont séparées par des écrans d’amiante pour permettre le décolmatage en marche. En effet, en marche normale, il n’y a que deux filtres en service. La pression à l’intérieur du réacteur étant contrôlée en continu, quand celle-ci monte au-dessus d’une valeur déterminée, on met en marche le troisième filtre, propre, tandis qu’on décolmate le filtre en service depuis le temps le plus long, en envoyant de l’air.
Figure 3
Concentration des produits de fission

P: purgeur d'air comprimé
R: rotamètre (1,5 à 15 m³/h)
PR: préchauffeur d'air de fluidisation
D: distributeur d'air (plaque inox fritté : 50 à 60 μ)
RR: réacteur de fluidisation en acier inoxydable
E: enceinte de filtration et détente en pyrex
T: Frémie d'alimentation de solide fluidisant
S: sortie des gaz filtrés vers ventilation
RP: régulateur de pression pour pulvérisateur
AS: Alimentation à niveau constant de la solution à concentrer
V: pulvérisateur
I: injection d'air pour décolmatage des filtres
AC: air comprimé
A: écran d'amiante
C: calorifuge en amiante et laine de verre
PA: produits solides
MP: mesure de pression
F: filtres d'acier inoxydable fritté (3) Pr:1μ
comprimé à contre-courant. L'opération peut être effectuée soit manuellement, soit automatiquement par des électrovannes. L'enceinte de détente est surmontée d'une trémie de chargement.

Au cours de nos études nous avons modifié l'appareillage pour permettre de mieux manipuler les particules fines. Pour soulager les filtres, et pour permettre éventuellement de recycler les particules fines dans le bas du réacteur (en dessous du pulvérisateur) nous avons enlevé des filtres de l'enceinte de détente, est à sa sortie, nous avons adjoint un cyclone. Nous avons placé des filtres à la sortie du cyclone (voir figure 4). La sortie de solide du cyclone comporte un sas muni de vannes tournantes permettant de soutirer les particules fines ou de les recycler.

![Figure 4](image)

_Détente-cyclone (filtres)_

A la sortie des filtres, les gaz passent dans un condenseur, puis dans une colonne garnie d'anneaux de Raschig où ils sont lavés à la soude diluée. Débits, températures et pressions sont contrôlés dans chaque partie de l'appareil.
2. Essais préliminaires

L'utilisation des pulvérisateurs dans le séchage des solutions de produits de fission par la méthode des lits fluidisés nécessite des solutions limpides. Les solutions provenant du retraitement des barreaux U-Mo à 1% de Mo ne peuvent être fortement concentrées sans apparition d'un précipité, ainsi que nous l’avons vu dans la première partie. Pour obtenir un volume de solide aussi faible que possible, nous avons essayé au début de notre expérimentation de sécher par fluidisation des solutions relativement diluées, une concentration plus forte nécessitant l’utilisation d’un complexant.

Dans ces solutions, le précipité d’anhydride molybdique apparaît au-dessus de 4 g de molybdène par litre.
Nous avons donc utilisé une solution contenant
- 4 g de Mo par litre,
- HNO₃ (3,7 N),
- les produits de fission sous la forme de leurs isotopes inactifs.

Les expériences ont été effectuées avec une volume de lit, au repos, de 600 cm³, la température variant de 250 à 400°C. Le débit de liquide, de 250 cm³/h est lié aux caractéristiques du pulvérisateur. Le lit de départ est constitué par de l’alumine calcinée. Nous avons pensé que dans un fonctionnement normal, nous pourrions remplacer le lit initial par des produits séchés. Mais du fait de la mauvaise tenue mécanique des particules formées par ces derniers, nous n’avons pu obtenir une marche satisfaisante dans ces conditions.

En effet, l’attrition des particules formées est si rapide que la densité du fluidisé diminue continuellement. Les grains qui ont grossi ne sont plus en suspension, par contre les particules formées de taille convenable se désagrègent au contact de la paroi du réacteur et par frottement mutuel.
Nous avons donc eu une grande quantité de particules fines produite; même le recyclage dans le réacteur ne permet aucun grossissement supplémentaire, la vitesse d’attrition étant supérieure à la vitesse de grossissement.

Pour maintenir un lit suffisamment dense dans les meilleures conditions, nous avons dû ajouter une charge inerte (de l’alumine) en continu, représentant un renouvellement du lit toutes les cinq heures de fonctionnement.

En augmentant la vitesse de production des grains (par le débit de pulvérisation), on peut certainement arriver à équilibrer leur vitesse de formation avec leur vitesse d’attrition, ce qui pourrait permettre de supprimer l’addition de produits inertes.

Cependant, comme nous avons constaté que les grains formés à partir d’une solution de produits de fission additionnée de nitrate ferrique présentaient une tenue mécanique nettement supérieure, nous avons préféré étudier le séchage de ces solutions.
3. Essais de séchage d'une solution de produits de fission contenant du molybdène et du fer

Comme nous l'avons décrit dans la première partie de cet exposé, l'addition de nitrate ferrique permet une concentration des solutions nitriques contenant du molybdène, sans précipitation de MoO₃.

Parmi les solutions de produits de fission concentrées, en présence de fer, nous avons adopté la solution contenant:
- 56 g/l de fer,
- 20 g/l de molybdène,
- HNO₃ 2M,
- et les produits de fission sous la forme de leurs isotopes inactifs, qui convient le mieux au séchage par fluidisation, tant au point de vue de la solidité des grains obtenus que par la stabilité de la solution, évitant ainsi le bouchage du pulvérisateur.

Les opérations étaient effectuées dans les conditions suivantes:
- température du réacteur 350°C
- débit d'air fluidisant (à froid) 8,5 m³/h
- débit de la solution 250 cm³/h
- débit d'injection de la solution 0,7 à 0,9 kg/cm²
- pression d'air de pulvérisation 2 kg/cm²
- lit initial (sable de Fontainebleau) (taille moyenne des grains 0,250 mm) 600 cm³.

Dans ces conditions, nous avons obtenu environ 25% du solide sous forme de particules fines recueillies à la sortie du cyclone; les 75% restants servent à faire grossir les grains du lit; les gros grains correspondant à l'accroissement du lit sont retirés en bas du réacteur.

Le solide formé dans le réacteur se dépose au début sur le sable, mais il se forme également des grains qui ne contiennent pas de sable. C'est ce qui permet de transformer le lit, complètement, en un lit de produit séché. Nous avons contrôlé cette transformation en dosant la silice dans les différents prélèvements effectués sur le lit, au fur et à mesure de son fonctionnement; nous avons ainsi constaté que la teneur en silice diminuait dans les proportions correspondant à une dilution par les produits solides introduits dans le lit (sans tenir compte des particules fines).

Après la disparition du sable, la granulométrie du lit est légèrement modifiée; en effet, le sable qui était surtout composé de particules d'un diamètre moyen de 0,250 mm est remplacé par des particules de produits de fission séchées ayant un diamètre moyen de 0,200 mm.

Au même moment, la densité apparente du lit augmente de 1,55 (pour le lit initial) à 1,8 - 1,9.

Pour supprimer la production de particules fines, nous avons considéré deux solutions: la première consistait à recycler des particules fines dans le bas du réacteur pour les faire grossir, mais l'élimination de ces particules est instantanée, et leur volume de circulation augmente rapidement. La deuxième solution consistait à redissoudre les particules fines, soit dans la solution à pulvériser, soit dans l'acide frais et à les réintroduire dans l'appareil. La vitesse de dissolution de ces particules étant relativement lente et une faible quantité restant insoluble, nous avons finalement opté pour leur stockage.
Le fonctionnement des filtres était satisfaisant. Nous n'avons jamais pu déceler de traces de fer ou de molybdène dans les condensats.

La fréquence du décolmatage des filtres était de 15 minutes ce qui correspondait à une augmentation de pression à l'intérieur du réacteur de 50g/cm².

Dans les condenseurs nous avons récupéré 52% de liquide par rapport au volume de liquide introduit, le restant étant récupéré dans la colonne de lavage. Comme nous avons utilisé l'air comme fluidisant, la récupération des vapeurs nitrées sous forme d'acide nitrique est relativement difficile du fait de la dilution des vapeurs nitrées et nécessite une colonne de recombinaison relativement importante, pour y assurer un temps de séjour des gaz assez long.

L'utilisation de vapeur surchauffée comme fluidisant pourrait pallier cet inconvénient.

Le comportement des produits de fission risquant de se volatiliser dans le réacteur ne sera étudié par des traceurs que dans l'installation semi-industrielle. Toutefois, en inactif nous avons essayé de déterminer leur comportement dans les conditions de fluidisation. Pour le molybdène nous n'avons pas constaté de volatilisation à la température de travail (350°C). Par contre, une grande partie du ruthénium se volatilise dans ces mêmes conditions.

Dans nos essais en inactif, nous avons constaté que le ruthénium se retrouve dans les concentrats de gaz sortants, et après la colonne de lavage nous n'avons pu le déceler. Naturellement, les essais par traceurs devraient encore confirmer ces résultats.

Le stockage des produits de fission sous forme solide pose le problème de l'évacuation de la chaleur due aux radiations. Nous avons donc effectué des mesures de conductivité thermique de ces produits, obtenus par fluidisation. Pour une température centrale de 130°C, nous avons obtenu: 1.10⁻⁵ cal/sec.°C.cm².cm

Dans nos essais en inactif, nous avons pu également démontrer que la méthode de concentration par lit fluidisé pourrait également s'appliquer à des solutions de produits de fission contenant le magnésium provenant de la dissolution des gaines.

En conclusion, notre étude montre que les solutions de produits de fission contenant du molybdène peuvent être concentrées dans des conditions acceptables avec une réduction de volume assez importante.

A titre de comparaison, nous donnons les concentrations en molybdène des produits finaux obtenus qui sont proportionnelles aux facteurs de concentration; on obtient finalement:
- en utilisant le fer comme complexant, une solution à 60 g/l de Mo,
- en utilisant l'acide phosphorique, une solution à 100 g/l de Mo,
- en utilisant la fluidisation, une poudre contenant 320 g/l de Mo.

Une autre solution est envisagée: l'incorporation des produits de fission et du molybdène dans des verres.

L'étude correspondante fait l'objet d'un autre rapport.
PROBLÈME DU STOCKAGE DES PRODUITS DE FISSION

RÉFÉRENCES

О ВЛИЯНИИ НИТРАТОВ НА СОСТАВ ПАРОВОЙ ФАЗЫ НАД ВОДНЫМИ АЗОТНОКИСЛЫМИ РАСТВОРАМИ

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СССР

Abstract — Résumé — Аннотация — Resumen

ON THE INFLUENCE OF NITRATES ON THE COMPOSITION OF VAPOUR PHASE OVER NITRIC ACID SOLUTIONS. The paper contains the experimental data for vapour liquid equilibrium and boiling-point temperatures at a pressure of 760 mm Hg, for part of the nitrate - nitric acid - water systems.

The authors study systems with nitrates of Al, Fe, Mg, Cu, Na and NH₄. They describe in general terms a manner of calculating the evaporation process in waste solutions obtained from the reprocessing of irradiated fuel elements.

The high-activity, nitric-acid waste solutions are formed during the extractive reprocessing of irradiated fuel elements. These solutions themselves constitute complex systems, composed of a series of nitrates, in addition to volatile components such as water and nitric acid.

Evaporation is usually carried out to reduce the volume of the waste solutions before burial, and in the course of evaporation, nitric acid is driven off. The nitrates in the waste solutions have a definite influence on the distribution of nitric acid between the vapour and liquid phases during evaporation.

The work described consists of an attempt to determine this influence for each nitrate, by investigating the vapour/liquid equilibrium in part of the nitrate - nitric acid - water systems.


Ils étudient des systèmes comportant des nitrates de Al, Fe, Mg, Cu, Na et NH₄. Ils donnent un aperçu général de la méthode de calcul du processus d’évaporation des effluents obtenus lors du traitement des cartouches de combustible irradiées.

Lorsque le traitement se fait par extraction, il se forme des solutions d’acide nitrique fortement radio-actives. Ces effluents représentent des systèmes très complexes qui contiennent, en dehors des éléments volatils (eau et acide nitrique), un certain nombre de nitrates.

D’une manière générale, on fait évaporer les effluents afin d’en réduire le volume avant l’enfouissement. L’évaporation entraîne également le dégagement de l’acide nitrique. Au cours du processus, les nitrates contenus dans les effluents exercent une certaine influence sur la distribution de l’acide nitrique entre la phase vapeur et la phase liquide.


О ВЛИЯНИИ НИТРАТОВ НА СОСТАВ ПАРОВОЙ ФАЗЫ НАД ВОДНЫМИ АЗОТНОКИСЛЫМИ РАСТВОРАМИ. В статье представлены экспериментальные данные по равновесию пар - жидкость и температурам кипения при давлении 760 мм рт.ст. в части систем: нитрат - азотная кислота - вода.

Изучены системы с нитратами Al, Fe, Mg, Cu, Na, NH₄. Дается в общей форме метод расчета процесса упаривания обзорных растворов от регенерации облученных теплопостелляемых элементов.

При экстракционной регенерации облученных теплопостелляемых элементов образуются высокоактивные азотнокислые обзорные растворы. Эти растворы представляют собой многокомпонентные системы, содержащие, кроме летучих составляющих (вода и азотная кислота), ряд нитратов.

Общим с целью сокращения объема перед захоронением обзорные растворы упариваются. Одновременно при упаривании происходит отгонка азотной кислоты. Нитраты, содержащиеся в обзорных растворах, оказывают определенное влияние на распределение азотной кислоты между паровой и жидкой фазами в ходе упаривания.

В настоящей работе делается попытка выяснить это влияние для каждого из нитратов путем изучения равновесия пар - жидкость в части тройных систем: нитрат - азотная кислота - вода.
INFLUENCIA DE LOS NITRATOS EN LA COMPOSICIÓN DEL VAPOR DESPRENDIDO DE SOLUCIONES ACUOSAS DE ÁCIDO NÍTRICO. En la memoria se presentan datos experimentales sobre el equilibrio vapor-líquido y sobre los puntos de ebullición a 760 mm de mercurio correspondientes al sistema ternario nitrato-ácido nítrico-agua.

Se estudiaron los sistemas con los nitratos de Al, Fe, Mg, Cu, Na y NH₄. Se expone a grandes rasgos un método de cálculo del proceso de evaporación de los efluentes formados durante la regeneración de los elementos combustibles irradiados.

Cuando el tratamiento se lleva a cabo por extracción, se forman soluciones de desechos nítricos de elevada actividad. Estas soluciones configuran sistemas de múltiples componentes que, además de los compuestos volátiles (agua y ácido nítrico), contienen una serie de nitratos.

Generalmente, a fin de reducir el volumen antes de proceder a enterrarlo, esos residuos líquidos se someten a una evaporación. Simultáneamente con la evaporación tiene lugar una destilación de ácido nítrico. Los nitratos contenidos en los desechos líquidos ejercen cierta influencia sobre la distribución del ácido nítrico entre la fase vapor y la fase líquida en el curso de la evaporación.

En la memoria se procura determinar esa influencia para cada uno de los nitratos mediante el estudio del equilibrio vapor-líquido en el sistema ternario nitrato - ácido nítrico - agua.

МЕТОДИКА ИССЛЕДОВАНИЯ

Равновесие пар-жидкость определялось на пароциркуляционном приборе типа Отмера. Рабочий объем кипятильника прибора составлял ~200 мл, объем ловушки конденсата ~ 5 мл.

Состав рабочего раствора определялся по составу и количеству исходных компонентов. Содержание азотной кислоты в конденсате определялось титрованием щелочью.

Точность данных по равновесию пар-жидкость составляет 0,5 -1%, в зависимости от содержания соли.

Температура кипения растворов определялась на эбулиоскопе с насосом Коттрея ртутным термометром (цена деления 0,2°С).

Давление поддерживалось постоянным с помощью маностата в пределах ±1 мм рт.ст.

В качестве исходных материалов для исследования применялись: перегнанная с H₂SO₄ азотная кислота (~70%), нитраты марки "ХЧ" и дистилилированная вода.

ЭКСПЕРИМЕНТАЛЬНЫЕ ДАННЫЕ И ИХ ОБСУЖДЕНИЕ

В таблице 1 представлены данные по равновесию пар-жидкость и температурам кипения при давлении 760 мм рт.ст. для части следующих систем:

<table>
<thead>
<tr>
<th>Система</th>
<th>Пар</th>
<th>Жидкость</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (NO₃)</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>Fe (NO₃)₃</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>Mg (NO₃)₂</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>Cu (NO₃)₂</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>NaN₃</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>HNO₃</td>
<td>H₂O</td>
</tr>
</tbody>
</table>
Таблица 1
ДАННЫЕ ПО РАВНОВЕСИЮ ПАР-ЖИДКОСТЬ И ТЕМПЕРАТУРАМ КИПЕНИЯ

<table>
<thead>
<tr>
<th>Давление, мм рт.ст</th>
<th>Состав жидкой фазы</th>
<th>Системы</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X вес %</td>
<td>C вес %</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0,063*</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>102,5</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>104,2</td>
</tr>
<tr>
<td>40</td>
<td>6,63</td>
<td>114,4</td>
</tr>
<tr>
<td>50</td>
<td>16,4</td>
<td>123,8</td>
</tr>
<tr>
<td>760</td>
<td>0,26</td>
<td>102,05</td>
</tr>
<tr>
<td>10</td>
<td>1,12</td>
<td>104,1</td>
</tr>
<tr>
<td>20</td>
<td>1,58</td>
<td>108,0</td>
</tr>
<tr>
<td>30</td>
<td>4,10</td>
<td>110,1</td>
</tr>
<tr>
<td>40</td>
<td>11,70</td>
<td>116,5</td>
</tr>
<tr>
<td>50</td>
<td>29,2</td>
<td>125,3</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>1,15</td>
</tr>
<tr>
<td>10</td>
<td>4,12</td>
<td>107,1</td>
</tr>
<tr>
<td>20</td>
<td>5,41</td>
<td>102,4</td>
</tr>
<tr>
<td>30</td>
<td>13,09</td>
<td>114,1</td>
</tr>
<tr>
<td>40</td>
<td>28,92</td>
<td>120,7</td>
</tr>
<tr>
<td>50</td>
<td>54,6</td>
<td>128,6</td>
</tr>
</tbody>
</table>

* Состав пара рассчитан по уравнению \( Y_M = K \cdot X_M \) при \( K = 0,0079 \)
Приведенные в таблице 1 данные показывают, что при добавлении нитратов к системе $\text{HNO}_3 - \text{H}_2\text{O}$ температура кипения в системе увеличивается (соблюдается 1-й закон Коновалова), а равновесные пары обогащаются азотной кислотой и тем в большей степени, чем выше концентрация нитрата.

Высаливающее действие нитратов на азотную кислоту является, в основном, следствием двух причин:

1) гидратация ионов нитратов, в результате которой связывается часть молекул воды;

2) смещение ионного равновесия азотной кислоты под действием вводимого одноименного иона $\text{NO}_3^-$.

Обе эти причины приводят к увеличению эффективной концентрации азотной кислоты (или, что то же самое, недиссоциированной части кислоты), т.е. к увеличению ее содержания в паровой фазе.

Естественно, что высаливающее действие различных нитратов неодинаково (рис.1). К сожалению, имеющиеся данные по гидратации ионов и диссоциации азотной кислоты в присутствии нитратов недостаточны для определения влияния указанных причин для каждой соли.

Рис.1

Влияние нитратов на равновесие пар - жидкость в системе $\text{HNO}_3 - \text{H}_2\text{O}; (x = 20\%_\text{o})$;

1 - $\text{Al(NO}_3\text{)}_3$; 2 - $\text{Fe(NO}_3\text{)}_3$; 3 - $\text{Mg(NO}_3\text{)}_2$; 4 - $\text{Cu(NO}_3\text{)}_2$;
5 - $\text{NaN}_3$; 6 - $\text{NH}_4\text{NO}_3$

Однако уже сейчас можно отметить, что порядки расположения нитратов по силе высаливающего действия на азотную кислоту и по способности катионов нитратов к гидратации совпадают: $\text{Al(NO}_3\text{)}_3 - \text{Fe(NO}_3\text{)}_3 - \text{Mg(NO}_3\text{)}_2 - \text{Cu(NO}_3\text{)}_2 - \text{NaN}_3 - \text{NH}_4\text{NO}_3$.
Следует в то же время отметить, что растворимость указанных нитратов в водных растворах азотной кислоты падает с ростом ее концентрации, т.е. кислота высаливает соль. На основании этого можно сформулировать следующее: если (при прочих равных условиях) с увеличением концентрации азотной кислоты в системе нитрат – $\text{HNO}_3 – \text{H}_2\text{O}$ раствора нитрата падает (кислота высаливает соль), то равновесные пары в этой же системе обогащаются кислотой (соль высаливает кислоту). Отмеченное явление взаимовысаливания, по-видимому, имеет общий характер и может служить для качественной оценки влияния соли на равновесие пар-жидкость в двойной системе по данным о растворимости соли в двойном растворителе.

О РАСПРЕДЕЛЕНИИ АЗОТНОЙ КИСЛОТЫ В ПРОЦЕССЕ УПАРИВАНИЯ СБРОСНЫХ РАСТВОРОВ

Для очистки соковых паров от радиоактивности при упаривании обычно используются противоточные тарельчатые колонны*. Число тарелок колонны определяется при этом требуемой степенью очистки. Для количественной характеристики процесса упаривания представляет интерес распределение азотной кислоты между паром ($Y_v$) и жидкостью ($X_b$), уходящими из колонны. При расчете ректификационной колонны встречаются обычно с обратной задачей: задана степень разделения смеси, и требуется определить необходимую для этого эффективность колонны.

Задачу о распределении азотной кислоты можно решить в общем виде графически, используя две зависимости между искомыми величинами: $Y_v$ и $X_b$.

1) $Y = f(x)$ - уравнение материального баланса.
2) $Y = \phi(x)$ - зависимость между составами пара и жидкости, уходящими из колонны с заданной эффективностью (при различных значениях $X_b$).

Координаты точки пересечения кривых, изображающих эти зависимости на диаграмме $Y - X$, дадут искомые составы.

Если эффективность колонны будет эквивалентна одной теоретической тарелке (испаритель), то зависимость $Y = \phi(x)$ совпадает с кривой равновесия $Y = F(x)$ (рис.2).

В другом частном случае, когда число теоретических тарелок колонны равно бесконечности, указанная кривая $Y = \phi(x)$ смещается относительно кривой равновесия таким образом, что, при одинаковых составах жидкой фазы, $Y$ меньше равновесного на величину $\frac{E}{V}$ (рис.3).

В случае конечного числа тарелок в колонне графическое решение несколько усложняется. Для построения зависимости $Y = \phi(x)$ необходимо определить ряд соответствующих значений $Y_v$ и $X_b$ путем

* Колонной в дальнейшем будем называть систему из испарителя и колонны.
Схема графического решения испарителя (rmm = 1).

Графического построения на диаграмме Y-X заданного числа теоретических тарелок при нескольких произвольных положениях рабочей линии колонны, имеющей угол наклона к оси X с тангенсом, равным L/V.

Однако, если колонна имеет эффективность большую 2-3 теоретических тарелок, то приведенное выше графическое решение для случая конечного числа тарелок дает практически те же результаты, что и более простое построение для бесконечного числа тарелок.

Выводы

1. Изучено равновесие пар - жидкость и температуры кипения в части тройных систем:

   $\text{Al (NO}_3\text{)} - \text{HNO}_3 - \text{H}_2\text{O}$

   $\text{Fe (NO}_3\text{)}_3 - \text{HNO}_3 - \text{H}_2\text{O}$
ВЛИЯНИЕ НИТРАТОВ НА СОСТАВ ПАРОВОЙ ФАЗЫ

\[
\begin{align*}
\text{Mg(NO}_3\text{)}_2 & \text{ - } \text{HNO}_3 \text{ - } \text{H}_2\text{O} \\
\text{Cu(NO}_3\text{)}_2 & \text{ - } \text{HNO}_3 \text{ - } \text{H}_2\text{O} \\
\text{NaNO}_3 & \text{ - } \text{HNO}_3 \text{ - } \text{H}_2\text{O} \\
\text{NH}_4\text{NO}_3 & \text{ - } \text{HNO}_3 \text{ - } \text{H}_2\text{O}
\end{align*}
\]

2. Показано, что при добавлении нитратов к двойному растворителю азотная кислота - вода (в области изученных концентраций):
   а) паровая фаза над ним обогащается азотной кислотой;
   б) температура кипения смеси возрастает.

3. Отмечено явление взаимоиспаривания азотной кислоты (в паровую fazu) и нитратов (в твердую fazу).

4. Показана связь между высыхающим действием нитратов и способностью их катионов к гидратации.

5. Предложен в общем виде способ расчета процесса упаривания азотнокислых растворов, позволяющий на основе данных по равновесию пар - жидкость, количественно оценить распределение азотной кислоты в процессе переработки обрывающихся растворов от регенерации облученных тепловыделяющих элементов методом упаривания.

**ОБОЗНАЧЕНИЯ**

\( X \) — содержание азотной кислоты в жидкой фазе (без учета соли)
\( Y \) — содержание азотной кислоты в паровой фазе
\( C \) — содержание соли в жидкой фазе.

**ИНДЕКСЫ**

\( F \) — питание
\( B \) — кубовой остаток
\( L \) — флегма
\( V \) — пары
\( M \) — мольный
LA SÉPARATION DES PRODUITS DE FISSION COMME SOLUTION DÉFINITIVE DU STOCKAGE DES DÉCHETS FORTEMENT RADIOACTIFS

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CENTRE D’ÉTUDES NUCÉAIRES, SAACLAY

Abstract — Résumé — Аннотация — Resumen

FISSION-PRODUCT SEPARATION AS A FINAL SOLUTION TO THE PROBLEM OF STORING HIGHLY RADIOACTIVE WASTE. At the 1955 Geneva Conference; it was suggested by Glueckauf that the problems presented by solutions of concentrated fission products could be dealt with by isolating caesium-137 and strontium-90 with a decontamination factor of at least $10^4$ so that, after conventional effluent processing, disposal could be effected in 10 to 20 years' time.

This paper considers the suggestion in the light of the present situation. Thanks to the progress made in methods of separating caesium and strontium it now seems feasible to obtain this factor of $10^4$ under industrial conditions.

The following methods are very promising:

(a) For caesium-137: precipitation by phosphotungstic acid, exchange using an ammonium salt of a heteropoly-acid, fixation using a zirconium phosphate; and

(b) For strontium-90: oxalate precipitation, extraction by di-2 ethyl hexylphosphoric acid, exchange using various salts, strontium sulphate, etc.

This progress in chemical techniques, backed up by advances in the industrial processing of effluents, indicate that Glueckauf’s proposal is technically possible.

In addition, the increasing use of large quantities of fission products, particularly in the SNAP programmes, justifies the outlay of capital, which will be recovered at least in part by the sale of the products made.

There is no doubt that refractory sources with a very high resistance to attack by all external agents, constitute the most satisfactory means of storage for products so dangerous and of such long half-life. We believe, therefore, that both technically and psychologically, storing by means of concentrated sources with strong cladding is the most reliable method.

A comparison of this method with that of fixation in glass is worthy of full and detailed examination.

LA SÉPARATION DES PRODUITS DE FISSION COMME SOLUTION DÉFINITIVE DU STOCKAGE DES DÉCHETS FORTEMENT RADIOACTIFS. Glueckauf avait formulé, à la Conférence de Genève en 1955, l’hypothèse qu’une solution définitive aux problèmes posés par les solutions de produits de fission concentrés pouvait être trouvée dans l’isolement du césium-137 et du strontium-90 avec un facteur de décontamination d’au moins $10^4$, ce qui permettrait d’envisager le rejet, après un traitement d’effluents classique, au bout d’une période de 10 à 20 ans.

Le but du mémoire est de faire le point de cette question en l’année 1962.

Les progrès réalisés dans les méthodes de séparation du césium et du strontium permettent d’envisager l’obtention de ce facteur $10^4$ dans des conditions exploitables industriellement.

Des méthodes pleines de promesses sont:

a) Pour le césium-137, la précipitation par phosphotungstic acid, l’échange sur un sel d’ammonium d’un hétéropolyacide, la fixation par un phosphate de zirconium.

b) Pour le strontium-90, la précipitation d’oxalate, l’extraction par l’acide di-2-éthyl-hexylphosphorique, l’échange sur des sels variés, sulfate de strontium, etc.

Ces progrès chimiques sont renforcés par les progrès réalisés dans le traitement industriel des effluents et permettent de considérer comme techniquement possible la solution préconisée par Glueckauf.

Parallèlement, le développement de l’utilisation de grandes quantités de produits de fission, particulièrement dans les programmes SNAP, justifie des investissements qui seront au moins partiellement récupérés par la vente des produits fabriqués.

Il est certain que des sources réfractaires, à résistance très élevée à tous les agents d’agression extérieurs, constituent le mode de stockage le plus satisfaisant pour des produits aussi dangereux et d’aussi longue période.
LA SEPARACIÓN DE LOS PRODUCTOS DE FISIÓN COMO SOLUCIÓN DEFINITIVA DEL PROBLEMA DEL ALMACENAMIENTO DE LOS DESECHOS DE ELEVADA RADIACTIVIDAD. En la Conferencia de Ginebra de 1955, Glueckauf formuló la hipótesis de que los problemas planteados por las soluciones de productos de fisión concentrados podrían resolverse aislando el cesio-137 y el estroncio-90 con un factor de descontaminación mínimo de $10^4$, lo que, después de un tratamiento de efluentes ordinario permitiría proceder a la evacuación al cabo de un período de 10 a 20 años.

La finalidad de esta memoria es exponer el estado de la cuestión en 1962.

Los progresos realizados en los métodos de separación del cesio y del estroncio permiten esperar la obtención del mencionado factor $10^4$ en condiciones industrialmente explotables. He aquí los métodos que ofrecen mejores perspectivas:

a) Para el cesio-137: la precipitación mediante el ácido fosfowolfránico, el intercambio a base de una sal de amonio de un heteropolisodio, la fijación mediante un fosfato de circonio,
b) Para el estroncio-90: la precipitación del oxalato, la extracción mediante el ácido di-2-etilhexilfosfórico, el intercambio a base de sales diversas, sulfato de estroncio, etc.

Estos progresos en el terreno de la química, a los que se suman los progresos realizados en el tratamiento industrial de los efluentes, permiten considerar técnicamente posible la solución propuesta por Glueckauf.

Al mismo tiempo, el desarrollo de la utilización de grandes cantidades de productos de fisión, particularmente dentro del marco de los programas SNAP, justifica la inversión de capitales que serán recuperados, por lo menos parcialmente, mediante la venta de los productos fabricados.

Es evidente que las fuentes refractorias, de muy alta resistencia frente a todos los agentes exteriores de ataque, constituyen la forma de almacenamiento más satisfactoria para productos tan peligrosos y de período tan prolongado. Los autores consideran, pues, que desde el punto de vista técnico y psicológico el empleo de fuentes concentradas con abundante revestimiento es el medio de almacenamiento que ofrece mayores garantías.

Valdría la pena efectuar un estudio completo y detallado del método descrito comparándolo con el método de incorporación de los desechos a masas vitreas.
LA SÉPARATION DES PRODUITS DE FISSION

INTRODUCTION

La possibilité de résoudre définitivement le stockage de produits de fission en séparant le césium -137 et le strontium -90 est discutée sur un exemple numérique en examinant le travail d'une installation complète, c'est-à-dire une usine de retraitement des combustibles irradiés couplée à une installation de récupération de césium -137 et de strontium -90, suivie d'une station de traitement des effluents des deux premières installations, l'existence de cette station de traitement des effluents (STE) constituant le fait particulier rendant possible l'application des principes de traitement proposés.

On montre que ces principes de traitement sont valables et que le rejet pourrait être effectué après dix ans de stockage par les solutions classiques actuelles (uranium naturel inférieur à 1500 MWj/t).

Le problème des transuraniens est évoqué.

Cet exposé a surtout pour but de souligner la complexité de la question et de montrer que des facteurs de tous ordres étant pris en considération, cette solution paraît viable.


Il est important de rappeler tout d'abord les étapes du traitement que subissent les produits de fission après dissolution des combustibles irradiés.

Au cours de la récupération du plutonium et de l'uranium, les produits de fission se divisent en deux lots:

I. la quasi totalité est stockée en solution après concentration,
II. une petite quantité de ces produits de fission trop dilués pour être concentrés est rejetée directement ou après traitement dans une station de traitement des effluents.

L'ensemble des opérations précédentes s'effectue après une décroissance des produits de fission qui n'excède pas un an. La suggestion du Dr. Glueckauf était de séparer le césium et le strontium de la partie I.

Le schéma du traitement proposé est le suivant (figure 1):

1. Traitement du césium -137

a) Un traitement chimique va produire le césium-137, suivi, si nécessaire, d'un traitement additionnel de décontamination qui fournira le facteur de décontamination désiré.

b) Au cours du traitement de récupération, une certaine quantité d'effluents à rejeter immédiatement sera produite. On peut l'évaluer à une fraction des effluents de l'installation de retraitement des combustibles irradiés pour tous les produits de fission, sauf pour le césium -137 qui
Figure 1
Schéma de traitement complet.
exigera un traitement additionnel pour l'obtention du facteur de décontamination désiré pour le césium -137. Puis ces effluents passeront par la station de traitement des effluents avant le rejet.

2. Traitement du strontium-90

Il est strictement identique à celui du césium -137.

3. Traitement final des solutions de fission

Après un stockage de l'ordre de dix ans, les solutions de fission débarassées de la majeure partie de leur césium et de leur strontium seraient rejetées après avoir passé par le STE.

En appelant TCI le traitement des combustibles irradiés pour la récupération de l'uranium et du plutonium, EU l'élimination ultime, c'est-à-dire l'opération qui, après la production d'un produit de fission, permet l'obtention du facteur de décontamination désiré, TE l'opération classique de décontamination des effluents dilués, nous arrivons au schéma de principe fourni par la figure 1.

Nous avons illustré le schéma de traitement précédent par un exemple numérique en prenant comme hypothèse de travail les valeurs suivantes:
- Nous avons supposé que l'installation TCI était capable de fournir $10^6$ c/a de césium -137 et de strontium -90.
- Nous avons admis qu'une usine de traitement irradié faisait 0,05% d'effluents de l'activité initiale et que les éléments combustibles étaient traités au bout de quatre mois de refroidissement.
- Nous avons pris pour valeurs du facteur de décontamination d'une station de traitement d'effluents, les valeurs suivantes:

<table>
<thead>
<tr>
<th>Élément (137Cs, 90Sr, 106Ru, 144Ce et terres rares)</th>
<th>Facteur de décontamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>137Cs</td>
<td>100</td>
</tr>
<tr>
<td>90Sr</td>
<td>100</td>
</tr>
<tr>
<td>106Ru</td>
<td>5</td>
</tr>
<tr>
<td>144Ce et terres rares</td>
<td>1000</td>
</tr>
</tbody>
</table>

Nous avons adopté, comme caractéristiques de l'installation de production de produits de fission, les valeurs suivantes:

a) Le traitement des solutions de fission a lieu après deux ans de décroissance.

b) Nous avons admis que le traitement du 137Cs libérait en effluent, en produits de fission mélangés, 0,01% de l'activité traitée (sauf pour le 137Cs pour lequel il est prévu une épuration spécifique).

c) Nous avons admis que la production de 90Sr libérait 0,01% de l'activité totale traitée en produits de fission mélangés (sauf en 90Sr pour lequel il est prévu une épuration spécifique).

d) Les deux épurations spéciales précédentes, ainsi que l'élimination ultime du 137Cs et du 90Sr des solutions de fission, sont capables de fournir un facteur de décontamination de $10^4$ par rapport à l'activité initiale traitée.
DISCUSSION DU SCHÉMA DE TRAITEMENT

Le fait de tenir compte de l'existence d'une station de traitement des effluents associée à l'installation de retraitement des combustibles, TCI, et à celle de récupération de $^{137}$Cs et $^{90}$Sr, IRPF, fait apparaître les faits suivants:

-On peut admettre pour les rejets totaux en activité, pour la récupération de $^{137}$Cs et $^{90}$Sr, le même ordre de grandeur que le rejet de l'installation de retraitement des combustibles irradiés.

-La quantité de boues actives produites par la STE étant directement fonction des volumes liquides traités sera peu augmentée par ce nouvel apport venant de IRPF, car ceux-ci sont peu importants par rapport à ceux du TCI.

-Dans l'hypothèse de Glueckauf, les concentrations maxima admissibles du $^{90}$Sr et du $^{137}$Cs étant très diffuses ($^{90}$Sr : $10^{-7}$ μc/l, $^{137}$Cs : $2 \cdot 10^{-4}$ μc/l), il serait possible théoriquement de ne rechercher un FD de $0,5 \cdot 10^2$ pour le $^{137}$Cs que lorsqu'on recherche parallèlement $10^6$ pour le $^{90}$Sr.

Dans cette hypothèse, le STE devrait récupérer 99% des $10^4$ c de $^{137}$Cs qui lui parviennent annuellement.

Or, après une durée de stockage convenable, le rayonnement des boues actives provenant de la STE est presque uniquement dû au $^{137}$Cs [3].

Faire passer de $10^4$ à $10^6$ c, dans les boues de la STE, le césium-137 dû à l'IRPF, équivaut à transformer complètement la conception des STE actuellement utilisées.

Il faut donc décontaminer le $^{137}$Cs avec le même facteur de décontamination que le $^{90}$Sr, sauf si les possibilités de rejet d'une installation sont très favorables. On peut alors profiter du fait que le traitement généralement appliqué dans les STE est spécifique pour le $^{137}$Cs, pour ne pas le faire; ceci amènera à rejeter le $1/100$ de l'activité totale manipulée en $^{137}$Cs et la nocivité relative du $^{137}$Cs rejetée deviendra 50 fois plus importante que celle du $^{90}$Sr.

En conclusion, le schéma (figure 1) complet de traitement montre clairement qu'un stockage de l'ordre de 10 ans est suffisant pour des rejets après traitement en STE. Dans l'hypothèse d'un stockage de 10 ans, les produits de fission $^{90}$Sr et $^{106}$Ru ont des toxicités relatives immédiates équivalentes.

LE PROBLÈME DES TRANSURANIENS

Nous ne nous proposons pas de traiter dans cette publication tous les cas se présentant lorsqu'on fait varier la nature du combustible et le «burn up». Il a été montré [4, 5] que dans le cas d'uranium naturel irradié d'un flux de $10^{13}$ n/cm$^2$.s jusqu'à 1500 MWJ/t, la contribution du curium-242 et de l'américium-241 à la toxicité des produits de fission est négligeable.

Il importe de souligner seulement ici:

a) que les facteurs de décontamination d'une STE pour Am, Cm et Pu sont excellents et toujours supérieurs à $10^3$. 
LA SÉPARATION DES PRODUITS DE FISSION

b) Nous verrons, quand nous examinerons les traitements de récupération du $^{90}$Sr, que les actinides peuvent être extraits en même temps que le $^{90}$Sr.

D'autre part, nous verrons que le procédé d'extraction du strontium-90 permet aussi de séparer les actinides avec les terres rares.

MÉTHODES DE PRÉPARATION ET DE SÉPARATION ULTIME POUR LE $^{137}$Cs ET LE $^{90}$Sr.

1. Tout le schéma de la figure 1 repose sur la possibilité d'obtenir un facteur de décontamination de $10^4$. Cela est-il possible dans des conditions industrielles?

2. Quels sont les problèmes posés par les déchets solides provenant de l'élimination ultime qui peuvent représenter le 1/100 de l'activité totale manipulée en $^{90}$Sr et $^{137}$Cs?

A. Césium -137

1. Méthode de production

Nous ne reviendrons pas longuement sur les diverses méthodes possibles de séparer le césium -137.

Nous nous contenterons de souligner l'intérêt des méthodes séparant le césium-137 en milieu acide, c'est-à-dire essentiellement celles qui utilisent la précipitation ou l'échange sur un sel d'hétéropolyacide.

Une méthode de précipitation peut ne laisser que 1% du césium initial. A fortiori, une méthode d'échange comme celle préconisée par VAN SMIT [6] donnera un rendement au moins aussi bon.

Par contre, la quantité de césium présent dans les effluents divers peut être de l'ordre de 10% de l'activité totale du césium manipulé.

2. Elimination ultime

La méthode utilisée devra fournir un FD de $10^2$ sur les solutions de fission et de $10^3$ sur les effluents du procédé.

Deux genres de méthodes paraissent actuellement possibles.

a) Celles qui utilisent l'échange sur un sel d'ammonium d'un hétéropolyacide, soit en colonne [6], soit en lit fluidisé [7].

b) Celles utilisant la bonne fixation du césium sur un échangeur d'ion (et particulièrement sur le phosphate de zirconium).

Naturellement, la majeure partie de l'activité récupérée au cours de ces éliminations ultimes doit être recyclée dans la partie production du césium-137.

Il est assez raisonnable, malgré tout, d'admettre que 1% du césium initial restera comme déchet solide au stade de l'élimination ultime en vue d'un stockage permanent.

Il sera donc souhaitable que le 1% du césium restant (soit $10^4$ c/a) soit stocké sous la forme la plus condensée possible (cela est réalisable avec les deux types de méthodes précédemment choisies).
Extrait du 90 Sr par l'acide di-2-éthylhexylphosphorique.

Figure 2

Extraction du 90 Sr par l’acide di-2-éthylhexylphosphorique.
LA SÉPARATION DES PRODUITS DE FISSION

B. Strontium -90

1. Méthode de production

Parmi les quelques méthodes possibles (perception des escales, etc.) celle qui paraît offrir le plus de possibilités est l'extraction par les esters phosphoriques, par exemple par l'acide di-2-éthylhexylphosphorique.

Nous avons représenté (figure 2) un schéma de traitement de récupération du $^{90}$Sr par solvant.

Cette méthode présente les avantages suivants:

a) Le procédé étant continu, les lavages sont réduits au minimum.

b) On peut obtenir par le même procédé la production et l'élimination ultime du $^{90}$Sr. Il suffit de rajouter un peu de strontium entraîneur pour garder le même coefficient de partage pour le strontium.

Les terres rares et les actinides se trouvent séparés dans la même opération et rassemblés, si on le désire, dans un volume faible par rapport au volume initial, ce qui pourrait conduire à préconiser le traitement des produits de fission après un refroidissement plus long que deux ans.

Il est néanmoins certain que l'on n'échappe pas à la nécessité d'une fixation de type échange d'ion pour conserver le facteur de décontamination de $10^4$ pour le strontium -90.

PERSPECTIVE A LONG TERME

Si on essaie d'étudier le même problème d'un point de vue mondial, il est pratiquement impossible d'analyser aussi loin que précédemment. En effet, la nature chimique et radiochimique des stocks de produits de fission existant dans le monde varieront fortement en fonction des combustibles nucléaires, des alliages ou composés employés, des « burn up » obtenus.


Ces réserves faites, il est néanmoins nécessaire de souligner que les performances demandées restent valablement les mêmes d'un point de vue mondial, si on reprend les valeurs préconisées par RODGER [7], c'est-à-dire les quantités de produits de fission existant au bout de cinquante ans d'accumulation.

En calculant la proportion de chaque produit stocké avec un stockage de 10 ans (et de 20 ans), nous obtenons les résultats donnés au tableau I.

Il est clair que les volumes nécessaires à la dilution des rejets supputés après traitement STE seraient convenables, compte tenu du nombre de points de rejet en mer qui existerait dans le monde.

Le stockage avant rejet devrait être compris entre 10 et 20 ans, le $^{106}$Ru étant le produit de fission critique.

En conclusion, nous dirons que les possibilités d'application de la proposition de Glueckauf mérite de retenir toute l'attention des spécialistes, car les performances demandées aux procédés et aux installations (FD $10^4$) sont loin d'être impensables en regard des avantages que l'on peut en escompter, c'est-à-dire:
<table>
<thead>
<tr>
<th>Isotope</th>
<th>Quantités accumulatees en 50 ans</th>
<th>Concentr. max. permises en μc/cc</th>
<th>Concentr. max. permises en curie/km³</th>
<th>Quantités rejetées après 10 ans de stockage</th>
<th>Volume nécessaire pour diluer à la dose de tolérance en km³</th>
<th>Quantités rejetées après 20 ans de stockage</th>
<th>Volume d'eau nécessaire pour diluer à la dose de tolérance en km³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>sans avec</td>
<td>STE</td>
<td>STE</td>
<td>STE</td>
</tr>
<tr>
<td>95 Zr</td>
<td>$1.3 \times 10^{11}$</td>
<td></td>
<td></td>
<td>STE nég.</td>
<td>STE</td>
<td>STE</td>
<td>STE</td>
</tr>
<tr>
<td>144 Ce</td>
<td>$1.1 \times 10^{11}$</td>
<td>$10^{-4}$</td>
<td>$10^{5}$</td>
<td>$2 \times 10^{4}$</td>
<td>200</td>
<td>0,2</td>
<td>$3 \times 10^{3}$</td>
</tr>
<tr>
<td>156 Ru</td>
<td>$1 \times 10^{11}$</td>
<td>$10^{-4}$</td>
<td>$10^{5}$</td>
<td>$2 \times 10^{7}$</td>
<td>1000</td>
<td>200</td>
<td>$3 \times 10^{4}$</td>
</tr>
<tr>
<td>147 Pm</td>
<td>$5.1 \times 10^{10}$</td>
<td>$2 \times 10^{-3}$</td>
<td>$2 \times 10^{3}$</td>
<td>$3 \times 10^{5}$</td>
<td>1600</td>
<td>3,2</td>
<td>$2 \times 10^{5}$</td>
</tr>
<tr>
<td>90 Sr</td>
<td>$8.6 \times 10^{10}$</td>
<td>$10^{-6}$</td>
<td>$10^{5}$</td>
<td>$6 \times 10^{4}$</td>
<td>8000</td>
<td>50</td>
<td>$3 \times 10^{4}$</td>
</tr>
<tr>
<td>137 Cs</td>
<td>$8.1 \times 10^{10}$</td>
<td>$2 \times 10^{-4}$</td>
<td>$2 \times 10^{5}$</td>
<td>$5.6 \times 10^{4}$</td>
<td>20</td>
<td>0,2</td>
<td>$3 \times 10^{4}$</td>
</tr>
</tbody>
</table>

NOTA: Les quantités rejetées pour le 137Cs et 90Sr ont été prises après le traitement d'élimination ultime (FD = 10⁴)
LA SÉPARATION DES PRODUITS DE FISSION

- utilisation de stockage liquide uniquement à moyen terme,
- récupération du $^{137}\text{Cs}$ et du $^{90}\text{Sr}$ sous une forme utilisable et offrant les garanties les plus grandes du point de vue de la sécurité.

RÉFÉRENCES


DISCUSSION

E. GLUECKAUF (Chairman): It is true that separation of the long-lived isotopes caesium and strontium make the bulk remaining after prolonged storage easier to handle and this view is also accepted in the paper by TOMLINSON*. However, it does not follow that one would wish to discharge these solutions into the sea, and to do so is certainly against the policy of the UKAEA. Firstly, it is now considered inadequate to use considerations of maximum permissible concentrations as a criterion on which to decide disposal to the environment. Instead, one has to decide on the basis of the total amounts released, and consider these in relation to possible locally applicable natural concentration processes which might take significant amounts of activity back to man. Such assessments, which have to be made for every individual locality, are very laborious.

Secondly, even if such an assessment eventually permitted discharge of these effluents into the sea as perfectly safe - and personally I think that it could be safe - one can see neither the need nor any economic incentive for dispersing these comparatively small volumes of concentrated solutions in the sea. The UKAEA is satisfied that keeping them either in stainless steel containers or in the form of glasses would not significantly increase the cost of nuclear power.

J. LEFEVRE (on behalf of R. RAGGENBASS): In the description of our treatment system, we have stressed the existence of an effluent treatment station. In speaking of discharge to the environment we have in mind only the surface solutions, after treatment in this station, whereas almost all the activity remains in the sludges, stored in solid form. Moreover, the intermediate storage of 10 – 20 years considerably reduces the overall activity of the mean-life fission products remaining after the separation of Cs$^{137}$ and Sr$^{90}$.

* TOMLINSON, R.E., "HANFORD high-level waste management", These proceedings.
As regards your second point, we think the net saving achieved by recuperating fission products such as Cs\(^{137}\) and Sr\(^{90}\) may at some future date justify this form of treatment, although the capital cost of the treatment is higher. In our view, the method certainly deserves consideration along with the various other methods suggested for the ultimate treatment of fission products for storage.

N. E. BREZHNEVA: How many theoretical stages are necessary for the complete separation of strontium and the rare earths? What type of extractor do you intend using and what concentration of di-2 ethyl hexyl phosphoric acid is used?

L. LEFÉVRE: The theoretical number of stages depends on the composition of the solution treated (iron, sodium, etc. content). The separation factors are between 10 and 30 for strontium at pH 4 and from 20 to 100 for cerium at pH 2. The number of theoretical stages can be calculated from those values.

The apparatus used for the laboratory research is a battery of mixing decanters, with which it is possible to check the various extraction phases. This type of apparatus seems to us to present advantages up to the pilot stage, in view of the information which it can provide on the progress of extraction. When an industrial installation is required, investigations will be made to determine the appropriate equipment (choice between pulsed column, battery of mixing decanters, etc.).

Under the conditions with which we are concerned, the composition of the organic phase is \( \frac{0.3 \text{ M } \text{D}_{2}\text{EHPA}}{0.15 \text{ M } \text{TBP}} \) in dodecane.

F. DUHAMEL: This is in connection with what Mr. Glueckauf said and it is not at all a criticism of the excellent paper we are considering. I would only like to point out that, as Mr. Belter mentioned in his review of United States practice*, by 1980 mankind will have several thousand million curies of fission products. Assuming that we extracted caesium and strontium for useful purposes and that the caesium and the strontium were equitably distributed throughout the population, each man would have several curies of fission products. Therefore the problem of protection will not have been solved, because these various sources are not going to decay sufficiently rapidly. They have half-lives longer than the artificial radioisotopes used for practical applications and it will therefore be necessary to take very serious measures to protect mankind.

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* BELTER, W. G., "Present and future programmes in the treatment and ultimate disposal of high-level radioactive wastes in the United States of America", These proceedings.
ULTIMATE STORAGE OF HIGH-LEVEL WASTE SOLIDS AND LIQUIDS IN SALT FORMATIONS

OAK RIDGE NATIONAL LABORATORY, TENN.

Abstract — Résumé — Аннотация — Resumen

ULTIMATE STORAGE OF HIGH-LEVEL WASTE SOLIDS AND LIQUIDS IN SALT FORMATIONS. Salt formations offer an attractive site for the ultimate storage of high-level liquid and solid wastes. Salt formations are impermeable, have good structural strength and good thermal conductivity.

Laboratory experiments and field tests in a Kansas mine have shown that: (1) the thermal conductivity and diffusivity of impure rock salt in situ (0.011 cal/cm·sec/°C and 0.026 cm²/sec at a peak salt temperature of 60°C) are within 10% to 20% of the laboratory values for single crystals; (2) elevating the temperature of 3000 gal (US) of waste in a 7½-ft square cavity of 65°C did not upset the structural stability of the mine room, even though the floor-to-ceiling dimensions decreased by 1/2 in at a distance of 5 ft from the cavity; (3) evaporation of solution with subsequent condensation on the walls produces some alteration of the cavity; (4) adsorption of the waste solution on to crushed salt appears to retard both cavity alteration and the production of radiolytic decomposition gases; (5) radiation doses to be expected in an actual disposal operation will not be great enough to significantly affect the structural stability of the rooms.

The major remaining uncertainty is the effect on structural stability of elevating the temperature of large areas of a mine. A theoretical and experimental investigation of this problem is currently under way.

Temperature-rise calculations have been performed for the storage of wastes from a 6-t/d fuel-processing plant. For liquids the waste was assumed to be adsorbed onto granular salt in rooms with recessed floor. The net mine area required to limit the waste-temperature rise to 70°C varied from 34 acres per year for 120-day-old wastes to 5 acres per year for 30-yr old wastes. If the wastes are stored in solid form above the floor, the acreage requirements are reduced by a factor of 2.3. For cylindrical vessels stored in holes in the mine floor, calculations, based on an infinite array of line sources, showed that, in general, for wastes cooled longer than three years the space requirements are the same as for solids above the floor.

Current studies are primarily concerned with the disposal of packaged solids and will culminate with a demonstration in a salt mine, probably during 1965.

STOCKAGE DEFINITIF DE DÉCHETS SOLIDES ET LIQUIDES DE HAUTE ACTIVITÉ DANS DES FORMACTIONS SALINES. Les formations salines présentent beaucoup d’intérêt pour le stockage définitif de déchets liquides et solides de haute activité. Elles sont imperméables, elles sont résistantes et elles offrent une bonne conductibilité thermique.

Des expériences en laboratoire et des essais dans une mine du Kansas ont montré que: a) les valeurs de la conductibilité thermique et du coefficient de diffusion de la roche saline impure in situ (0.011 cal/cm·s·°C et 0.026 cm²/s pour une température de pointe du sel de 60°C) ne représentent que de 10 à 20% des valeurs mesurées en laboratoire pour des monocristaux; b) le fait de porter à 65°C la température d’un volume d’environ 12 000 l de déchets placés dans une cavité carrée de 2,25 m de côté n’a pas compromis la stabilité de la chambre de mine, bien que la distance entre le sol et le plafond ait diminué de 1,25 cm à 1,50 m de la cavité; c) l’évaporation de la solution suivie d’une condensation sur les parois provoque certaines altérations de la cavité; d) l’adsorption d’une solution de déchets par du sel écrasé retardait à la fois l’altération de la cavité et la production de gaz provenant de la décomposition radiolytique; e) les doses de rayonnement aux- quelles il faut s’attendre dans une opération réelle d’élémination de déchets ne sera pas suffisamment grande pour affecter sensiblement la stabilité des chambres de mine.

* Analytical Chemistry Division.
** Chemical Technical Division.
Le point principal sur lequel il subsiste encore des doutes est l'influence sur la stabilité de la mine d'une élévation de la température de grandes surfaces. Des recherches théoriques et expérimentales sur ce point sont en cours.

Des calculs d'élévation de température ont été faits pour le stockage de déchets provenant d'une usine de traitement de combustible irradié traitant 6 t par jour. Pour ce qui est des liquides, on suppose qu'ils seront adsorbés par le sel granulaire formant le fond surbaissé des cavités. Pour limiter l'élévation de température des déchets à 70°C, la surface nette de la mine doit varier de 13 hectares par an pour des déchets vieux de 120 jours à 2 hectares par an pour des déchets vieux de 30 ans. Si les déchets sont emmagasinés sous forme solide sur le sol de la mine, on pourra diviser les surfaces ci-dessus par 2,3. Si on stocke des récipients cylindriques dans des trous creusés dans le sol de la mine, des calculs fondés sur une disposition linéaire infinie des sources montrent que pour des déchets désactivés depuis plus de trois ans la surface nécessaire sera en général la même que pour des solides disposés sur le sol.

Les études en cours portent essentiellement sur l'élaboration d'une méthode de stockage des déchets solides et liquides de haute activité. Elle doit être basée sur des calculs de la stabilité de la mine en cas d'élévation de température des déchets.

Les études en cours portent essentiellement sur l'élaboration d'une méthode de stockage des déchets solides et liquides de haute activité. Elle doit être basée sur des calculs de la stabilité de la mine en cas d'élévation de température des déchets.
de desechos en la sal triturada retarda al parecer tanto la alteración de la cavidad como la formación de gases por descomposición radiolítica; e) las dosis de radiación que cabe esperar durante una operación de evacuación efectiva no serán bastante elevadas como para afectar en forma apreciable la estabilidad estructural de las cámaras.

El principal factor de incertidumbre es el efecto de una elevación de temperatura en grandes superficies de una mina sobre su estabilidad estructural. Este problema se está estudiando actualmente teóricamente y experimentalmente.

Por otra parte, se ha calculado el ascenso de temperatura que produciría el almacenamiento de los desechos procedentes de una planta de tratamiento de combustible de 6 t de capacidad diaria. En el caso de los líquidos, se supuso que los desechos serán absorbidos por rocas salinas de estructura granular, en cámaras con depresiones en los pisos. La superficie neta de mina necesaria para limitar a 70°C el ascenso de temperatura de los desechos varía entre 34 acres/año para los desechos de 120 días, y 5 acres/año para los desechos de 30 días. Si los desechos se depositan en forma de sólidos sobre el piso de la mina, la superficie necesaria se reduce 2,3 veces. En el caso de recipientes cilíndricos almacenados en cavidades practicadas en el piso de la mina, los cálculos basados en una disposición de las fuentes en hileras infinitas demuestran que, en general, el espacio necesario para desechos "enfriados" durante más de tres años es igual que para los sólidos colocados sobre el piso.

Los estudios actualmente en curso versan principalmente sobre la evacuación de sólidos envasados y, como culminación de los mismos, se proyecta realizar en 1965 una demostración en una mina de sal.

INTRODUCTION

In September of 1955, at the request of the Reactor Development Division of the USAEC, the Earth Sciences Division of the National Research Council discussed the disposal of high-activity-level radioactive wastes in geologic structures. As a result of these deliberations, storage in natural salt formations was proposed as perhaps the most promising method [1].

Some of the advantages of natural salt formations as repositories for radioactive wastes are:

1. Salt is essentially impermeable due to its plastic properties;
2. Salt is widely distributed and abundant, underlying about 500 000 square miles in the United States and with known reserves greater than $6 	imes 10^{18}$ t [2, 3];
3. The cost of developing space can be as low as 15 cents/ft$^3$ [4, 5];
4. The thermal conductivity of salt is good (2.5 BTU hr$^{-1}$ ft$^{-1}$ °F$^{-1}$ at 200°F) [6];
5. Salt formations in the United States are located in areas of low seismicity;
6. The compressive strength of salt is similar to that of concrete or about 3 000 lb/in$^2$.

In spite of the apparent advantages of natural salt formations for disposal of high-level wastes, questions that required answers before an actual storage operation could take place were in brief: (1) to what degree will the structural properties of salt be altered by heat and radiation, (2) will there be interactions between liquid waste and salt, and (3) can the off-gas problems be handled?

LARGE-SCALE TESTS WITH LIQUID WASTES [7-9]

The installation in a mine in Kansas of two large-scale field tests designed to provide answers to some of the questions was reported at the IAEA Conference on the Disposal of Radioactive Wastes, November, 1959 [10].
Objectives

The major objectives of these tests were: (1) to check the validity of theoretical heat-flow calculations, (2) to measure the effects of heat on plastic flow of the salt, (3) to determine the nature and extent of chemical interactions between the liquid waste and the salt, and (4) to investigate possible changes in size and shape of cavities.

Waste composition

The waste chosen for use in these experiments chemically simulated the first-cycle raffinate from the Purex solvent extraction system as it existed in 1958 but did not include any radioactive material. The solution had the following composition:

$$7.0 \text{ M, } \text{NO}_3^-; 0.75 \text{ M, } \text{SO}_4^{2-}; 0.5 \text{ M, } \text{Fe}^{3+}; 0.3 \text{ M, } \text{Na}^+; 7.7 \text{ M, } H^+.$$  

This waste was used for one experiment and was neutralized with 50% NaOH to a pH of approximately 10.5 for the other to simulate the neutralized waste presently being stored in carbon steel tanks. Waste was assumed to be generated at a rate of approximately 800 gal/t of uranium processed, with heat generation based on an assumed cooling time of two years, burn-up of 10 000 MWD/t, and 33 MW/t specific power. Fission product heating was simulated by passing alternating current through the solution.

Test cavities

The experiments utilized two 7.5-ft-square by 10-ft-deep cavities excavated in the floor of the mine. The size of the cavities was selected so that the surface area, when the cavity was filled to a 7.5-ft depth (approximately 3 000 gal), would be equal to that of a 10-ft-diam. sphere, thus permitting correlation of experimental thermal data with theoretical heat calculations based on spherical cavities.

Operation

Initial power input to each cavity was 5760 W, with the input being reduced about 50 W every 30 d. The experiment with neutralized waste was placed in operation on 6 January, 1960, and the acid-waste experiment on 18 January, 1960. The acid-waste experiment was terminated on 2 August, 1960, after 197 day's operation. The neutralized waste experiment was terminated on 1 February, 1961, after 392 day's operation.

Heat flow

Calculations based on the equivalent sphere, assuming complete mixing of waste, predicted a maximum temperature rise of 50°C. Temperature rises actually achieved are shown in Fig.1. In the acid-waste cavity, where convective mixing was good, the maximum average waste temperature rise was 42°C. In the neutralized-waste cavity, which contained a viscous sludge,
Fig. 1

Average temperature rise in waste
the maximum average temperature rise was 52°C. Temperature rises out in the salt formation were also in good agreement with the theoretical calculations. Perfect agreement would not be expected, since (1) the sphere only approximates the cube, (2) heat transfer from the floor to the mine air would not be the same as for conduction in salt, and (3) there are horizontal shale and anhydrite bands in the cavity walls.

The theoretical time-space temperature rise in an infinite medium containing a spherical heat source can be normalized such that distances from the sphere are in terms of sphere radii. When plotted on logarithmic graph paper, the thermal conductivity and diffusivity of the medium can be determined by superimposing experimental temperature rises obtained with spherical sources.

In the case of the 7.5-ft cube of neutralized waste, the localized heating in the precipitate makes such a comparison invalid. The acid-waste cavity, however, gives a reasonably good check if the comparison is confined to portions of the curves that represent a temperature rise greater than 1°C and time less than 20 d after start-up. (The accuracy of the temperature recordings is approximately ± 0.5°C, and after 20 d the heat loss through the floor becomes appreciable.) The data from the acid-waste test are plotted in Fig. 2 along with theoretical curves for a 10-ft-diam. sphere with the ordinate and abscissa adjusted so that the cavity-wall curves approximately coincide. It will be noticed that the 2.5- and 8-ft-out curves show good agreement with the theoretical for the 10-ft-diam. sphere. The 0.5-ft-out curve does not agree so well, perhaps because of an inaccurately placed thermometer. From this comparison, the calculated thermal conductivity is 2.6 BTU hr⁻¹ ft⁻¹ °F⁻¹, and the diffusivity 0.10 ft²/hr. The BIRCH and CLARK [6] values for single salt crystals at 60°C, the peak salt temperature reached in the experiment, are 2.8 BTU hr⁻¹ ft⁻¹ °F⁻¹ and 0.10 ft²/hr, respectively.
Plastic flow

Rock salt flows plastically under elevated temperature and pressure; and thus, for any given mine disposal operation, there will be a limit to the allowable temperature rise if a desired degree of structural stability is to be maintained. When a cavity or room is developed in salt, there is immediate plastic flow which results in decreased cavity dimensions. As time progresses, the rate of flow decreases, but it may never cease in cases where the elastic limit is exceeded. The problem is to determine the maximum allowable temperature rise which will ensure that the room does not close to an undesired extent in a specified period of time.

Gauges to measure changes in room dimensions were installed around the 7.5-ft-square cavities and at other locations in the mine. Results obtained from the gauges around the neutralized-waste cavity are shown in Fig. 3. The upper curve shows the total deformation from floor to ceiling at a point about 5 ft from the edge of the waste cavity. The portion of the curve from 0 to 110 d represents the flow that was taking place before heating. If this portion of the curve is extrapolated at a constant slope, it indicates that the floor and ceiling will meet in about 900 yr. Actually, since the rate of flow decreases with time, the time for closure would be expected to be much greater and, in fact, the room may never close. The portion of the curve from 110 d up to about 400 d represents the time that the salt temperature was rising due to application of heat to the waste. From 400 to 500 d the temperature of the salt under the gauge was essentially constant at the maximum value reached. (The temperature rise of the salt beneath

![Fig. 3](image-url)

Total deformation for various gauge locations around neutralized-waste cavity.
the gauge varied with depth and distance from the waste cavity, but the highest rise immediately adjacent to the cavity was approximately 45°C. At 10-ft out the highest temperature rise was about 10°C.) During the period from 400 to 500 d the flow rate was essentially the same as it was before heating, thus indicating that raising the salt temperature a few degrees did not upset the structural equilibrium of the room. Immediately upon shutting off the power to the waste, the flow rate became negative and during the cooling period part of the deformation was recovered. After the salt had returned to ambient temperature (at about the end of the curve), the flow rate again reversed its sign, and returned to the approximate value which it had before heating. The net effect of heating the salt around the cavity for a period of about one year has been the introduction of an offset of about 0.5 in in the normal cumulative deformation curve.

The calculated thermal expansion of the salt beneath the gauge, if it all took place in the vertical direction, is about 0.5 in. However, the fact that complete contraction did not take place when the temperature returned to ambient indicates that the expansion or flow was largely inelastic.

Chemical interactions

Shale impurities in the salt contain oxidizable material which will react with HNO₃ at ambient temperature to produce volatile oxides of nitrogen and CO₂. No interaction has been observed between anhydrite and the acid-waste solution. The slight attack of acid Purex waste solution on the Haynes Alloy No. 25 cavity cover will also produce small amounts of the oxides of nitrogen. The aqua regia reaction would be expected to produce NOCl and Cl₂ [11]. No reactions were expected and none were observed in the cavity containing neutralized Purex waste.

Samples of the gaseous products were taken at the beginning of the experiment (temperature 22°C) and at regular intervals up to the maximum temperature reached by means of evacuated 250-ml bottles.

Gas production in the acid cavity became substantial only between 50 and 60°C. The vapour contained no detectable NOCl at 51°C but reached 7 vol. % at 60°C. A further rise in temperature to 63.7°C resulted in an NOCl content of 18%. There were traces of N₂O and NO₂ from the beginning of the experiment and these rose to about 10% at 63.7°C. CO₂ reached a peak concentration of 4% at about 60°C. Routine analysis of off-gases from the acid cavity did not positively show the presence of chlorine; however, when a sample of the gases was collected in a cold trap, chlorine was present.

Laboratory studies have shown that there is a close relation between the free-acid content of acid Purex waste and gas production [11]. The free-acid content was monitored at two locations during the rising-temperature phase of the experiment and the data obtained indicated the progress of the reaction in the solution during the heating process. The change was very small until a temperature of approximately 60°C was reached. The reaction in the solution below 60°C is primarily between HNO₃ and the oxidizable components of the shale and with carbonates present in the shale and possibly in the salt. At approximately 60°C the aqua regia reaction begins, and the free acidity dropped from 6.9 M to 6.6 M. A further drop in acidity would have been expected if the temperature had gone higher.
Alteration of cavity size and shape

The changes in the cavities produced by the experiment were documented in three ways: (1) by direct measurement; (2) by weighing the salt redeposited during the experiment; and (3) by photographs.

The shape and dimensions of the cavities used to contain the acid and neutralized Purex waste solutions were altered during the course of the experiment by erosion, both above and below the liquid level and by salt recrystallization. Both phenomena would be anticipated in a system where a thermally hot liquid is contained in a medium that is highly soluble in the liquid. Erosion of the walls of the acid-waste cavity resulted from physical dissolution as well as chemical attack. The degree of erosion below the liquid level in the neutralized waste pit was minimal. There was considerable erosion above the liquid level in both cavities.

**Acid waste cavity**

In the acid cavity, from the liquid level at 2.5 ft to about 9 ft below the mine floor, the wall was partially covered with salt crystallized from the waste solution. Localized attack resulted in pitting of the walls to as much as 8 to 9 in. There was no apparent system to these points of deep attack; however, they appeared to parallel the bedding planes. The bottom of the cavity was covered by a thick layer of dense recrystallized salt. The material reached a depth of 16 in near the wall and was about 4 in thick near the centre.

Approximately 7400 lb of material (recrystallized salt and some shale) was chipped from the walls and floor of the acid cavity. If this amount of material is considered to have dissolved from the walls, it represents an average penetration of 1.9 in. If the unattacked area at the bottom of the cavity is eliminated from the computation, the average penetration is 2.5 in.

**Neutralized-waste cavity**

In the neutralized-waste cavity there was deep erosion of the wall just below the rim due to a malfunctioning condensate collection system. The anhydrite band, beginning about 10 in and continuing to 15 in below the mine floor, was undisturbed. Below the anhydrite band, salt mixed with shale 15 to 21 in down, was eroded to maximum depths of 15 to 18 in. Recrystallized salt was deposited on the wall from about 21 in to 30 in (the liquid level). This deposit was thickest just at the liquid level, bridging out over the solution to distances of several inches. Below this, the wall was covered by 2 to 3 in of crystalline salt down to the precipitate occupying 22 to 24 in at the bottom.

It was not possible to measure as accurately the amount of recrystallized salt in the neutral cavity since the sludge in the bottom of the cavity may have contained some salt and large pieces of salt were removed from the bridged-over area during cover and electrode disassembly and may have become mixed with the sludge. Approximately 5600 lb of salt were chipped from the walls, and if this is assumed to have been removed evenly from the upper two feet of the walls, the depth of erosion would be about 8 in.
LABORATORY STUDIES ON DISPOSAL OF LIQUIDS

When aqueous solutions are exposed to high levels of radiation, some of the water is radiolytically decomposed producing a hazardous mixture of hydrogen and oxygen.

A study of the radiolytic stability of representative waste solutions was undertaken in order to determine the degree of radiolysis that could be expected under storage conditions, as well as the solution conditions which affect changes in the rate and degree of radiolysis. The solutions were irradiated in a Co^{60} facility, and the results are limited, therefore, to the effects of gamma radiation (1.17 and 1.33 MeV) from an external source. Each solution type was irradiated under three conditions: (1) no salt added, (2) salt saturated, and (3) salt saturated plus excess salt. The irradiations were carried out in sealed tubes which included built-in mercury manometers to indicate the internal pressure.

At absorbed doses of around 10^9 rad the tubes reached equilibrium pressures in the range of 3 to 10 atm, depending on the composition of the waste solution (Table I). It is probably not feasible to maintain a pressure head of a few atmospheres in salt structures over long periods of time; therefore containment in closed systems with the expected pressure build-up is

<table>
<thead>
<tr>
<th>Type</th>
<th>Condition</th>
<th>Steady-state pressure (atm.)</th>
<th>Yield (ml of gas per ml of solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 M Purex</td>
<td>A</td>
<td>3.55</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3.64</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>9.4</td>
<td>4.90</td>
</tr>
<tr>
<td>3.5 M Purex</td>
<td>A</td>
<td>3.85</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>5.01</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>9.4</td>
<td>4.90</td>
</tr>
<tr>
<td>Semineutral</td>
<td>A</td>
<td>2.94</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>5.68</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.88</td>
<td>4.28</td>
</tr>
<tr>
<td>Neutral Purex</td>
<td>A</td>
<td>4.58</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>2.68</td>
<td>0.91</td>
</tr>
<tr>
<td>Formaldehyde denitrated</td>
<td>A</td>
<td>2.06</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>11.9</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>11.6</td>
<td>6.62</td>
</tr>
</tbody>
</table>

*No salt added.
*bSalt saturated.
*cSalt saturated plus excess solid salt.
*dOriginal samples damaged - data incomplete.
not practical. It was found that a hydrogen atmosphere over the solutions will reduce the steady-state pressure to atmospheric level, but this, too, is impractical. Known recombination catalysts increase their efficiency with increasing pressure and the minimum pressure at which favourable rates of recombination are promoted are again too high for use in salt structures. At present, therefore, the containment of liquid wastes in salt cavities can be expected to result in the production of a steady stream of radiolytic gases, principally hydrogen and oxygen.

In a different approach to minimizing radiolysis, the effect of suspending the waste solution in the interstices of crushed salt was studied. Waste solution was poured over crushed salt in the ratio of 1 ml of waste to 5 g of salt. On exposure to Co\textsuperscript{60} radiation, no pressure build-up was seen as long as the liquid remained in the interstices. As the dose approached 10\textsuperscript{8} rad, a liquid phase formed over the top of the salt layer in most of the tubes. This phase separation was accompanied by a build-up in pressure. In order to minimize possible wall effects, the same irradiation was repeated with larger tubes containing five times more material. The same behaviour was observed, which strengthens the belief that phase separation is more closely tied in with radiation effects than container wall effects. Changes in the particle size did not alter the radiolytic process. When coarse salt particles (1/4 in mesh) were used, there were relatively large volumes of free solution in the voids between the particles. Despite the existence of such locales of free solution, no radiolytic pressure built up as long as the free liquid was overlain by a layer of salt.

When waste solution was sorbed in the lattices of vermiculite and attapulgite, the radiolytic behaviour was similar. The maximum pressure build-up was 20 mm Hg at 10\textsuperscript{8} rad.

It is believed that if the salt is not saturated, but only wetted with the waste solution, the liquid may not migrate to the surface of the salt layer, thus preventing the net production of significant quantities of radiolytic gases.

The results of the laboratory studies with the waste solutions in the interstices of crushed salt also indicate that very little cavity alteration would be expected with this type of storage.

FIELD AND LABORATORY STUDIES ON DISPOSAL OF SOLIDS

Previous studies on heat dissipation and structural stability are directly applicable to solids disposal. The chief differences between liquid and solids disposal is that with solid wastes there will be a greater allowable temperature rise and there should be little or no off-gases.

High-level packaged solid wastes may take almost any form, but likely container-shapes might be parallelopipeds, rods, or cylinders, either solid or hollow. If the packages are placed in racks on the floor of sealed mine rooms such that it may be assumed that all heat is transferred to the salt by radiation and convection, then the shape of the container is not important in determining peak temperature rises in the salt.

In an actual disposal operation, there would be certain advantages in placing the waste containers in holes in the floor rather than on the floor. If the holes were deep enough that the tops of the containers were several
feet below the floor and concrete plugs were placed on top of the containers, or the holes back-filled with crushed salt, there would be adequate radiation shielding to enable the use of a manually operated waste carrier. In this case the size and shape of the container will be important in determining the peak salt temperature and radiation dose in the immediate vicinity of the container.

Heat flow and structural stability

In order that most efficient use be made of the mine space, it is desirable to allow the salt temperature to rise as high as practical. For cylindrical containers filled with high-temperature-calcined solids, in some cases, peak salt temperatures of more than 300°C would not result in excess waste temperature. It is thus desirable to establish if salt temperature can be allowed to go this high.

The salt from the mine in Hutchinson, Kansas, contains numerous small inclusions of water (up to 1 wt.%). When chunks of this salt are heated in the laboratory to temperatures of 250 to 280°C they explode violently, releasing the water as steam. Since the resultant salt particles vary in size from about 1 in down to 1/8 in or less, if this shattering occurs in situ it may result in poorer thermal conductivity in the shattered zone and consequent increased waste temperature rise. Field experiments to investigate this phenomenon are currently being run with electrical heaters in 5-ft-long, 6-in-diam. cylinders which simulate calcined-waste containers.

There are as yet no satisfactory theoretical solutions to the problem of the structural behaviour of salt in mines (plastic flow, strength of pillars, etc.) as a function of load on the pillars, salt temperature, and other variables. Sufficient empirical data are available to allow at least approximate predictions of the structural behaviour of mine openings at ambient temperature. Data on structural conditions existing at various locations in eight different salt mines in the United States were correlated with calculated pillar loads. Depths of the mines ranged from 650 to 1100 ft and percentage salt extractions from about 40 to 80%. Calculated pillar loads, based on the percentage extraction and an assumed 1 lb/in²-ft of overburden, ranged from about 1100 to 4000 lb/in². For calculated pillar loads less than 3000 lb/in², there was a minimum amount of structural flow, even after several decades. For pillar loads greater than 4000 lb/in² there was considerable closure of the openings along with floor heaves, roof falls, and heavy pillar spalling.

When short-cooled wastes (less than 3 years old) with a rapidly decaying heat-generation rate are placed in the floor, the principal structural effect will be similar to that obtained in the large field test with liquids, i.e., expansion of the floor in the vertical direction. However, with older wastes in a large disposal operation, peak salt temperatures may not be reached for several years, and by this time the ceiling and pillars will be nearly as hot as the floor. Since the pillars are supporting the overburden pressure and it is known that, for a fixed pressure, at higher temperatures the plastic flow is greatly accelerated, it might be expected that the room will close in some finite time. Studies are now being carried out which are designed to provide some means of predicting this effect.
Radiation dose

The effect of radiation on single alkali halide crystals is well known, and there appears to be a finite limit to the amount of radiation damage possible. The maximum degree of decomposition of NaCl crystals is indicated to be approximately 0.1% [12]. However, the physical properties of rock salt, as found naturally, could change to a much greater degree. The response to radiation of dome and bedded rock-salt aggregates was studied at ORNL by determining the stress-strain relation [13]. Only with irradiations of more than \(10^8\) r was there any indication of a decrease in compressive strength (about 10% drop at \(5 \times 10^8\) r).

Calculations of the dose that might be expected in disposal of 2-year-cooled calcined solids in the floor were made. Salt doses as high as \(5 \times 10^8\) r would not accumulate at distances of more than one foot from the waste containers. Since the floor does not have to support the overburden pressure and the dose to the pillars is insignificant, radiation would not be expected to affect the structural stability of the rooms.

Laboratory tests at 28°C of an unirradiated aggregate sample and an aggregate irradiated to \(5 \times 10^8\) r indicated less than 10% reduction in the thermal conductivity due to radiation.

SPACE REQUIREMENTS FOR DISPOSAL IN SALT

The mine space required for disposal in salt formations will be determined by the maximum allowable salt-temperature rise. The allowable rise will be limited by the boiling point for liquid wastes, by the decomposition temperature for solid wastes, and by the effects of increased temperature on the structural properties of salt.

If it is assumed that disposal of wastes will be in relatively large rooms, e.g., 50 x 100 ft, peak waste temperatures in the centre of a room may not be too different from that in a layer or slab with infinite horizontal dimensions. Temperature calculations based on the infinite slab will be conservative in that waste will be produced at a finite rate and, thus, the actual slab will contain wastes whose average heat-generation rate will be somewhat lower than that currently being added. Additionally, probably not more than 60% of the gross mine area will actually contain wastes, the remainder being taken up by passageways and roof supports.

As a part of the economics study reported by ROBERTS [14], space requirements were calculated for a disposal operation handling the wastes from the entire nuclear power economy predicted to be in operation in the United States in 1975 (continuous operation of 15 000 MWe capacity). Seventy-five percent of the reactors are assumed to be fuelled with uranium and 25% with thorium. The uranium fuel is reclaimed in a Purex process and the thorium in a Thorex process. Wastes are assumed to be stored either as calcined solids in 10-ft-long cylinders with diameters of 6, 12, or 24 in, or as liquids adsorbed on crushed salt.

Solids above floor

Mined areas for storage of calcined solid wastes above the floor of rooms in salt deposits were calculated with temperature limits of 1650°F at the
cylinder axis and 400°F at the surface of the salt room. The rooms were assumed to lie in the same horizontal plane, and the dissipation of heat into the salt was calculated on a digital computer with a code for the infinite slab geometry. Most of the heat was found to be transferred from the vessels to the salt surface by radiation, and heat fluxes to the floor and ceiling were assumed equal. Permissible heat-generation rates subject to the limiting temperatures were calculated with parameters of waste type, vessel diameter, and mine area per vessel.

Minimum ages at burial and required mine areas per cylinder at the minimum age are given for the various waste types in Table II. The net yearly amount of mine space required for each waste type if buried at the minimum age varies from 1.26 acres/yr for acidic Thorex in 24-in-diam. vessels to 11.45 for reacidified Purex waste filled twice in 6-in-diam. vessels (Table III). Figure 4 shows the net mine area required to store solid wastes above the floor as a function of the age of the waste at the time of storage. It is assumed for this Figure that Purex and Thorex wastes are buried at the same age. Purex wastes account for 75% of the total area requirements.

Solids in the floor

With waste packages stored in holes in the floor, the slab calculation would determine the average salt temperature rise, but to obtain the perturbations produced by the packages another approach is necessary. If the packages are equally spaced on triangular centres, each package will be in the middle of a hexagonal area. If there are a large number of packages, all containing identical heat sources and all placed in the mine simultaneously, it may be assumed that no heat flows across the vertical boundaries of the hexagonal area. For cylindrical heat sources, if the hexagonal boundary is approximated by a circle, the problem reduces to that of a single finite-length cylindrical heat source in the centre of an infinitely long cylinder whose sides are perfectly insulated. For temperatures outside the heat-generating cylinder, an insignificant error will be introduced if the heat source is assumed to be a line in the centre of the cylinder.

An equation to fit these assumptions was derived for a decaying heat source and a code was written to allow computation on a digital computer. As in the case of solids stored above the floor, an additional calculation is required to obtain the temperature rise at the centre of the waste.

Space requirements to dissipate the fission product heat in the waste were calculated for cylinders of calcined waste buried in a vertical position in the floors of rooms in salt media. Acres per year of mined space required were calculated for Purex and Thorex wastes in acidic and reacidified forms in 6-, 12- and 24-in-diam. vessels and for an acidic Thorex glass in 6-in-diam. vessels buried at ages of 0.33 to 30 yr.

The maximum allowable temperatures in the salt and in the calcined wastes were chosen to be 400°F and 1650°F, the same as they were in the calculation of space requirements for the storage of calcined wastes above the floor in the salt rooms. The cylindrical vessels, 10 ft in length, were assumed placed into vertical holes 33% larger in diameter than the vessel diameter (e.g., 8-in-diam. holes for 6-in-diam. vessels) and 15 ft in depth, with the top 5 ft occupied by salt or concrete plugs for shielding purposes.
### Table II

**Minimum Burial Ages* and Required Mine Area per Vessel at Minimum Age for Calcined Purex and Thorex Wastes in Salt Rooms**

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Vessel diam. = 0.5 ft</th>
<th>Vessel diam. = 1.0 ft</th>
<th>Vessel diam. = 2.0 ft</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min. age (yr)</td>
<td>Area (ft²/vessel)</td>
<td>Min. age (yr)</td>
</tr>
<tr>
<td>Acidic Purex</td>
<td>1.07</td>
<td>280</td>
<td>3.05</td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>0.33</td>
<td>142</td>
<td>0.84</td>
</tr>
<tr>
<td>Reacidified Purex filled</td>
<td>0.33</td>
<td>215</td>
<td>0.84</td>
</tr>
<tr>
<td>Acidic Thorex</td>
<td>0.33</td>
<td>128</td>
<td>1.1</td>
</tr>
<tr>
<td>Reacidified Thorex</td>
<td>0.33</td>
<td>28.5</td>
<td>0.33</td>
</tr>
<tr>
<td>Reacidified Thorex filled</td>
<td>0.33</td>
<td>43.0</td>
<td>0.33</td>
</tr>
<tr>
<td>Acidic Thorex glass</td>
<td>0.33</td>
<td>100</td>
<td>--</td>
</tr>
</tbody>
</table>

* Ages at burial < 0.33 year not considered since this is assumed as the age at which the uranium and thorium are processed.
### TABLE III

**YEARLY MINED SPACE REQUIREMENTS FOR CALCINED WASTES STORED IN SALT ROOMS***

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Net yearly space required (acres/yr)</th>
<th>Vessel diam. 0.5 ft</th>
<th>Vessel diam. 1.0 ft</th>
<th>Vessel diam. 2.0 ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Purex</td>
<td>5.9</td>
<td>3.6</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>11.4</td>
<td>6.9</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Reacidified Purex filled</td>
<td>11.4</td>
<td>6.9</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Acidic Thorex</td>
<td>4.1</td>
<td>2.0</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Reacidified Thorex</td>
<td>4.1</td>
<td>4.1</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Reacidified Thorex filled</td>
<td>4.1</td>
<td>4.1</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Acidic Thorex glass</td>
<td>4.1</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

* At minimum permissible burial age.

---

Net area requirements for Purex waste range from 20 acres/yr at 0.65 yr to about 2 acres/yr at 30 yr age at burial. Corresponding results for Thorex wastes are 10 and 0.7 acres/yr. The primary effects of the form of the waste (acidified, reacidified, glass) and vessel diameter are to limit the minimum burial age, although area requirements may be affected by factors of 2-3 by waste form and vessel size near the minimum burial ages. For acidic Purex in 12- and 24-in-diam. vessels and acidic Thorex in 24-in vessels at all ages, space requirements are greater than those for the case of storage above the floor. The area requirements for the various forms...
of waste in 6-in-diam. vessels are shown in Fig. 5. Minimum burial ages for the various combinations of waste type and vessel diameter are shown in Table IV. In the case of above-floor storage, the minimum burial ages

![Fig. 5](image)

Net mine area requirements for storage of 6-in-diam. vessels in floor

**TABLE IV**

**MINIMUM BURIAL AGES* IN YEARS FOR CALCINED PUREX AND THOREX WASTES IN THE FLOOR OF SALT ROOMS**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5 ft</td>
<td>1.0 ft</td>
<td>2.0 ft</td>
</tr>
<tr>
<td>Acidic Purex</td>
<td></td>
<td>2.3</td>
<td>5.5</td>
<td>30</td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>0.7</td>
<td>2.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>1.0</td>
<td>3.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>filled twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidic Thorax</td>
<td>0.6</td>
<td>1.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Reacidified Thorax</td>
<td>0.33</td>
<td>0.33</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Reacidified Thorax</td>
<td>0.33</td>
<td>0.6</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>filled twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidic Thorax glass</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

* Ages < 0.33 year not considered.
were determined by the waste-temperature requirement, but with storage in the floor, the salt-temperature requirement (400°F) is limiting in all cases.

Liquids

With liquid wastes there is no minimum burial age since the peak temperature can be controlled by dispersion. The limiting temperature is the boiling point of the waste. An ambient of 75°F was assumed and a 125°F waste-temperature rise was allowed. Storage in liquid form increases the area requirements over that for storage of solids above the floor by a factor of 2.3. This factor is made up of a factor of 2.6 difference in the assumed maximum allowable temperature rise combined with the better heat dissipation properties of the salt at the lower temperature.

ECONOMICS OF SOLIDS DISPOSA L IN SALT

In order to determine which variables are important contributors to the cost of storage of solids in salt mines, a conceptual design was developed and some approximate cost figures calculated.

In the conceptual design the waste container shipping cask is removed from a rail truck and carried into a hot cell which encloses the top of the waste shaft. Waste containers are then unloaded into a storage area, from which they are removed for lowering down the shaft into a motorized carrier at the working level of the mine. The carrier moves out to the current disposal area, lowers the container into a hole in the floor, and backfills the hole with fine crushed salt. Concurrently with this operation, salt is being mined in another corridor.

Figure 6 shows one quadrant of the 1-mile square area, which is assumed to be served by one set of shafts. The operation will be conducted

![Plan-view: one quadrant of one-square-mile disposal area](image-url)
so that the salt mining is completely isolated from the disposal operations. Disposal operations personnel and equipment will use the mining shaft for ingress and egress, however.

Ventilating air will come down a compartment in the mining shaft, a portion being split off into the disposal tunnel. The disposal tunnel air will travel completely around the quadrant and exit up the waste shaft. The air will be drawn from the shaft, through the hot cell, through an absolute filter, and up a 200-ft stack.

In order that ventilating air never passes a filled storage area before it reaches the current working area, the disposal operations will start at the most remote point and work back toward the shaft. One quadrant will be filled at a time.

The criteria of isolation and ventilation require that a double tunnel be driven completely around the quadrant and that the rooms outside the peripheral tunnel be excavated before disposal operations start.

The net yearly space requirements for storage of the various waste combinations have been given in the previous section. The gross requirements are dependent on the allowable salt extraction for a specified stability condition. If no fission-product heat were involved, then the extraction as a function of depth based on observations of existing mines would be adequate. With the presence of heat, the dimensional changes of the rooms due to thermal expansion and plastic flow must also be considered. The problem of predicting the thermal closure of a cavity in salt has not been completely resolved, but an approximate calculation was made for purposes of this study.

Cost figures were calculated for disposal at a depth of 1000 ft for two conditions of stability, one with very small structural flow and 2.5% dimensional closure due to thermal flow, and one with considerable structural flow and 100% thermal closure of the rooms. These figures for typical waste combinations are shown in Table V for waste ages at burial of 1, 3, 10, and 30 yr. The costs of developing peripheral tunnels and storage space are based on an assumed cost of $2.00/t for salt removal. Shafts and life-of-shaft items were amortized over the time required to fill the entire square mile (8.5 yr for 1-year's cooling with 2.5% closure to 89 yr for 30 yr cooling with 100% closure).

Total costs ranged from $6 \times 10^{-3}$ mill/kWh(e) for 100% room closure with 30-yr-cooled wastes to $30 \times 10^{-3}$ mill/kWh(e) for 1-year's cooling and 2.5% closure. The cost of removal of salt is 60% to 85% of the total costs. It might be possible to sell the salt, thus reducing costs. Of the remaining costs, only operating costs appear to be appreciably more important than the others.

SUMMARY AND CONCLUSIONS

In summary, it may be said that the storage of high-level radioactive wastes in salt mines appears attractive. Further investigation of methods of controlling radiolytic gas production and of minimizing cavity alteration are required for liquids disposal. For solids disposal the chief remaining uncertainty is the combined effect of heat and overburden pressure on the structural stability of mined openings.
TABLE V
COST OF STORING WASTE IN HOLES IN FLOOR OF MINE AT DEPTH OF 1000 ft
FOR REPRESENTATIVE CASES

| Waste age and combination | Storage* space | Peripheral* tunnels | Head facilities | Mine facilities | Mine facilities | Mine facilities | Mine facilities | Mine facilities | Mine facilities | Mine facilities | Mine facilities | Operation | Total |
|---------------------------|----------------|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|
| 1 year                    |                |                     |                |                |                |                |                |                |                |                |                |             |
| Reacidified Purex 6-in -diam. vessels | 21.70 | 3.94 | 1.09 | 0.73 | 0.24 | 0.19 | 0.28 | 0.59 | 1.90 | 30.60 |
| Acids Thorex 6-in -diam. vessels | 10.70 | 1.41 | 0.48 | 0.33 | 0.24 | 0.08 | 0.28 | 0.59 | 1.90 | 16.00 |
| 2.5% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 100% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 3 year                    |                |                     |                |                |                |                |                |                |                |                |                |             |
| Acids Purex 6-in -diam. vessels | 10.60 | 1.94 | 0.63 | 0.43 | 0.24 | 0.11 | 0.28 | 0.18 | 1.05 | 15.40 |
| Acids Thorex 12-in -diam. vessels | 5.25 | 0.75 | 0.35 | 0.24 | 0.06 | 0.28 | 0.15 | 1.05 | 8.40 |
| 2.5% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 100% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 10 year                   |                |                     |                |                |                |                |                |                |                |                |                |             |
| Reacidified Purex filled twice 12-in -diam. vessels | 8.25 | 1.54 | 0.53 | 0.36 | 0.24 | 0.09 | 0.28 | 0.15 | 1.05 | 12.50 |
| Acids Thorex 12-in -diam. vessels | 4.06 | 0.61 | 0.33 | 0.24 | 0.06 | 0.28 | 0.15 | 1.05 | 7.00 |
| 2.5% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 100% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 30 year                   |                |                     |                |                |                |                |                |                |                |                |                |             |
| Acids Purex 12-in -diam. vessels | 6.29 | 1.20 | 0.44 | 0.31 | 0.24 | 0.08 | 0.28 | 0.15 | 1.05 | 10.00 |
| Acids Thorex 24-in -diam. vessels | 3.10 | 0.51 | 0.31 | 0.24 | 0.06 | 0.28 | 0.15 | 1.05 | 6.00 |
| 2.5% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |
| 100% closure              |                |                     |                |                |                |                |                |                |                |                |                |             |

* Assumes cost of removing salt = $2.00/t.
STORAGE OF WASTE SOLIDS AND LIQUIDS IN SALT FORMATIONS

Tests with liquid wastes in large cavities showed that some cavity alteration may be expected.

With neutralized waste there is no chemical gas production, but, with acid waste, chlorine and nitrosyl chloride are produced at temperatures above 60°C. If it is desired to raise the temperature to 100°C, chemical gas production can be avoided by reducing the acidity to 4 M or less. Reaction of the acid wastes with shale also produces small quantities of nitrogen oxides and CO2.

A serious limitation for storage of liquids appears to be radiolytic production of hydrogen and oxygen. A method that appears to hold promise for overcoming this problem, as well as the problem of cavity alteration, is to adsorb the solution on a granular material.

Field heat-flow experiments have indicated that the thermal conductivity and diffusivity of rock salt in place are only 10 to 20% lower than those of single natural crystals. Laboratory tests at 28°C of an aggregate irradiated to $5 \times 10^6$ r indicated approximately 10% lower conductivity than that of a similar unirradiated sample. This relatively close agreement lends confidence to theoretical calculations of temperature rise based on single-crystal values of conductivity and diffusivity.

Preliminary estimates of the cost of a large-scale disposal operation in salt (about 0.01 mill/kWh(e)) show that such an operation is economically compatible with competitive nuclear power.

REFERENCES

B. KOLYCHEV: With the burial of liquid wastes, is there no danger that the water vapours formed may wash out the dome of the cavity, causing the whole cavity to rise, so to speak, until it reaches the surrounding rock?

R.L. BRADSHAW: Yes, we feel that the disposal of free liquids will produce cavity alteration and possibly migration of the cavity. However, laboratory studies have indicated that if the liquid is adsorbed on granular materials, such as crushed rock salt, cavity alteration can be minimized and perhaps eliminated. We plan to run some hot-cell tests designed to answer this question.

F. DUHAMEL: What is your opinion of storage in salt formation from the viewpoint of earthquake hazards?

R.L. BRADSHAW: In the United States, most of the suitable salt deposits are located in areas of low seismic activity. An additional safety factor is inherent in the plastic nature of salt when under high pressure. If a fracture is produced in the salt formation by a seismic occurrence it will tend to be self-healing, due to plastic flow. This is not generally true of other common rocks, such as limestone.

R. ROMETSCH: How does the cost of transporting the wastes to the salt-mine compare with the cost of storage in the mine?

R.L. BRADSHAW: This question is answered in detail in the paper by J.J. PERONA et al. on economic evaluation of tank storage and pot calcination*. I might say, though, that the costs are roughly the same as for disposal in salt. A typical shipment cost might be about $10\times10^{-8}$ mill/kWh(e).

P. ZIMAKOV: In your oral presentation you dealt mainly with liquid wastes. I would like to know your views on the burial of solid wastes in salt formations.

R.L. BRADSHAW: It is true that most of our efforts initially were concerned with liquid waste and I spent a large portion of the time here this morning discussing liquids, but we are currently studying solids and we feel that solid wastes will be the first to be disposed of in salt formations. We have not abandoned hope of burying liquid wastes also in salt, but there are still some problems to be solved. We feel that solids could be disposed of now if we had them, and we are proposing to run a demonstration with solid wastes, perhaps by 1965.

We shall not be prepared to say that we can dispose of liquids until we are sure that we can solve the problems of cavity alteration, migration and radiolytic gas production. With solid wastes, there is no radiolytic gas problem and there is not such a rigid limit to the permissible temperature rise. In liquid wastes, the temperatures must be kept below boiling point; whereas with the solid wastes they can be allowed to go much higher without decomposing our material. For instance, the so-called pot-calcined solid that we are studying at Oak Ridge National Laboratory is produced at a temperature of about 900°C, so that if our storage temperatures are kept below this point, we can expect to get little or no decomposition of the solid waste.

* PERONA, J.J. et al., "Economic evaluation of tank storage and pot calcination of power-reactor fuel-reprocessing rates", These proceedings.
D.W. CLELLAND: Have you compared the cost of storage in concrete cells at the reprocessing site with that of storage in salt deposits? The latter system might be less favourable because of new-site charges as well as the transport costs, referred to by Mr. Rometsch.

R.L. BRADSHAW: No, we have not yet made this comparison, though we do expect to make such a study as part of the Engineering, Economic and Hazards Evaluation which is currently under way at the Oak Ridge National Laboratory.

It may well be that the cost of the complete operation up to and including disposal in salt will be more than that of a comparable operation with disposal in concrete cells. However, we feel that ultimate disposal methods must be compared on a hazards, as well as an economic, basis. If we were able to assign a monetary value to the hazards, we feel that salt disposal would be the cheaper method. This, of course, is a matter of opinion, which can only be settled when the economics and hazards study has been completed.
III

SOLIDIFICATION AND FIXATION OF LIQUIDS
BY CALCINATION

(Part 1)
CONTINUOUS CALCINATION OF HIGH-LEVEL RADIOACTIVE WASTES BY MEANS OF A ROTARY-BALL KILN

W. H. REGAN, L. P. HATCH AND R. F. DOMISH
BROOKHAVEN NATIONAL LABORATORY, UPTON, LONG ISLAND, N. Y.

Abstract — Résumé — Аннотация — Resumen

CONTINUOUS CALCINATION OF HIGH-LEVEL RADIOACTIVE WASTES BY MEANS OF A ROTARY-BALL KILN. The calcination of high-level, high salt content, aqueous wastes to convert the bulk salts to stable solid forms offers important advantages in ultimate waste disposal, namely, major reduction in waste volume and general simplification of long-range waste-storage problems. Among the types of wastes commonly considered for calcination are those produced in the aqueous reprocessing of aluminium alloy and zirconium-alloy fuels and in the reprocessing of fuels clad with stainless steel or having stainless-steel matrices. Decomposition of the bulk salts thus involved, namely, aluminium nitrate, zirconium fluoride and ferric nitrate to their respective oxides introduces a number of serious operations problems many of which stem from the formation of highly radioactive solids with substantial proportions in the small, or low micron, range.

One promising type of calciner, which is under development at the Brookhaven National Laboratory operates on the principle of a rotary-ball kiln. Basically, the unit consists of a slowly rotating horizontal tube or kiln externally heated by means of electric resistance heaters. Feed is introduced into the kiln by means of a distribution nozzle and falls on a hot, shallow bed of metal balls, which aid in heat transfer and prevent the formation of large agglomerates during calcination. The calcined solids overflow from the discharge end of the kiln into a powder receiver.

The calciner is designed for continuous operation, to give good transfer of heat to the interior of the kiln and to reduce problems of controlling radioactive dust to a bare minimum. Since no non-condensable gases are added to the system, excellent dust control is accomplished by direct condensation of off-gases followed by passing the small non-condensable portion through a scrubber and absolute filter.

An engineering scale calciner has been constructed at Brookhaven and is at present being used to carry out equipment and process development studies. The rotary kiln is 8 in in diam., has a heated length of 7 ft and is designed to calcine approximately 6 gal/hr of waste.

The paper presents an outline of the essential features of the Brookhaven calciner, with particular emphasis on the development of a rotary gas seal, together with a discussion of the results of operation of the pilot plant with simulated non-radioactive aluminium nitrate waste feed.
Ce four est conçu pour une marche continue et une bonne transmission de la chaleur vers l'intérieur du four; il vise à réduire au minimum les problèmes de contrôle de la poussière radioactive. Vu qu'on n'ajoute au système aucun gaz non condensable, on peut contrôler la poussière d'une façon très satisfaisante en condensant directement les gaz d'échappement et en faisant passer la faible partie non condensable par un dispositif d'épuration et un filtre absorbant.

On a construit à Brookhaven un four expérimental qui est actuellement utilisé pour la mise au point du matériel et des opérations. Ce four rotatif a un diamètre de 20 cm et une longueur de 2,1 m; il peut calciner environ 22 l de déchets à l'heure.

L'auteur donne un aperçu des caractéristiques essentielles du calcinateur de Brookhaven, en insistant particulièrement sur la mise au point d'un joint rotatif pour les gaz; il commente en outre les résultats du fonctionnement de l'installation pilote avec une charge simulée de déchets inactifs (nitrates d'aluminium).

CALCINACIÓN CONTINUÁ DE DESECHOS DE ELEVADA RADIACTIVIDAD EN UN HORNO DE BOLAS ROTATORIO. La calcinación de desechos líquidos de elevada radiactividad con alto contenido de sales, que permite convertir esos sales a granel en sólidos compactos, ofrece notables ventajas para la evacuación definitiva de los desechos, a saber, una reducción considerable del volumen y una simplificación general de los problemas de almacenamiento a largo plazo. Entre los tipos de desechos que se consideran adecuados para el tratamiento por calcinación, figuran los productos en la regeneración acusa de los combustibles de aleación de aluminio y aleación de circonio y en la regeneración de los combustibles con revestimiento de acero inoxidable o provisiones de matrices de acero inoxidable. La descomposición de las sales formadas en estos procesos, a saber, el nitrato de aluminio, el fluoruro de circonio y el nitrato férrico, para formar los óxidos respectivos, plantea una serie de arduos problemas de tratamiento, muchos de los cuales deben a la formación de sólidos de elevada radiactividad que aparecen. en proporciones apreciables, bajo forma de partículas de dimensiones del orden de algunos micrones.
Un dispositivo de calcinación que promete dar buenos resultados, actualmente en curso de perfeccionamiento en el Brookhaven National Laboratory, se basa en el principio del horno de bolas rotatorio.Consta esencialmente de un homo en forma de tubo horizontal animado de un lento movimiento de rotación, y calentado externamente por resistencias eléctricas. El material se introduce en el homo por medio de una boquilla de distribución y cae sobre un lecho caliente, poco profundo, de bolas metálicas, que facilitan la transmisión del calor y evitan la formación de conglomerados voluminosos durante la calcinación. Los sólidos calcinados pasan por el extremo de descarga del homo y pasan a un acumulador de polvo.

Este homo de calcinación está concebido para funcionamiento continuo, para alcanzar una buena transmisión de calor en su interior y para reducir al mínimo los problemas de control del polvo radiactivo. Como no se agregan al circuito gases no condensables, ese control del polvo puede efectuarse en forma muy satisfactoria mediante la condensación directa de los gases de salida y del paso de la pequeña porción no condensable a través de un dispositivo depurador y un filtro absoluto.

Se ha construido en Brookhaven un homo de calcinación en escala experimental que se utiliza actualmente para efectuar estudios tendientes a perfeccionar el equipo y las operaciones. El diámetro de ese homo rotatorio asciende a 8 pulg (20 cm), la longitud de la zona calentada es de 7 pies (2,1 m) y la capacidad de calcinación, de 6 gal (22 l) de desechos por hora, aproximadamente.

En la memoria se describen las características esenciales del homo de calcinación de Brookhaven, destacándose especialmente los ensayos realizados en busca de un cierre giratorio para gases, a la vez que se exponen los resultados del funcionamiento de la instalación piloto con una carga simulada de desechos inactivos de nitrato de aluminio.

INTRODUCTION

Investigation of rotary-kiln calcination as a step toward the ultimate disposal of high-level radioactive wastes was initiated at Brookhaven National Laboratory in 1955, when emphasis was first being placed on the processing of wastes containing high concentrations of bulk salts by means of fixation in stable solids. Specifically, the need for the calcination step arose in the course of a development study on the adsorption and fixation of fission products on mineral ion-exchange media because of the interference offered by the bulk ions Al^{3+} and Zr^{4+}. Calcination followed by leaching offered an effective means for eliminating this interference, since aluminium and zirconium form highly insoluble oxides and, thus, could be readily separated from the soluble fission products, notably strontium and caesium, which were not firmly fixed in the bulk oxides [1].

Rotary-kiln calcination was selected from a number of possible methods because it appeared to offer the best means of achieving the combined goals of continuous operation, dust control through condensation of off-gases, efficient heat input, and uniformity of product. Although a basic disadvantage was inherent in this concept, namely the requirement for a rotary seal, the potential advantages were considered to substantially outweigh this disadvantage. That conclusion still appears to have been a sound one [2].

It should be noted that calcination has commonly come to be regarded as a final waste-treatment step in ultimate disposal, rather than as an adjunct step with another means of fixation in solids. Accordingly, the development programme at Brookhaven was reoriented toward calcination as an end in itself, since it does accomplish the highly practical objectives of substantial reduction in waste volume and conversion to a non-corrosive, immobile state. The fact remains, however, that the two long-lived fission products, strontium-90 and caesium-137, are readily leached from the bulk oxides, and the calcined products must therefore, be stored in carefully selected environments [3].
This paper presents the results obtained in carrying out a development programme on the rotary-kiln calciner at Brookhaven National Laboratory and discusses the design and operation of a pilot-plant scale unit with simulated aluminium nitrate waste feed.

**ROTARY BALL KILN CALCINER**

The calciner is basically a heavy-walled 8-in metal tube supported horizontally by means of tires which run on rollers, and is heated by means of a resistance furnace. At one end of the kiln, the diameter is reduced abruptly to a 4-in section which serves as the product discharge tube and forms the inner boundary of the rotary seal. The discharge tube terminates within a housing on the stationary side of the rotary seal which, in turn, is connected through 3-in pipe and flexible bellows to the product receiver and the off-gas system. The waste feeder is attached to the stationary housing and extends through the discharge tube into the kiln. The kiln is approximately a quarter filled with 1\(\frac{1}{4}\)-in metal balls which form a weighted bed and serve to prevent the build-up of cakes of partially calcined product.

**OFF-GAS STUDIES**

One of the foremost requirements in the calcination of radioactive wastes is a very high degree of control of dust entrained in the off-gases. However, since only a very small fraction of the gases produced in the calcination of the wastes is non-condensable, it has been possible to achieve very high degrees of dust control by simple condensation of the off-gases. In addition, the low rate of gas flow through the calciner itself minimizes the entrainment of dust in the off-gases. Dust control was first studied with a modified version of a commercially built calciner shown in Fig. 1 [4]. The rotating tube is 6\(\frac{1}{4}\)-in in diam. with a 36-in heated zone and is equipped with simple face-type seals with the rotating face held in contact with the stationary face. Dust studies were carried out to determine the following: (1) the volume flow-rate of the non-condensable off-gases in proportion to the feed rate, (2) the quantities of dust entrained in these off-gases, and (3) the effectiveness of condensation as a means for dust removal from a gas stream. The results of these studies are given in Table I.

In conformity with the results of earlier analyses, the volume of non-condensable gases leaving the condenser was found to be very low. Moreover, the data showed that the concentrations of dust in the off-gases were extremely small. The off-gases were finally passed through a \(\frac{4}{8}\)-in-diam. Millipore filter, rated at 0.45\(\mu\), with no detectable increase in pressure drop across the filter during periods of operation up to 5\(\frac{1}{2}\)hr. The amount of dust collected on the filter was too small to measure by weighing, and the filter and aluminium oxide were put into solution and the quantity of aluminium determined spectrophotometrically. Actually, no baffles, cyclones or other dust arresting units were built into the discharge section of the calciner, and roughly 1\% of the product was carried over to the condenser. Of this amount only about 10\(^{-4}\)\% passed through the condenser[7].
### TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of run hr</th>
<th>$\text{Al}_2\text{O}_3$ produced g</th>
<th>Dust collected on filter g</th>
<th>Non-condensables, $*_{\text{ft}^3}$</th>
<th>Dust collected per $\text{ft}^3$ non-condensables g</th>
<th>g Dust collected per g $\text{Al}_2\text{O}_3$ produced</th>
</tr>
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<tbody>
<tr>
<td>1 in. H$_2$O vacuum</td>
<td>1</td>
<td>5.33</td>
<td>2510</td>
<td>$1.7 \times 10^{-5}$</td>
<td>3.22</td>
<td>$5.28 \times 10^{-6}$</td>
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<tr>
<td>2</td>
<td>5.18</td>
<td>2440</td>
<td>$2.6 \times 10^{-5}$</td>
<td>6.6</td>
<td>$3.94 \times 10^{-6}$</td>
<td>$1.065 \times 10^{-8}$</td>
</tr>
<tr>
<td>3</td>
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<td>1085</td>
<td>$1.32 \times 10^{-5}$</td>
<td>2.05</td>
<td>$6.45 \times 10^{-6}$</td>
<td>$1.34 \times 10^{-8}$</td>
</tr>
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<td>2 in. H$_2$O vacuum</td>
<td>4</td>
<td>2.8</td>
<td>1320</td>
<td>$1.5 \times 10^{-6}$</td>
<td>3.8</td>
<td>$3.94 \times 10^{-7}$</td>
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<tr>
<td>5</td>
<td>3.5</td>
<td>1650</td>
<td>$1.0 \times 10^{-6}$</td>
<td>4.32</td>
<td>$2.31 \times 10^{-7}$</td>
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<tr>
<td>3 in. H$_2$O vacuum</td>
<td>6</td>
<td>3.0</td>
<td>1412</td>
<td>$2.1 \times 10^{-6}$</td>
<td>4.395</td>
<td>$4.77 \times 10^{-6}$</td>
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<tr>
<td>7</td>
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<td>5.22</td>
<td>$9.20 \times 10^{-6}$</td>
<td>$3.4 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

* Air leakage through seals for the seven runs averaged 0.451 ft$^3$/hr.
COLD PILOT-PLANT CALCINER

The 6-in calciner served well for the initial dust studies but was unsuitable for the over-all development programme. Accordingly, a pilot-plant scale rotary calciner, shown in Fig. 2, was designed and constructed. The kiln, constructed of Inconel-X [5], is 8 in in diam. and has a heated length of 7 ft. The furnace, rated at 40 kW, is designed for a kiln-operating temperature of 700°C with a feed-rate of 5 gal/hr of simulated aluminium nitrate waste. The kiln is rotated at 1-5 rpm by means of an electric motor and a chain-and-sprocket drive. The feed is pumped into the unit normally at a rate of 3-5 gal/hr, and calcined oxide product, which overflows the kiln, moves through the 4-in diam. discharge tube and falls into the 30-gal heated powder receiver. The off-gas system, shown in Fig. 3, consists of a heated off-gas line, two cyclone separators, and the condenser followed...
by a scrubbing tower, mist trap, filter and flowmeter. In a commercial plant, nitric acid would be recovered from the condensate by distillation and the still bottoms containing the dust would be recycled to the kiln, as shown in the schematic flow-sheet, Fig. 4, or otherwise suitably disposed.

ROTARY-SEAL DEVELOPMENT

As already pointed out, one of the most critical problems stemming from the rotary-kiln concept is the development of a satisfactory rotary seal. Due to the high temperature and radiation environment in which the seal must operate, and the presence of abrasive dust in the kiln, the protection against excessive wear and galling of moving parts was of paramount importance.

The initial seal which was installed and tested on the pilot-plant calciner was a circumferencial type utilizing segmented graphite rings held in contact with the rotating 4-in discharge tube by means of garter springs [6]. A diagram of this seal is shown in Fig. 5. The unit actually consists of two sets of sealing rings spaced apart and contained in a housing which was supplied with superheated steam under moderate pressure, thereby providing a barrier to the escape of dust and kiln off-gases. Any leakage occurring in
Fig. 3
Off-gas system of rotary-calciner pilot plant

Fig. 4
Rotary-calciner flow-sheet
the seal would, therefore, consist of a slight flow of steam from the seal housing into the kiln, which operated at subatmospheric pressure, and a similar flow of steam from the seal housing to the outside. This seal was found to be unsatisfactory, since chemical attack on the graphite due to the oxides of nitrogen combined with inability of the segments to adjust to mechanical misalignment resulted in gross leakage through the seal, thereby
eliminating any significant differential pressure between the housing and the interior of the kiln.

A face-type seal, with contact maintained between the rotating and stationary faces by means of a bellows, was installed in the plant after modification of the seal housing. This commercial type of seal, shown in Fig. 6, allows for considerable adjustment of the stationary face to conform to the position of the rotating face. However, like the first, this seal had the disadvantage of considerable leakage due to excessive wear at the sealing surfaces, again preventing any significant pressure from being maintained in the steam chamber. Furthermore, this seal can be replaced and maintained only with considerable difficulty and probably would not be suitable for a radioactive installation.

In view of the results with the first two seals a seal-development programme was undertaken at Brookhaven. To facilitate preliminary testing of various types of rotary seals without interfering with pilot-plant operations, the simplified rotary calciner shown in Fig. 7 has been rebuilt specifically for seal testing purposes. Two seals have been designed and constructed for testing, both utilizing the principle of a very small gap between the moving and stationary parts to avoid wear and galling. As before, the seals provide for a steam plenum between two sealing members.
In one seal, Fig. 8, which is now being tested, a gap of approximately 0.002 in is maintained between two flat faces by means of rollers mounted at the periphery. The steam plenum, formed by a \( \frac{1}{4} \) -in groove cut in one face, serves to distribute the steam uniformly to the gaps between the sealing surfaces. With positive pressure of 2 lb/in\(^2\) in the steam plenum, steam consumption does not exceed 24 lb/hr. Only a portion of this steam adds to the volume of the condensate, since steam flows to the atmosphere as well as to the kiln. Under these conditions the velocity of the steam through the 0.002-in gap is several thousand feet per minute.

Figure 9 is a photograph of the seal mounted on the seal-test calciner. The non-rotating portion of the seal and the end housing to which it is attached are somewhat free floating, thereby permitting it to follow any slight eccentricity in the rotating face. An end thrust of approximately 300 lb is maintained on the non-rotating part by means of a compressed air cylinder to insure the proper positioning of the two halves of the seal assembly. Since the roller shafts are mounted at an angle to the seal faces, adjustment of...
the gap width is accomplished by screwing the three roller shafts in or out of the roller mounting blocks.

Several helium leak tests have been performed on the rotary seal with the kiln at operating temperature and rotating, but with the feed turned off. Helium was metered into the kiln at a flow-rate of 10 ft³/hr while a sampling probe was held on the outside of the seal and close to the gap. No leakage was detected although the mass spectrometer of the leak detector was said to be sensitive to one part in two million.

In the other seal, which is of the radial type, a small gap is maintained between the outer surface of the discharge tube of the kiln and the inner surfaces of a series of floating rings. These rings are spaced apart to form a labyrinth, as shown in Fig. 10 and are capable of some radial movement to adjust to the position of the rotating tube. As in the other designs, steam is introduced midway in the seal assembly. All of the seals tested so far incorporate a loose packing of stainless-steel wool around the rotating discharge tube to provide an initial barrier to the migration of dust toward the main seal.
SOLUTION FEEDER STUDIES

Initially, feed was introduced into the calciner through a simple water jacketed tube insulated on the outside to prevent condensation. Although this type of feeder proved satisfactory with low feed rates, there was an unsatisfactory tendency for cake formation, due to local cooling, in the vicinity of the feeder at feed approaching the design capacity of the unit. Accordingly, it was decided to investigate nozzles which would distribute the feed over a larger area of the kiln surface.

Atomization of the feed was found to be unsatisfactory, since it resulted in the production of relatively large quantities of dust and excessive carry-over of fines in the off-gas system. Spray nozzles giving various flow patterns such as narrow-angle solid cone, flat, and multiple solid streams were then investigated. Various orientations of the nozzles within the kiln are being tried and feed-pressure variation is being used to obtain a more uniform distribution.

The Rotary Calciner Pilot Plant is so designed that the limitation on the feed-processing rate is the effective heat input to the kiln from the furnace rather than in the associated equipment such as the condenser, scrubber, etc. An excessive feed rate to the kiln manifests itself by causing the formation of a cake in the over-fed zone. Since the cake is a heat insulator, its presence is noted by changes in the heat input rate and temperature profile of the kiln. Obviously the distribution of the feed solution has an important influence on the maximum feed rate that can be sustained. Two
methods have been used successfully for removing cakes; one method is to shut off the feed for a while to allow the heat to penetrate and calcine the cake, and the other is to cool the kiln and use water.

PREPARATION FOR A 1000-hr RUN

A 1000-hr run is to commence in the autumn of this year during which the pilot plant will be operated around the clock and on weekends except for brief shut-downs to change powder receivers and perform routine maintenance chores. The rotary-gap seal will be mounted on the pilot plant in place of the present bellows type, metal-to-metal contact seal. The long run will give an opportunity to gather process and operating data for use in the design of a rotary calciner demonstration plant for studies with high-level radioactive wastes at Hanford.

REFERENCES


DISCUSSION

J. A. BUCKHAM: In terms of capacity or geometry, how large a rotary kiln do you envisage using for calcining radioactive material, and what factors limit its size?

W. H. REGAN: A preliminary design study was carried out some time ago on a calciner for processing wastes at the rate of 100 gal/hr. It was estimated that the kiln needed for this output had to be approximately 3 ft in diam, by 20 ft in length. No problems are foreseen in constructing and operating a unit of this size and no thought has been given to units with larger processing rates.

N. BREZHNEVA: I have three questions. What percentage of solids removal is obtained in the rotary-kiln calcination process? Is the dust which is carried away soluble in the condensate? And what activity is obtained in the condensate at the end of the calcination process?

W. H. REGAN: Decontamination factors of $10^6$ - $10^8$ are obtained for the solids. Whilst the dust is not soluble to a large extent, the activity of
the solids, particularly caesium and strontium, will be rapidly leached out by the highly acid condensate.

The condensate may be decontaminated by evaporation. One stage of evaporation would make the condensate suitable for re-use in the processing plant; a second evaporation stage might be required if the condensate was to be discharged to the environment. Evaporator bottoms would be returned to the calciner.

R. BONNIAUD: In your oral presentation you mentioned that the condensate contained 1% dust, yet the condenser is preceded by a dust separator (cyclone). What percentage of dust is retained in the cyclone, or what total percentage of dust escapes from the calciner?

W.H. REGAN: The 1% figure you refer to was obtained from experiments with the small 6-in calciner, which did not contain a cyclone separator. Since the degree of dust carryover will be influenced by the type of solution feeder used, and since a satisfactory solution feeder for the pilot plant calciner has only recently been developed, little or no information is available at the moment. However, this type of data will be obtained during the forthcoming 1000-hr run.

S. LINDHE: Could you say anything about the expected lifetime of the kiln? There may be considerable erosion and corrosion on the balls and walls of the kiln.

W.H. REGAN: A study was carried out in 1958 and detailed results have been given in a report numbered 5 in the bibliography. Generally speaking, the erosion rate was found to be quite small. The best metals are the high-nickel alloys. Moreover, there is not much limitation on the thickness of the kiln walls and I can easily conceive of a kiln having walls 1/4 - 1/2 in thick.
CALCINATION OF RADIOACTIVE WASTE IN MOLTEN SULPHUR

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Abstract — Résumé — Аннотация — Resumen

CALCINATION OF RADIOACTIVE WASTE IN MOLTEN SULPHUR. The Savannah River Laboratory is developing a novel process based on the unique properties of sulphur for converting radioactive wastes to a solid form of low solubility for "ultimate" disposal. In this process the aqueous acidic wastes are reacted with molten sulphur at 150°C so that the water and volatile acids are driven off and the chemical compounds present in the waste are calcined and/or chemically reduced. The resulting sulphur-waste slurry is then heated at 400 to 444°C for from 1 to 5 hr to drive off sulphuric acid and residual water and further calcine and/or reduce the chemical compounds in the sulphur-waste slurry. In these steps the molten sulphur serves as a heat-transfer medium, prevents the entrainment of the radioactive solids in the steam and reaction gases and eliminates the volatilization of radioactive ruthenium by preventing the formation of the tetroxide.

Laboratory scale runs with concentrated high activity waste as feed (1.3 \times 10^9 \text{ c/(min·ml)}, 2.0M Al(NO_3)_3, and 1.5M HNO_3) have shown that only one part in approximately 100 000 parts of the activity in the feed is carried overhead in the off-gas in these process steps.

After the completion of the high-temperature treatment, the sulphur-waste slurry is cooled to 120-150°C and transferred as a liquid to the final containment system where it is allowed to solidify. Although it is our intent to protect the containment system against the action of water, the resistance of the solidified sulphur-waste slurry to the action of water has been used as a measure of the effectiveness of this process.

Small cylinders of the solidified slurry have been prepared from simulated wastes containing Al(NO_3)_3 or dissolved stainless-steel nitrates with tracer levels of Sr and Cs, and for concentrated high-activity waste containing Al(NO_3)_3. These cylinders have been exposed to water over extended periods of time. Leaching rates are calculated as though there is complete removal of material from a surface layer. Rates of 10 to 20 mil/yr, or less, have been observed after an initial period of 6 to 8 weeks at moderately higher rates.

CALCINATION DE DÉCHETS RADIOACTIFS DANS LE SOUFRE FONDU. Le Laboratoire de Savannah River met actuellement au point une méthode nouvelle fondée sur les propriétés exceptionnelles du soufre qui permettent de transformer des déchets radioactifs en solides peu solubles, en vue de procéder à leur élimination définitive. Selon cette méthode, on fait réagir les déchets liquides acides avec du soufre fondu à 150°C: l'eau et les acides volatiles sont chassés, puis les composés chimiques présents dans les déchets sont calcinés et/ou réduits chimiquement. La suspension soufre-déchets ainsi obtenue est alors chauffée pendant une durée de 1 à 5 h à une température de 400 à 444°C afin de chasser l'acide sulfurique et l'eau résiduelle et de poursuivre la calcination et/ou la réduction des composés chimiques dans la suspension soufre-déchets. Au cours de ces opérations, le soufre fondu sert de milieu calóporteur, empêche l'entraînement des solides radioactifs dans la vapeur et les gaz de la réaction et prévient la volatilisation du radioruthénium en empêchant la formation du tétraoxyde.

Des essais en laboratoire avec des déchets concentrés de haute activité (1.3 \times 10^9 \text{ c/min·ml}, Al(NO_3)_3, 2.0 M et 1.5 M HNO_3) ont montré qu'environ un centième seulement de l'activité présente dans la matière premère est emporté par le gaz qui se dégage au cours de ces opérations.

Une fois terminé le traitement à haute température, le soufre-déchets est refroidi à 150 ou 120°C et on la laisse solidifier dans le milieu d'isolement final, où la matière se solidifie. Bien que les auteurs aient l'intention de protéger le milieu d'isolement contre l'action de l'eau, ils ont étudié la résistance de la suspension solidifiée soufre-déchets à l'action de l'eau pour vérifier l'efficacité du procédé.

On a fabriqué de petits cylindres de la suspension solidifiée obtenue à partir de déchets simulés qui contenaient Al(NO_3)_3 ou de nitrates formés par dissolution de l'acier inoxydable, avec des traces de Sr et Cs, ainsi que de déchets concentrés de haute activité qui contenaient Al(NO_3)_3. Ces cylindres ont été exposés à l'action de l'eau pendant de longues périodes. On a calculé les vitesses de lixiviation comme s'il y avait élimination complète de matière sur une couche superficielle. Les vitesses enregistrées correspondent à des
values of 0.25 to 0.50 mm par an, plus, après une période initiale de six à huit semaines durant laquelle on a enregistré des vitesses légèrement supérieures.

CALCINANDO DE Desechos Radiactivos en Azufre Fundido. En el Savannah River Laboratory se está perfeccionando un procedimiento basado en las peculiaridades del azufre que permiten transformar los desechos radiactivos en sólidos de baja solubilidad, aptos para una evacuación "definitiva". Según dicho procedimiento, los desechos acuosos ácidos se hacen reaccionar con azufre fundido a 150°C, con lo cual se expulsa el agua y los ácidos volátiles, mientras que los compuestos químicos presentes en los desechos quedan calcinados, y/o químicamente reducidos. La suspensión azufre-desechos así formada se calienta entonces entre 400° y 444°C, durante 1 a 5 h, para expulsar el ácido sulfúrico y el agua residual y los compuestos químicos se vuelven a calcinar o a reducir, o ambas cosas a la vez, según convenga, en la suspensión azufre-desechos.

En estas operaciones, el azufre fundido actúa como medio de transmisión del calor, impide el arrastre de sólidos radiactivos en el vapor y los gases de la reacción y suprime la volatilización del rutenio radiactivo, al impedir la formación del tetraóxido respectivo.

Los ensayos de laboratorio efectuados con desechos de elevada radiactividad (1.3 * 10^9 c y/min ml, Al(NO₃)₃, 0 M 1.5 M HNO₃) han demostrado que tan sólo una cienmilésima parte, aproximadamente, de la actividad presente en la carga es arrastrada por el gas desprendido en estas operaciones.

Una vez terminado el tratamiento a alta temperatura, la suspensión azufre-desechos se enfria hasta 120 ó 150°C y se transporta en forma de líquido al sistema de confinamiento final, donde se la deja solidificar. Aunque los autores tienen el propósito de proteger el sistema de confinamiento contra la acción del agua, han utilizado la resistencia de la suspensión solidificada azufre-desechos a la acción del agua como medida de la eficacia del procedimiento.

Se prepararon pequeños cilindros de suspensión solidificada de desechos simulados que contenían Al(NO₃)₃, o los nitratos formados disolviendo acero inoxidable, con vestigios de Sr y Cs, así como de desechos concentrados de elevada actividad que contenían Al(NO₃)₃. Estos cilindros se expusieron a la acción del agua durante períodos prolongados. Se calculan las velocidades de lixiviación como si se eliminara totalmente el material de una capa superficial. Las velocidades registradas oscilan entre 10 y 20 milésimas de pulg/ año, o menos, después de un período inicial de 6 a 8 semanas durante el cual adoptan valores algo más elevados.
INTRODUCTION

The Savannah River Laboratory is actively exploring an apparently novel approach to the treatment and storage of radioactive waste [1]. In this concept, the unique properties of elemental sulphur are used (1) to convert wastes to solids of low solubility and (2) to store these solids in a solid matrix of the sulphur.

In the evaluation of the somewhat indefinite criteria that are now held for the "ultimate" disposal of waste [2], the following principles are now generally accepted:

(1) Two separate factors are important: the physical form in which the waste is to be stored, and the location (containment or geographical or both) where the wastes will be stored.

(2) For safest storage, (a) the waste should be converted to a physical form which reduces the probability that the radioactivity can be brought back into contact with people, animals, or plants and (b) the location should be chosen with the same objective.

(3) The treatment process and its product should reduce the solubility of the radioactive components in water to a minimum, since no practical location can positively guarantee total removal from contact with ground water for all time.

(4) The treatment should be simple and must not produce water- or air-borne contamination at the process location.

Several processes and products have been extensively developed to meet these objectives. The better known are the various processes to convert wastes to glass-like solids, to contained amorphous solids in durable retorts, or to finely divided solids. The glass-like solids are generally regarded as approaching the ultimate in the integrity of the activity-containing product. However, these glasses are susceptible to some radiation damage, the glass recipe itself must be carefully tailored to individual variations in waste composition and the processes involve high temperatures with attendant problems with volatile fission products. Elemental sulphur appears to produce a product similar in basic nature to the glasses, but offering marked advantages in processing, handling and cost.

In the process that is envisioned and is partially evaluated in this study, waste is heated in molten sulphur to drive off free and combined water and to decompose compounds, such as sulphates and nitrates, that might evolve gases. The sulphides and oxides that are formed are in general much less soluble in water than are the starting materials, which are thoroughly converted at or below the moderate temperature of the boiling point of sulphur, 444°C. No problem with volatile fission products is expected from waste-sulphur reaction mixtures at this temperature, although small amounts of entrainment similar to that from an evaporator will be present. The liquid sulphur provides a fluid, readily handled medium for the reaction and for transfer of the resultant solids as a slurry. The slurry can be cast into blocks, either contained or uncontained, in which the solid waste is dispersed in the resultant matrix of solid sulphur. Being elemental, the sulphur does not undergo radiation damage as do even such stable inorganic compounds as the components of glasses. Pure sulphur is an inexpensive commodity that is readily available anywhere in the world. The process re-
quires little modification to handle wastes of a wide variety of compositions, a distinct advantage in a situation in which different fuels must be processed.

The use of sulphur to process, handle and store radioactive wastes shows promise as a satisfactory product for long-term storage, with significant process advantages and possibly cost advantages over such alternatives as those now under consideration for producing calcined wastes. This concept is being vigorously extended by thorough evaluation of the engineering aspects of process technology and demonstration of the optimum form and resultant behaviour of the final products.

SUMMARY

Promising results of calcination have been obtained by a two-step process in which aqueous radioactive waste is dehydrated and denitrated in a molten sulphur bath at 150°C and is then heated for 1 to 5 hr in the range between 400°C and boiling point (444°C). Since sulphur reaches its minimum viscosity (6.6 centipoises) at about 150°C, disengagement from the reaction mass of the large quantities of water vapour and gas evolved during the first step is most readily accomplished at this temperature. Both steps are carried out with continuous agitation.

Appreciable quantities of water-soluble sulphates are formed by the calcination at 150°C of "stainless-steel nitrates". The subsequent high-temperature step converts most of the sulphates to sulphides (Table IV); the final product is a mixture of the oxides and sulphides. The best product mixtures have been made by heating at 444°C for periods of 3 to 5 hr (Table V). Cylinders cast from mixtures made under these conditions, and containing in the sulphur a 9 to 24-M (0.53-1.33 g/cm³) concentration of compounds derived from stainless steel, have remained intact after eight months in water at 22°C. (For convenience, cation concentrations in the sulphur are expressed as the molarity that the species in the feed would have if they entered the product unchanged). During the eight-month period, the leaching rate that was indicated by tracers of strontium and caesium remained below 10 mil/yr, which is the limit of detection in these particular experiments. These leaching and stability tests are continuing.

In the case of solutions that initially contain Al(NO₃)₃ and HNO₃, the product of the 150°C calcination is a mixture of Al₂O₃ and Al₂(SO₄)₃. The sulphate is reduced to the oxide very slowly, and appreciable quantities of it still remain after the high-temperature treatment (Table I). Despite the presence of sulphate, both tracer level and high-level wastes were leached by water at acceptably low rates that decreased with time, as long as the concentration of aluminium compounds in the sulphur remained below approximately 5M. The best results were obtained by heating either at 400°C for 5 hr or at boiling point for 1 hr (Table II). The leaching rate of such a sample of high-activity waste at an aluminium concentration of 4.7M in sulphur is approaching 15 mil/yr after five months of immersion, as indicated by removal of γ activity, Fig. 6. Furthermore, the β activity is leaching at only 2 mil/yr, and plutonium at 1 mil/yr (Table III).

* mil/yr = 0.001 in/yr
The three runs with high-activity aluminium waste as aqueous feed (22 c/l of γ) demonstrate one of the important advantages expected for the process; only one part in 100,000 of the activity in the feed was carried out of the calcining vessel with the off-gas. Since analysis of the activity that did leave the vessel showed that the composition was identical to that of the bottoms, it can be concluded that entrainment, rather than volatilization of fission products such as ruthenium, was responsible for the small amount of activity in the off-gas equipment.

Preliminary experiments have been made with simulated wastes that contained zirconyl nitrate and with solutions simulating concentrated waste from the Purex process. The zirconyl nitrate was converted to oxide, and the resulting 7.5-M product is stable in water and leaches at rates of about 10 mil/yr. Treatment of Purex waste containing sodium nitrate has not yet been as successful as treatment of the preceding wastes. The best product so far is that obtained at the end of the 150°C step; although the sample is still intact after immersion for six months, the leaching of tracers is occurring at the rate of 100 mil/yr.

DISCUSSION

In order to investigate the use of the unique properties of sulphur in connection with a process for the calcination and storage of radioactive waste, a number of small-scale experiments have been carried out. These experiments and the relevant properties of sulphur are described in the following pages.

Properties of sulphur [3-11]

The melting point of sulphur ranges from 112.8 to 120°C, depending upon the crystalline form at the time of melting. The viscosity of liquid sulphur decreases to 6.6 centipoises as the temperature is increased to about 155°C (Fig. 1), but increases abruptly to 93 000 centipoises at 188°C, then decreases again above 188°C. At atmospheric pressure, sulphur boils at 444°C. Figure 2 shows the vapour pressure of sulphur as a function of temperature [3, 6].

The addition of 0.77 wt. % I₂ to sulphur reduces the peak viscosity to about 300 centipoises and displaces the peak from 188°C to about 265°C. Small amounts of other additives such as H₂SO₄ or organic material have a similar effect on viscosity.

At the melting point, the specific gravity of liquid sulphur is approximately 2.0.

The thermal conductivity of sulphur varies from 0.155 BTU/(hr)(ft)°F at 21°C to 0.133 BTU/(hr)(ft)°F at 95°C. Preliminary measurements on some of the product mixes indicate that the thermal conductivity will not be increased by more than a factor of two by the presence of inorganic solids at the concentrations to be expected in the waste mixtures.

The ignition point of sulphur vapour in air ranges from 248 to 266°C, depending on the method of measurement [3].

Elemental sulphur has tension and compression characteristics slightly superior to those of conventional concrete [4].
Fig. 1
Viscosity of liquid sulphur

Fig. 2
Vapour pressure of sulphur.
Experimental equipment

The calciner, Fig. 3, was a stainless-steel vessel 4 in diam. and 5 2\(\frac{1}{4}\) in high with four 3/8-in baffles. A flanged cover-plate contained openings for the agitator shaft, feed inlet, off-gas line, thermocouple well and safety valve. The vessel was equipped with electrical heating facilities and the sides and cover were insulated. The stainless-steel agitator shaft was sealed by a carbon-bearing surface. The agitator was a four-bladed paddle, 2 2\(\frac{1}{4}\) in long and 3/4 in high and was located 1\(\frac{1}{4}\) in from the bottom of the vessel.

The calciner is shown connected to the remaining equipment of the system in the photograph, Fig. 4. The system was maintained under a slight vacuum during operation. The off-gas from the calciner (piece 8 in Fig. 5) passed through a sulphur condenser of 3/4-in stainless-steel tubing to a glass surge pot. The latter two equipment items were maintained at 150°C with electrical resistance heating. The gas stream passed from the surge pot through a water-cooled glass condenser, from which the condensable vapours were collected in a condensate receiver. The non-condensable gases
were passed through a glass scrubber, 4 in in diam, and 10 in high, packed to a depth of 6 in with 3-mm glass beads and filled to a depth of 9 in with water. The gases leaving the scrubber went to a vacuum pump where they were contacted with oil in the pump. The oil served as another off-gas scrubber and was monitored for activity buildup.

Experimental procedure

Simulated wastes were fed at a controlled rate to the vessel containing molten sulphur (150°C) while the vessel agitator was turning at 600 rpm. The mixture was held at 150°C for about 15 min to allow time for the release of gases. The resulting mixture was then heated slowly to temperatures ranging from 250°C to boiling point (444°C) and held at the selected temperature for 1 to 5 hr with agitation. The resultant slurry was then solidified by "casting" the slurry and cooling.

To determine the effect of water on the physical properties of the simulated products, uniform samples were taken after various heating periods;
solidified and placed in water at 22°C; a few samples were placed in water at 50 and 80°C. These samples were in the form of right cylinders, 1.25 in in diam. and about 1.5 in high. Leaching tests were performed by immersing these cylinders (about 30 cm$^3$ of solid product) in 175 cm$^3$ of water. The leaching rate was determined by adding a radioactive tracer to the simulated aqueous waste and then measuring as a function of time the activity of the water in contact with the solid product mixture. From these data and the original surface area of the sample, a penetration rate in mil/year (1 mil/yr = 0.001 in./yr) was calculated on the assumption that penetration occurred uniformly on the surface. Cracking of the sample causes a higher leaching rate since more surface is exposed, but the initial surface area was used in all calculations.

Results

**Simulated waste containing aluminium nitrate**

Simulated waste solution containing 2.4 M Al(NO$_3$)$_3$ was fed to the calciner at rates of 5 to 10 cm$^3$/min. Initially, the sulphur level in the calciner was such that 3/4 of the vessel volume was available for disengagement of water vapour and off-gas (300% "freeboard"). As concentrations rose above 7.5-M aluminium, the product mix became so viscous that gas disengagement difficulties made it necessary to lower the feed rate.

Analysis of the off-gas indicated that appreciable quantities of NO, NO$_2$, and SO$_2$ and/or SO$_3$ were given off during the 150°C step, with a mole ratio of nitrogen oxides to sulphur oxides of about 10. Since water was removed before analysis, there was no quantitative indication as to the amount of SO$_3$, although a barium test of the condensate was positive for sulphate; it is not known whether SO$_3$ is formed directly during denitrification or by the reaction $\text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{NO}$. Analysis of the product formed at 150°C indicated that greater than 99% denitrification of the feed was obtained. With heating of this product to temperatures between 350 and 444°C, more gas was evolved, consisting mainly of SO$_2$ and/or SO$_3$; the ratio of nitrogen oxides to sulphur oxides was about 1:10. (Thermal decomposition of Al(NO$_3$)$_3$·9H$_2$O without sulphur is complete at 460°C and results in Al$_2$O$_3$ [12].) Analyses of samples digested for 5 hr at 150, 250, 350, 400, and 444°C (Table I) show that the ratio of Al$_2$O$_3$ to Al$_2$(SO$_4$)$_3$ increases with digestion temperature. Two reactions that evidently take place during heating are as follows:

\[
2\text{Al(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} + 3\text{S} \underset{150^\circ\text{C}}{\rightarrow} \text{Al}_2(\text{SO}_4)_3 + 6\text{NO} + 2x\text{H}_2\text{O}
\]
\[
2\text{Al(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} + 3\text{S} \underset{150^\circ\text{C}}{\rightarrow} \text{Al}_2\text{O}_3 + 6\text{NO} + 3\text{SO}_3 + 2x\text{H}_2\text{O}
\]

No uncontrolled reactions are expected, since both of these reactions are endothermic as written when $x$ represents at least nine waters of hydration.

The lowest leaching rate of specimens in water was obtained with samples containing approximately 5 M aluminium and treated at 400°C for
TABLE I
ANALYSIS OF ALUMINIUM WASTE CALCINED IN SULPHUR

<table>
<thead>
<tr>
<th>Precasting heating</th>
<th>Mixture heated at 150°C during addition of 2.4 M aluminium waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C) (hr)</td>
<td>Al in casting, (M)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>250</td>
<td>5</td>
</tr>
<tr>
<td>350</td>
<td>5</td>
</tr>
<tr>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>444</td>
<td>5</td>
</tr>
<tr>
<td>444</td>
<td>5</td>
</tr>
</tbody>
</table>

* Elemental sulphur was removed by dissolution in carbon disulphide.

In immersion tests of these castings containing tracer concentrations of Cs\(^{137}\) and 5.2 M aluminium, the leaching rates were in the range of 10 to 20 mil/yr for the period from two to eleven months (Table II); the sample in Fig. 5E has only one crack after a year in water. Immersion tests of castings with Sr\(^{85}\) as tracer and containing 7 to 8 M aluminium showed anomalously low leaching rates (less than 10 mil/yr) for treatment at 400°C for periods from 1 to 5 hr. However, castings made after heating at the boiling point (444°C) brought the leaching rates indicated by Sr\(^{85}\) into agreement with the rates indicated by Cs\(^{137}\) for similar compositions and treatments. Cracking of the product mixtures when exposed to water may be caused by hydration of the Al\(_2\)(SO\(_4\))\(_3\). The reason for the increased cracking and faster leaching observed with samples digested at 444 rather than 400°C is not understood.

**High-activity waste containing aluminium nitrate**

Three calcinations were made with one-year-old waste from a separations plant process, so that a more representative evaluation of the technique could be made than is allowed by simulated wastes. Gamma activity in the waste was 22 c/l, beta activity was 108 c/l, and plutonium activity was 2.3 × 10\(^7\) disintegration/min-cm\(^3\). The calcining procedure was identical to that for the simulated waste except that the feed rate was 2.0 cm\(^3\)/min. The previous results with simulated waste allowed the exploration of conditions to be narrowed. Runs 1 and 3 were carried out at 444°C for one hour and the aluminium concentration in Run 1 was allowed to reach only 4.7 M, whereas the concentration in Run 3 reached 7.2 M aluminium. Run 2 was performed at 400°C for 5 hr, with a final aluminium concentration of 8.3 M.
TABLE II
QUALITY OF CASTINGS OF SIMULATED ALUMINIUM WASTE IN SULPHUR
Mixture heated at 150°C during addition of 2.4 M aluminium

<table>
<thead>
<tr>
<th>Precasting heating</th>
<th>Al in casting</th>
<th>Tracer</th>
<th>Leaching in water at 22°C</th>
<th>Condition of immersed casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>(hr)</td>
<td>(M)</td>
<td>(d)</td>
<td>(mil/yr*)</td>
</tr>
<tr>
<td>400</td>
<td>1</td>
<td>4.4</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>Cs</td>
<td>0-140 30→65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>Sr</td>
<td>0-168 &lt;10</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>3</td>
<td>5.2</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>Sr</td>
<td>0-168 &lt;10</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>5</td>
<td>5.2</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.2</td>
<td>Cs</td>
<td>0-28 52</td>
<td>28-336 ~45</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>Cs</td>
<td>0-140 ~200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>Sr</td>
<td>0-168 &lt;10</td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>1</td>
<td>7.4</td>
<td>Cs</td>
<td>0-56 37</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>Cs</td>
<td>0-56 145</td>
<td>56-168 75→45</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>Sr</td>
<td>0-56 20</td>
<td>56-224 60→90</td>
</tr>
<tr>
<td>444</td>
<td>3</td>
<td>8.2</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>Cs</td>
<td>0-56 25</td>
<td>56-280 70→100</td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>Sr</td>
<td>0-35 ~400</td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>5</td>
<td>7.4</td>
<td>None</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8.9</td>
<td>Cs</td>
<td>0-56 ~250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.7</td>
<td>Cs</td>
<td>0-48 1350→70</td>
<td></td>
</tr>
</tbody>
</table>

* The limit of analytical accuracy is 10 mil/yr for the tracer experiments. The arrow between two rates indicates the direction of change during the period (mil/yr = 0.001 in/yr).
In each of the three runs, only one part in approximately 100 000 parts of the activity in the feed was carried overhead, as shown by measurement of activity in the scrubbing solutions and in the other off-gas equipment. Analysis showed that the activity was caused by entrainment of particulate matter rather than volatilization of RuO$_4$. Such low activity carry-over is in marked contrast to the highly-active gas streams experienced with other calcination techniques.

Duplicate castings were made with product slurry from each of the three runs. Leaching rates were somewhat more consistent than those observed with simulated wastes. As shown in Fig. 6 and Table III, leaching rates for the samples of high aluminium concentration (Runs 2 and 3) fell during the initial two months, then rose during the next three months. Examination at the end of this time showed a network of cracks on the surfaces of the samples. In contrast, the leaching rate of the 4.7-M aluminium samples
### TABLE III

**CALCINATION OF HIGH-ACTIVITY ALUMINIUM WASTE IN SULPHUR**

Mixture heated at 150°C during addition of waste to sulphur. Waste was 2.0 M Al(NO₃)₃ and 1.6 M HNO₃, with 22 c/l of γ, 108 c/l of β, and $2.3 \times 10^7$ d/(min)(cm³) of Pu.

<table>
<thead>
<tr>
<th>Aluminium concentration in product, M</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.7M</td>
<td>8.3M</td>
<td>7.2M</td>
</tr>
</tbody>
</table>

**Heating**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time, hr</th>
<th>Fraction of activity in gas-cleaning equipment</th>
<th>Leaching rate in water at 22°C, mil/yr (duplicate samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>Beta</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1/(5.4 \times 10^4)$</td>
<td>$1/(5.9 \times 10^4)$</td>
</tr>
</tbody>
</table>

|                 | γ       | β       | Pu |
|                 |        |        |    |
| 0-7             | 75-71  | 12-10  | 3-2 |
| 7-14            | 41-53  | 5-7    | -   |
| 14-21           | 57-49  | 8-7    | 1-1 |
| 21-28           | 37-37  | 5-5    | -   |
| 28-35           | 27-27  | 4-4    | -   |
| 35-42           | 27-27  | 4-4    | -   |
| 42-49           | 29-29  | 4-4    | -   |
| 49-56           | 18-20  | 3-3    | 1-1 |
| 56-63           | 23-19  | 4-3    | -   |
| 63-70           | 20-20  | 3-3    | -   |
| 70-77           | 17-18  | 2-2    | -   |
| 77-84           | 20-16  | 2-2    | -   |
| 84-98           | 16-16  | 2-2    | -   |
| 98-112          | 13-15  | 2-2    | -   |
| 112-126         | 13-14  | 2-2    | 1-1 |
| 126-140         | 15-13  | 2-2    | 1-1 |
| 140-154         | 13-15  | 2-2    | 1-1 |

**Note:** Leach water changed at end of each interval.

* mil/yr = 0.001 in/yr.
Leaching rate of calcined high-activity waste. The major constituent of the waste was Al(NO₃)₃. The curves represent average values indicated by γ-activity (Table III). (Values corresponding to Pu activity are much lower).

(Run 1) continued to fall throughout the exposure period and examination revealed smooth surfaces on the duplicate samples. Of additional importance, the leaching rate of plutonium was much lower than that of other radioactive constituents. These calcinations with high activity waste confirm that the best product is obtained at aluminium concentrations of about 5 M, with heating in the range of 400°C to the boiling point of sulphur.

Simulated waste containing "stainless-steel nitrates"

Feed solution containing 2.9 M stainless-steel nitrate (2.1 M Fe⁴⁺⁺⁺, 0.5 M Cr⁴⁺⁺⁺, 0.3 M Ni⁺⁺⁺) was fed at 10 cm³/min to the agitated calciner vessel containing molten sulphur at 150°C. Initially, the sulphur level was such that there was about 300% freeboard for the disengagement of water vapour and off-gas. Feed was continued until the concentration in the product mixture reached the range of 10 to 24 M stainless-steel salts. At this concentration the mixture was still rather fluid, so no upper limit to the concentration of solids in the product mixture was reached.

Greater than 99% denitration was estimated from chemical analysis of the 150°C product. About 30 wt.% of the dispersed waste was water soluble and consisted largely of sulphates. Ferrous sulphate was identified by X-ray diffraction as a major constituent. The remainder of the iron was presumed to be present as insoluble oxide. Ferrous sulphate and ferric oxide can result from the following two reactions of the nitrate with sulphur at 150°C:

\[
\begin{align*}
3\text{Fe(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} + 5\text{S} & \overset{150^\circ\text{C}}{\longrightarrow} 3\text{FeSO}_4 + 9\text{NO} + 2\text{SO}_3 + 3x\text{H}_2\text{O} \\
2\text{Fe(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} + 3\text{S} & \overset{150^\circ\text{C}}{\longrightarrow} \text{Fe}_2\text{O}_3 + 6\text{NO} + 3\text{SO}_3 + 2x\text{H}_2\text{O}
\end{align*}
\]
These reactions are endothermic as written, provided that at least 15 moles of water per mole of metal are present. Heating of the mixture for 3 to 5 hr at 444°C produced a product that was characterized by low leaching rates in water and a lack of cracking after immersion for over six months. During the high-temperature step small amounts of gas were evolved that contained SO$_2$ and/or SO$_3$ in appreciable concentrations. Chemical analysis of the solids after the high-temperature step indicated that most of the stainless-steel sulphates had been converted to sulphides (Table IV), and that the iron was present specifically as the disulphide, FeS$_2$. At 444°C both of the following reactions for iron may take place:

$$\text{FeSO}_4 + 3S \xrightarrow{444^\circ C} \text{FeS}_2 + 2\text{SO}_2$$
$$3\text{FeSO}_4 + 7S \xrightarrow{444^\circ C} 3\text{FeS}_2 + 4\text{SO}_3$$

The colour of the product from the 150°C calcination is yellow. This changes to black after the 444°C treatment due to the formation of the stainless-steel sulphides at the higher temperature.

Heating at the boiling point (444°C) with agitation for 3 to 5 hr produces the best castings for feeds containing stainless-steel nitrates (Table V). These castings, which were rapidly cooled, have not cracked after immersion for eight months. In tests of castings that contain tracer concentrations of Sr$^{85}$ and Cs$^{137}$, the rates of leaching of these isotopes demonstrated that the penetration of the castings by water is slow. The rate of penetration dropped to less than 10 mil/yr for Sr$^{85}$ and Cs$^{137}$ (the limit of analytical accuracy) during immersion periods, thus far, of eight months. The rates of less than 10 mil/yr are in contrast to rates of 250 to 1500 mil/yr for

**Table IV**

**ANALYSIS OF STAINLESS-STEEL WASTE CALCINED IN SULPHUR**

Mixture heated at 150°C during addition of waste to sulphur. Waste was 2.9 M in "stainless-steel nitrates" (2.1 M Fe$^{+++}$, 0.5 M Cr$^{+++}$, 0.3 M Ni$^{+++}$).

<table>
<thead>
<tr>
<th>Precasting heating</th>
<th>SS in casting, (M)</th>
<th>Combined sulphur in waste, wt.% (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C) (hr)</td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>400 1</td>
<td>5.0</td>
<td>32.9</td>
</tr>
<tr>
<td>400 3</td>
<td>5.6</td>
<td>47.2</td>
</tr>
<tr>
<td>400 5</td>
<td>5.0</td>
<td>49.4</td>
</tr>
<tr>
<td>400 5</td>
<td>6.0</td>
<td>45.3</td>
</tr>
<tr>
<td>444 3</td>
<td>13.8</td>
<td>42.2</td>
</tr>
<tr>
<td>444 5</td>
<td>24.0</td>
<td>47.6</td>
</tr>
</tbody>
</table>

(a) Elemental sulphur was removed by dissolution in carbon disulphide.
TABLE V
QUALITY OF CASTINGS OF SIMULATED STAINLESS-STEEL WASTE IN SULPHUR

Mixtures heated at 150°C during addition of waste to sulphur.
Waste was 2.9 M in "stainless steel" (2.1 M Fe++, 0.5 M Cr++, 0.3 M Ni+++).

<table>
<thead>
<tr>
<th>Precasting heating</th>
<th>SS in casting, (M)</th>
<th>Tracer</th>
<th>Leaching in water at 22°C (d) (mil/yr*)</th>
<th>Condition of immersed casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>(*C) (hr)</td>
<td></td>
<td></td>
<td>(d) (mil/yr*)</td>
<td></td>
</tr>
<tr>
<td>400 1</td>
<td>5.1</td>
<td>None</td>
<td>-</td>
<td>Cracked at 40 d. Ruptured at 278 d. (Fig.5A)</td>
</tr>
<tr>
<td>400 1</td>
<td>6.0</td>
<td>Cs</td>
<td>0-28 132 28-336 83-32</td>
<td>Sample broke in half at 24 d. No further changes (375 d).</td>
</tr>
<tr>
<td>400 3</td>
<td>5.6</td>
<td>None</td>
<td>-</td>
<td>Still solid (380 d).</td>
</tr>
<tr>
<td>400 3</td>
<td>6.0</td>
<td>Cs</td>
<td>0.56 67 56-336 &lt;10</td>
<td>Crumbled at base at 242 d.</td>
</tr>
<tr>
<td>400 5</td>
<td>5.0</td>
<td>None</td>
<td>-</td>
<td>Still solid (378 d).</td>
</tr>
<tr>
<td>400 5</td>
<td>5.6</td>
<td>Cs</td>
<td>0-28 44 28-336 &lt;10</td>
<td>Still solid (381 d). (Figure 5B)</td>
</tr>
<tr>
<td>444 1</td>
<td>10.6</td>
<td>Cs</td>
<td>0-28 37 28-224 &lt;10</td>
<td>Still solid (228 d).</td>
</tr>
<tr>
<td>444 1</td>
<td>10.0</td>
<td>Sr</td>
<td>0-224 &lt;10</td>
<td>Still solid (243 d) except for small cracks.</td>
</tr>
<tr>
<td>444 3</td>
<td>9.6</td>
<td>Cs</td>
<td>0-224 &lt;10</td>
<td>Still solid (235 d) except for two small cracks.</td>
</tr>
<tr>
<td>444 3</td>
<td>13.8</td>
<td>Sr</td>
<td>0-224 &lt;10</td>
<td>Still solid (237 d).</td>
</tr>
<tr>
<td>444 5</td>
<td>12.0</td>
<td>Cs</td>
<td>0-224 &lt;10</td>
<td>Still solid (236 d).</td>
</tr>
<tr>
<td>444 5</td>
<td>24.0</td>
<td>Sr</td>
<td>0-224 &lt;10</td>
<td>Still solid (232 d). (Fig. 5C)</td>
</tr>
</tbody>
</table>

* The limit of analytical accuracy is 10 mil/yr (mil/yr = 0.001 in/yr).
CASTINGS PREPARED FROM MOLTEN MIXTURES THAT WERE HEATED TO ONLY 350°C (NOT SHOWN IN THE TABLE).

Simulated waste containing zirconyl nitrate

In a preliminary experiment, an aqueous solution containing 0.6 M ZrO(NO₃)₂ was added to molten sulphur at 150°C at a rate of 5.6 cm³/min. The product mixture was visibly fluid at a concentration of about 7.4 M zirconium. The maximum feed-rate and maximum concentration of zirconium salts in the product were not determined.

Analysis showed that denitration was only 25% complete at 150°C but was completed after 5 hr at 444°C. The resulting compound is about 95% ZrO₂·2H₂O, with the remainder being anhydrous ZrO₂. It is interesting to note that data from the National Reactor Testing Station (Idaho) [13] show that complete thermal decomposition of ZrO(NO₃)₂ to the oxide occurs at 450°C without sulphur.

A casting containing 7.4 M zirconium was made from a slurry that was heated to 444°C for 5 hr. In immersion tests with tracer concentrations of Cs¹³¹, the leaching rate during two months of exposure so far has fallen from 30 to 12 mil/yr. There is one slight crack at the base of the casting; otherwise, the surface is smooth.

Simulated acidic Purex waste

An aqueous solution that simulated the concentrated waste from evaporators of the Purex process was calcined in a preliminary study of this material. The solution was 3.5 M in HNO₃ and 2.6 M in metallic ions; the latter were present as nitrates and consisted of 1.5 M Na⁺, 0.5 M Mn⁴⁺, 0.5 M Al⁶⁺, and 0.1 M Fe⁶⁺. The calcination procedure was again the 150°C step that was followed in most cases by prolonged heating at higher temperatures before casting a sample.

Analysis of the 150°C product showed that denitration was essentially complete and that all of the combined sulphur was present as sulphates. The presence of oxides was not certain, although from the results of aluminium calcination alone (Table I) the formation of Al₂O₃ would be expected.

For all of the tests made with this waste, the metallic ions were concentrated in the sulphur slurry to about 9 M and the castings were traced with Cs¹³⁷. In a reversal of findings with the previously described wastes, the best casting was obtained directly from the 150°C step, with no further heating. This sample is smooth and intact after six months in water, and the leaching rate has remained at about 100 mil/yr. Precasting treatment at 250°C for 5 hr produced a sample that showed small cracks after two months in water and has leached at about 250 mil/yr during three months of immersion. Samples from treatment at 350°C and at the boiling point for 5 hr were progressively poorer, the latter cracking at about two weeks; leaching rates of both were greater than 1000 mil/yr during the first month, though the rate of each had fallen to about 15 mil/yr by four or five months.

Sodium in this waste is presumably the cause of the generally poor properties of the castings, and the reason for the relatively good behaviour of the 150°C casting is not apparent.
Additional studies of product quality

The substitution of sand (SiO₂) of the same particle size (80-100 mesh) as the sulphides of stainless steel and in about the same concentration gave products with leach rates of approximately 20 mil/yr for both Csⁱ³⁷ and Sr⁸⁵. The mere fact that the bulk inert material has a low solubility is, therefore, not the only reason for the lower leaching rate of the stainless-steel samples. The lower leach rates exhibited by stainless steel sulphides in sulphur may be due to the fact that the sulphides are chemically bound to the sulphur matrix thus enhancing the stability of the castings.

Sulphur slurries that contained iron and nickel salts (without chromium) and were heated for 5 hr at 444°C gave products that were not as stable as those containing stainless-steel salts; the samples cracked after exposure to water for about 10 d and the leaching rates were higher than those for stainless-steel salts.

Since the chromium appeared to improve the quality of the product slurry, a test was made in which chromic nitrate was added to the aqueous feed of simulated aluminium waste. The sulphur slurry from the 150°C calcination was then heated at 444°C for 5 hr. The product, which contained 10 M aluminium salts and 2.5 M chromium salts, showed slight cracking after three days but was still relatively solid after three months. The sample must be exposed for a longer period before the effect can be determined. Other additives that were tried, such as boric acid and calcium nitrate, were clearly of no benefit.

A single test was made in which aluminium nitrate was added to the aqueous stainless-steel nitrates before calcination at 150°C; the slurry was heated at 444°C for 5 hr. The resulting product was 12.9 M stainless steel and 1.2 M aluminium. Despite the presence of the stainless steel, this sample cracked after exposure to water for one month and has shown leaching rates of 30 to 100 mil/yr for the two-month period to date.

Pure sulphur castings that contained 10⁻³ M Cs¹³⁷ or Sr⁸⁵ and were rapidly cooled in air did not exhibit any appreciable cracking but did have higher leaching rates than samples containing stainless-steel compounds. The initial rates were about the same, in fact, as those observed for the high activity waste containing aluminium. These results were not expected, since it was thought that absence of gross quantities of foreign material, such as aluminium compounds, would allow a better sulphur structure. The apparent anomaly may be caused by a weakening transformation in the crystal structure of sulphur which is blocked by gross quantities of additives, as illustrated by the following experiments. Casting of pure sulphur were held at 100°C for five days to ensure that most of the sulphur was converted to the monoclinic form, and then were held at 80°C for six days to obtain a conversion to the denser rhombic form; the castings developed major cracks and were brittle and porous. In contrast, sulphur waste castings that contained 4 to 8 M aluminium or 13.7 M stainless steel and that underwent the same extended heat treatments were tough and did not exhibit this poor behaviour.

Solid samples of calcined waste - sulphur that contained either aluminium or iron were irradiated to 3 × 10⁹ r in air without any changes in physical appearance.
CALCINATION OF RADIOACTIVE WASTE

Fig. 7
Photomicrographs of simulated waste in sulphur

Initial leaching rates in water at 80°C are 4 to 20 times higher than initial rates at 22°C for equivalent castings.
Castings containing aluminium and stainless steel were sectioned, polished and etched with carbon disulphide. Photomicrographs of the resulting surfaces are reproduced in Fig. 7, and show that the particles are separated by sulphur and are roughly spherical in shape.

Future programme

Because of the importance of the waste-disposal programme, development of detailed information is planned to ensure compatibility of the use of sulphur as a storage medium with the long-range goal of minimum surveillance of the stored waste. The present studies will be extended to include the use of additives and supplementary chemical treatments to enhance the stability of the castings in contact with water, and to include wastes resulting from the processing of (1) Zr-clad elements that are dissolved by HNO$_3$ -HF, (2) neutralized Purex wastes, and (3) the neutralized wastes that contain aluminium nitrate from the processing of aluminium-uranium alloy fuel.

In view of the quite favourable results obtained in the tests with acidic high-activity wastes containing aluminium, large-scale equipment will be designed for further tests with inactive solutions. Such tests will allow the development of appropriate techniques for operating the process remotely, as will be required with active wastes. In parallel with the preceding work, economic studies will be made of processing costs and of storing the resultant products in various forms, at various locations and under various conditions. Over-all, the intent is to determine fully the economics and the product stability that can be attained with calcined waste-sulphur, so that an optimum balance can be sought between processing costs and the desirability for long-term integrity of stored waste.

REFERENCES


CALCINATION OF RADIOACTIVE WASTE


DISCUSSION

W. LEVI: Have you any idea in what chemical form the various radio-nuclides are present in sulphur? In so far as they are present as sulphides they may become soluble by oxidation.

D.S. WEBSTER (on behalf of W. E. WINSCHER et al.): No, we do not yet know in what form they are present.

F. DUHAMEL: Have you studied the influence of the method of cooling the sample on the formation of fissures and on leaching?

D.S. WEBSTER: Yes, we have studied the influence of cooling rates on the properties of the castings, and can detect no effect so long as a calcined material is present. In contrast, when pure sulphur is held for several days in the monoclinic form (100°C) and then transformed to the rhombic form by retention for several days at 85°C, the casting shatters readily. We noted that the presence of foreign material apparently causes a direct conversion, on cooling, to the rhombic form.

D. W. CLELLAND: Do you foresee any application of the sulphur process in future storage schemes?

D.S. WEBSTER: The evaluation of waste calcination in sulphur is part of our future programme, but I do not yet know what place sulphur will have in that programme.

P. DEJONGHE: Did you perform the elution tests on samples as they occurred after cooling, or did you previously break the cylinders so as to expose the inner surface of the block? I am asking this because we found, in our work on asphalt insolubilization, that, on cooling, a film of asphalt is formed which protects the inner part of the block against elution and I am wondering whether the same, or a similar, phenomenon is observed with sulphur.

D.S. WEBSTER: We perform leaching tests on the samples without breaking them. The molten mixture is poured into glass beakers and allowed to solidify, after which the glass is broken away from the casting. Examination shows that the dispersed solids are exposed on all parts that were in contact with glass. Consequently there is no need to break the sample before immersion in water.

C. SOMBRET: During heating, the salts originally present in solution undergo transformation which may go as far as partial calcination. As the resulting products are not necessarily of the same density as sulphur, did you observe any separation in the mass of material, or was the distribution of substances uniform?

D.S. WEBSTER: Yes, the calcined products tend to settle in molten sulphur. However, if the concentration is sufficiently high the particles
are close-packed and there is no settling. In the case of the \( \text{Al(NO}_3\text{)}_3 \) feed, the necessary concentration is about 250 g/l of aluminium.

J. A. McBRIDE: How do you propose to store the sulphur products containing high-activity waste residues?

D.S. WEBSTER: This is something for future evaluation, but one solution would consist of pumping the molten slurry into the bedrock cavern already mentioned by Dr. Belter*.

J. A. BUCKHAM: Was the thermal conductivity value of 0.155 BTU/(hr)(°F)(ft) which you give in that section of the paper where you discuss your experimental conditions a handbook value for pure crystalline sulphur, or was it a measured value for the mixture produced by this calcination process?

D.S. WEBSTER: The value that I quoted was for pure sulphur. The addition of oxides or sulphides will increase the conductivity. In the case of stainless steel wastes at high concentrations, the conductivity will increase by a factor of 2 or 3.

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* BELTER, W.G., "Present and future programmes in the treatment and ultimate disposal of high-level radioactive wastes in the United States of America", These proceedings.
RADIANT-HEAT SPRAY CALCINATION STUDIES

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Abstract — Résumé — Аннотация — Resumen

RADIANT-HEAT SPRAY CALCINATION STUDIES. The radiant-heat spray calcination process for conversion of liquid wastes to solids is described and the design of a one-gallon-per-hour spray calcination unit coupled with a small melt pot, capable of being run separately as a pot calciner, is discussed. The units were designed to test the feasibility of the calcination process with actual Purex plant waste in terms of: the process as a unit operation, off-gas treatment, fission-product behaviour, condensate and calcined waste characteristics.

The entire system was made to fit into an available 7-1/2 ft x 15 ft x 15 ft tall, manipulator-equipped, shielded cell which is also described. Included in the design discussion are: the resistance heating of the spray calciner column, thermal insulation of the column, spray nozzle, method of nozzle replacement, induction heating of the melt pot, radioactivity scanner for the pot, off-gas processing system including condenser, scrubber and filters, off-gas sampling device, liquid sampling device, wash-down system, feed system, instrumentation and control methods.

The experience gained in operating the calciners and associated equipment is discussed.

Experimental results presented show the effectiveness of off-gas decontamination and behaviour of gross chemical constituents and some specific fission products.

CALCINATION PAR PULVÉRISATION ET CHAUFFAGE RADIANT. Les auteurs étudient le procédé de calcination par pulvérisation et chauffage radiant utilisé pour transformer les déchets liquides en solides; ils décrivent notamment une installation de calcination par pulvérisation (d'une capacité de 1 gallon par heure) accouplée à un petit creuset qui l'on peut utiliser séparément comme creuset de calcination. Cet ensemble a été conçu pour étudier la possibilité de calciner des déchets réels résultant du traitement Purex, en tenant compte des facteurs suivants: opérations dans un seul appareil, traitement des gaz d'échappement, comportement des produits de fission, caractéristiques du condensé et des déchets calcinés.

Tout l'appareillage a été installé dans une cellule blindée de 2,50 x 5 x 5 m, pourvue de manipulateurs, qui est aussi décrite dans le mémoire. Les auteurs traitent des questions suivantes: chauffage par résistance de la colonne de calcination, isolement thermique de la colonne, ajutage de pulvérisation, méthode de remplacement de l'ajutage, chauffage par induction du creuset, détecteur de radioactivité du creuset, système de traitement des gaz d'échappement (y compris le condensateur, l'épurateur et les filtres), échantillonnage des gaz d'échappement et des liquides, système de lavage, instruments et méthodes de contrôle.

Les auteurs font part de l'expérience acquise dans le fonctionnement des appareils de calcination et du matériel connexe.

Les résultats expérimentaux présentés montrent l'efficacité de la décontamination des gaz d'échappement et donnent un idée du comportement des principaux éléments chimiques constitutifs et de certains produits de fission.

ИССЛЕДОВАНИЯ НА КАЛЬЦИНАТОРАХ ФОРСУНОЧНОГО ТИПА С НАГРЕВАНИЕМ ТЕПЛОВЫМ ИЗЛУЧЕНИЕМ. Дается описание процесса форсуночного кальцинирования с нагреванием тепловым излучением для отверждения жидких отходов, а также обсуждается конструкция форсуночного кальцинатора производительностью 3,7 л/час; этот аппарат включает небольшой тигель для плавления, который может быть самостоятельно использован в качестве тигельной обжигательной печи. Аппарат был сконструирован для того, чтобы проверить возможность осуществления процесса кальцинирования на промышленной установке по переработке отходов "Пурекс-процесса" со следующих точек зрения: осуществление процесса в качестве единой операции, оборудование выделяемых газов, поведение продуктов деления, характерные особенности конденсата и кальцинированных отходов.

Вся система была сконструирована таким образом, чтобы она поместилась в защитную камеру площадью 2,26 x 4,57 м и высотой 4,57 м; оборудованную манипуляторами. Обсуждаются следующие вопросы: электрический нагреватель обжигательной колонки для форсуночного кальцинирования; термическая изоляция колонки; сопло форсунки; метод замены сопла; индукционный подогрев плавильного...
INTRODUCTION

The fixation of radioactive waste in a stable solid medium has been the subject of considerable effort by workers throughout the United States Atomic Energy Commission as well as by atomic energy organizations in other countries. Calcination of the waste is one of the methods being studied and several methods have been proposed to achieve calcination on a continuous basis. At Hanford, development work has been done on the fluidized-bed calciner [1, 2, 3], pot calciner [3, 4, 5, 6] and spray calciner [3, 7]. Since the latter two methods looked quite promising on the basis of "cold" work and engineering evaluation, it was decided to install in a shielded cell a dual-purpose unit which could be operated either as a spray calciner or as a pot calciner in order to test waste calcination with actual, full-level, radioactive wastes. It is hoped that out of the research will come a better understanding of the calcination characteristics of the radioactive waste, the associated off-gas treatment problems, thermal properties of the waste calcine and operational techniques and problems. This report briefly describes the hot-cell calciner equipment and its mode of operation.

DISCUSSION

Spray calcination

The spray-calcination process was suggested by work done at Oak Ridge, Tennessee (on the conversion of uranyl nitrate to UO₃) [8] and at the Pulp and
Paper Institute of Canada (initially for treatment of paper mill liquors) [9]. The process is somewhat similar to spray drying but differs in important respects and may be looked upon as a new, and very versatile, chemical engineering unit operation. The process has been called "radiant-heat spray calcination" (or simply spray calcination) by United States workers and the "atomized suspension technique" in Canada [9]. Investigation of its potential use for the calcination of radioactive wastes was initiated at Hanford about three years ago and has been under intensive development since that time. The spray-calcination method entails atomizing the liquid waste into the top of a tower, the walls of which are heated to a high temperature (ca. 800°C), and passing the resulting suspension of droplets down the column where the droplets undergo drying and calcination (Fig. 1). Separation of the calcined droplets from the off-gas is accomplished in our process with sintered metal filters. The calcined droplets are very small (mean particle size is 50 μ), and they pass as a powder into a heated pot below the column. In the pot, which is also the final storage container, the powder is melted by induction heating and then allowed to cool to a dense solid. In the Hanford cell arrangement, the same induction furnace is used for the pot-calcination heat source.

Pot calcination

The pot or batch calciner has received extensive development at Oak Ridge National Laboratory and considerable experimental work with Purex waste has also been done at Hanford [4, 5, 6]. The pot-calciner system is simple in principle. The feed is fed directly to the pot where it is dried and calcined. The pot is used as a final storage container as well. In the hot-cell installation, the off-gas system used for the spray calciner is used also for the pot calciner.
Process comparisons

Potential advantages of spray calcination for the treatment of radioactive wastes include: (1) the droplets have only a very low residence time (approximately 10 to 15 sec) in the heated zone of the calciner. It is believed that the brief duration of high-temperature exposure should minimize the volatilization of certain fission products (such as ruthenium and caesium). (2) As with pot-type calcination, the total volume of non-condensable off-gases is very low, compared to fluidized-bed calcination. Furthermore, and unlike pot calcination, the rate of off-gas evolution is constant. This considerably simplifies the sizing of the off-gas equipment. (3) The spray calciner, as demonstrated in "cold" pilot-plant runs, can operate satisfactorily with a wide range of feed compositions and even with slurries. Various additives (such as phosphate or borate) can be readily added to produce insoluble, glassy products or to promote chemical reactions during the calcination. An example of the latter is addition of a carbohydrate (sugar) to promote conversion of sodium nitrate to sodium carbonate. The major disadvantage of spray calcination is the relatively low density and "dustiness" of the powder product; however, this powder can be readily consolidated to a dense, monolithic form by use of a melt vessel.

The principle advantage of pot calcination is mechanical simplicity. Major disadvantages include: (1) poor heat transfer as solids build up concentrically in the pot from the wall inward; (2) non-uniform rate of off-gas release; and (3) with some feeds, foaming and uncontrolled exothermic reactions. The combination of a spray calciner with a melt pot combines many of the advantages of both continuous spray calcination and batch-pot calcination.

EQUIPMENT DESCRIPTION

The problem in the design of the hot-cell calcination equipment was to scale the calciner to fit an existing 7½ X 15 X 15-ft high cell (Fig. 2). Since the manipulators could only reach the 7-ft level, the calciner had to be short enough to allow the nozzle to be changed in case of pluggage. The previous unit used in "cold" studies was 8 in in diam, by 10 ft tall. In order to keep the particle hold-up time in the calciner approximately the same as in the cold unit, the hot-cell unit was made 10 in in diam, by 5 ft tall, and processing was limited to 1 gal/hr of liquid waste. The calciner was mounted on jacks so that it could be lowered for nozzle changing. The pot is a stainless-steel pipe 13 in tall by 5 in in diam, with suitable flanges and thermocouple wells. It will hold nearly one gallon of calcined waste. The off-gas equipment (Fig. 3) consists of a condenser, packed scrubber, electrostatic scrubber, silica gel absorber and two absolute filters. The off-gas is drawn from the calciner by an air jet and exhausts with the cell ventilation air (through additional filters and up a stack).

Heating

The spray calciner is heated by passing low-voltage, high-amperage alternating current through the 1/16-in Inconel shell. The upper two feet
High-level cell waste processing facility

Fig. 2

of the column constitute the drying zone and can be heated at a different rate to the bottom three feet. The voltage is controlled with variable transformers which feed step-down transformers. The large current is fed into the cell through a three-conductor copper step-plug and thence to bus bars (Figs. 4 and 5). The final connection to the column is made with large flexible cables which allow the column to be moved vertically. The bottom of the column is at ground potential and the top is electrically insulated from the top flange to allow metallic nozzle feed lines to be used. Sheath heaters are used to prevent steam condensation in the filter jack leg. The melt pot is heated by a 15-turn induction coil, mounted in a movable cart. The coil is fed from the 15-kVA motor generator outside the cell with water-cooled copper coaxial line through the 4-ft thick cell wall and thence by two flexible cables to allow for cart motion to position the pot under the spray calciner.

Temperature readings

The column temperature is taken from four thermocouples which press against the outside of the heated wall. Two of the thermocouples are used for the temperature control. The pot temperature is taken from two thermocouples in wells in the pot wall. Two additional thermocouples record the
Fig. 3
Calciner off-gas train

Fig. 4
Bus bars and calciner in high-level cell
temperature at the centre and mid-radius of the calciner pot (Fig. 6). The two thermocouples at the top of the pot are used for liquid-level control during pot calcination.

Nozzle changing

In order to change a feed nozzle, the column has to be low enough for the medium-duty manipulator to reach it. This is accomplished by removing the pot and lowering the column, which is mounted on air-motor-driven screw jacks (Fig. 6). After the column is down, the clean-out needle lever (Fig. 7) is swung out of the way, the feed and steam lines are disconnected, and the hold-down nut is removed. The nozzle then is removed from between the split hold-down screw and the new nozzle put in place. The nozzle has a stainless-steel, captive O-ring to seal against the seat on the top cover. The nozzle is a modified commercial nozzle*, in which the clean-out needle has been sealed in a stainless-steel bellows.

Decontamination

The entire column can be washed down by introducing a wide-angle spray through the nozzle port, a port in the jack leg and four ports in the top of

* Spraying Systems Co., Setup No. 12A.
Fig. 6
Pot calcination vessel.

Fig. 7
Top of spray calciner.
the filter section. Wash-down tests with the partially soluble simulated Purex calcines have been quite successful. The column can be made clean by washing with water alone. All the off-gas equipment has suitable inlet lines and drains for flushing. Each tank also has a spray head installed for wash-down.

Pot radioactivity scanner

A collimated radioactivity scanner is mounted on the cart (Fig. 8). The counter-balanced lead-shielded counting chamber can be positioned vertically and horizontally with the manipulator to scan the radioactive profile of the melt pot held in the cart. In this way an approximate indication of the melt and fluid level can be obtained.

Off-gas dust sampler

Between each stage of the off-gas system is a particle sampler (Fig. 9). Five samplers are used. Each consists of a membrane filter in a dispos-
able plastic holder. The filter can be introduced into the gas stream by the simultaneous operation of three valves driven by an air piston. All of the off-gas passes through the filter for a length of time sufficient to collect a countable sample. The efficiency with which a filter can be counted in its container is not as high as might otherwise be obtainable, but this technique will allow all operations to be done with manipulators.

Liquid sampler

Liquid sampling of all the tanks and of several of the process solutions, such as condensate and scrub streams, is accomplished by use of a vacuum sampler (Fig. 10). The sampling vial is pressed against a gasket and a vacuum drawn through the annular tube. The sample is drawn in through the central tube and goes out through the annular tube to a trap until the lines have been flushed. Back suction leaves a sample in the vial which is then stoppered and removed to the in-cell gamma spectrometer (Fig. 11).

The spectrometer is a 400-channel pulse-height analyser [10], and is extremely useful for detecting not only the radioactive isotope present but the quantity as well - without the necessity of removing samples from the cell.

OPERATION

The operation of the calciner is quite simple once the feed is prepared and the system is ready (tanks empty, sample filters in place, sample vials
When starting the spray calciner, steam is fed through the nozzle for a few minutes, and then the stainless-steel remote-head diaphragm pumps are primed and operated with water feed until the system is operating steadily, then the pump inlet is switched to the feed tank and waste is pumped to the nozzle at a flow-rate of about 1 gal/hr. The electric feed-pump motor is connected to a relay which will shut off the pump in case the steam flow stops - to insure that feed will not be backed up into the steam line (which leads to the outside of the cell).

Both the feed and the steam are screened to keep any small particles from plugging the nozzle jets. (This is not expected to be a problem in production-sized spray calciners, where much larger and less critical nozzles would be employed and only removal of coarse particles would be required). In case a plug occurs on the liquid side, a clean-out needle can be operated to clear the nozzle.

During operation the pot is scanned with the probe to determine melt level and close check is maintained of the temperatures and flow rates. Samples are taken as desired of both the process liquids and the off-gas. Occasionally the column is vibrated, and/or hammered, to loosen any cal-
Fig. 11

In-cell gamma analyser

THIN S.S. WINDOW & ALUMINIUM BETA SHIELD

LEAD GLASS WINDOW

MULTIPLIER PHOTOTUBE

NaI (Tl) CRYSTAL

LEAD SHIELD

LEAD COLLIMATOR

HIGH DENSITY CONCRETE

SAMPLE VIAL IN CARRIER

THIN S.S. WINDOW & ALUMINIUM BETA SHIELD

COLUMN FEED TANK

SCALE IN INCHES
cined powder which may adhere to the walls. After operation, the cooled pot is removed from the column and capped.

The feed pump is not used with the small pot calciner. Rather, a vacuum is drawn on the pot (3-5 in of Hg) and the pot is heated at low power. About one gallon of feed is added to the pot and boil-down is begun. Eighteen liters of concentrated Purex waste are then added over a 6-hr period of boil-down. Liquid level is determined from thermocouple readings and controlled manually by adjusting the power input to the induction coil. Feed-tank and condensate-tank float gauges are read frequently to keep an inventory of the liquid volume in the pot. The collimated counting probe is used as well, to determine the waste level in the pot. After boil-down and drying, heating is continued while calcination occurs. If there are large amounts of sulphates in the waste, heating is continued until they are decomposed. Off-gassing is most severe during this period and the greatest quantity of particulate matter appears in the off-gas system. Heating is continued until a rapid temperature rise at the centre of the pot indicates that the calcine has melted. The pot is then cooled (by running water through the induction heating coils) and the off-gas and feed lines removed and the ports capped off.

The filled pots are lifted out of the cart with a remote-controlled (General Mills Corp.) electric-motor driven manipulator and placed in storage where temperature and pressure, etc. can be observed as a function of time.

Off-gas system

The off-gas system (Fig. 3) is designed to serve two functions: (1) to achieve the high degree of decontamination (DF's of the order of $10^8$) which is necessary before the off-gases can be released to the atmosphere, and (2) to derive information on the chemical behaviour of the off-gas and on the efficiency of the various units in the off-gas train. On behalf of the second objective, the off-gas rack has been made flexible to permit replacing or by-passing the various units as may be required. The initial configuration is shown. A special alloy*, which is resistant to sulphate corrosion, is used for the condenser tubing. Caustic is used in the packed scrubber and fibre glass is used in the de-entrainer. Silica gel is used to absorb any moisture and ruthenium left in the gas before it passes through two "absolute" filters, which are used for back-up.

The second scrubber in the off-gas is called an "electrostatic bubble scrubber" [11]. It was designed to remove small particles from the gas and return them to a liquid phase for recycle. In the electrostatic bubble scrubber (Fig. 12) the gas is passed through a 20-kV corona discharge. The particles, upon being charged, are attracted to the liquid (which is at ground potential) as the gas bubbles through a plastic skirt via small holes into the liquid. Cold runs with this scrubber were very encouraging. De-entrainment factors of over 200 were obtained at the design flow-rate of 1.5 ft$^3$/min with exit-gas dust loadings of 0.5 mg/m$^3$.

* "Ni-o-nel", International Nickel Company.
All of the equipment was set up and run first as a mock-up. The units were placed in an area which corresponded with the cell floor area. Cold runs were made and all manipulator operations were tested from behind a dummy wall. After thorough "de-bugging" and minor modification, the equipment and much of the piping could be transferred directly from the mock-up to the cell, and transfer of the equipment took only a week. Additional hook-up and testing took about a month; thus the mock-up was very useful and saved valuable in-cell time.

In the mock-up runs with simulated Purex waste, both the spray calciner and pot calciner worked very well. Several runs were made in which off-gas particulate decontamination factors of $10^7$-$10^8$ were achieved in both spray and pot calcination. Sodium and iron were used as a basis for calculating the decontamination and in many cases they had reached the lower limit of analytical detection. Following completion of in-cell installation, several "cold" shake-down runs with synthetic waste were made to test equipment and train operators. These were followed by tracer-level runs, in which only sufficient actual waste was added to verify satisfactory operation of the off-gas system. These were then followed with full-level hot runs with Hanford Purex plant first-cycle waste. It is believed that this repre-
sents the first time that actual full-level separations plant waste have been calcined on anything approaching a pilot-plant scale.

In the full-level Purex runs decontamination factors to the off-gas of over $10^6$ were obtained. Ruthenium is the main contaminent; 20% appearing in the condensate, whereas other constituents are reduced by a factor of 1000 from the feed to the condensate. Residual ruthenium in the off-gas is sufficient in quantity to mask the counting of other fission products which implies a decontamination factor of greater than $10^8$ for them also.

REFERENCES

PILOT-PLANT STUDIES OF THE FLUIDIZED-BED WASTE CALCINATION PROCESS

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Abstract — Résumé — Аннотация — Resumen

PILOT-PLANT STUDIES OF THE FLUIDIZED-BED WASTE CALCINATION PROCESS. Studies have been conducted in 6- and 12-in diam. electrically heated fluidized beds and in a 24-in square NaK-heated bed and are being extended in the two larger units. Although exploratory studies demonstrated the feasibility of this process for stainless steel and zirconium fuel wastes, the overwhelming majority of the work has been with aluminium fuel wastes.

Feed rates from 5 to 150 1/hr per air-atomizing nozzle have been used with no perceptible tendency toward caking. capacity of all units has been limited by the rate of heat introduction through internal surfaces. Measured heat-transfer coefficients range from 40 to 110 BTU/(hr)(°F) (ft²), depending upon bed particle size and fluidized-bed density.

Particle size has been controlled by varying the atomizing air rate, the major factor governing particle attrition; quantitatively this effect is very dependent on the crystalline form of alumina produced. Various operating factors make significant differences in the rate of conversion of amorphous alumina calcine to the alpha (or, in isolated cases, gamma or iota) crystalline form. Particle attrition increases with alpha alumina content, hence, average bed particle size decreases and particle elutriation rate increases with increasing alpha content. High alpha-content beds are more dense and contain less nitrate, both desirable features. Sodium is a necessary feed ingredient for alpha alumina formation; its effect can be overcome by addition of boric acid to the feed. Addition of one of these components to the feed is recommended to obtain the desired product form.

Intra-particle porosity varies from 5 to 60% and is a direct function of bed temperature (from 250 to 550°C) and feed concentration (from 0.8 to 2.0M aluminium), but not a significant function of any other variable. Superficial fluidizing velocities from 0.5 to 2.5 ft/sec have been used; best results are obtained with velocities under 1.0 ft/sec.

Studies have been made with and without condensing the off-gas stream and with near-total recycle of non-condensible off-gas for fluidization. The latter method of operation shows promise for minimizing atmospheric contamination.

Performance data from preliminary operation of a 48-in diam. Demonstrational Waste Calcining Facility are reported.
J. A. BUCKHAM and J. A. McBRIDE

moins de nitrate, deux caractéristiques considérées comme favorables. Le sodium est un élément nécessaire pour la formation d'aluminé alpha; on peut en éliminer l'effet en ajoutant de l'acide borique à la charge. Pour obtenir un produit de la forme désirée, il est recommandé d'ajouter un de ces éléments à la charge.

La porosité intragranulaire varie de 5 à 60%; elle est en fonction directe de la température du lit (de 250 à 550°C) et de la concentration de la charge (de 0,8 à 2,0 M d'aluminium), mais elle est peu influencée par les autres variables. On a utilisé des vitesses de fluidisation allant de 15 à 75 cm/s; les meilleurs résultats ont été obtenus pour des vitesses inférieures à 30 cm/s.

Les études ont été effectuées avec et sans condensation des gaz d'échappement et avec recyclage pour ainsi dire total des gaz d'échappement non condensables. Cette dernière méthode est intéressante du fait qu'elle permet de réduire au minimum la contamination atmosphérique.

Les auteurs présentent les résultats obtenus au cours des essais d'une installation de démonstration de 1,20 m de diamètre.

ИЗУЧЕНИЕ ПРОЦЕССА КАЛЬЦИНИРОВАНИЯ ОТХОДОВ В ДВИЖУЩЕМСЯ СЛОЕ НА ОПЫТНОЙ УСТАНОВКЕ. Исследования были проведены в кальцинаторах с движущимся слоем диаметром 14,2 и 28,4 см с электрическим подогревом, а также в кальцинаторах с площадью слоя 56,8 см с NaK-нагревателем. В настоящее время эти исследования проводятся также и на двух более крупных установках. Хотя предварительные исследования показали возможность применения этого процесса для обработки отходов от переработки топливовмещающих элементов в оболочках из нержавеющей стали и циркония, подавляющее большинство опытов было произведено на отходах от переработки топлива в алюминевой оболочке.

Были использованы скорости подачи материала от 5 до 150 л/час на каждое распылительное сопло, причем не наблюдалось заметной тенденции к оседанию. Емкость всех установок ограничивалась скоростью проникновения тепла через внутренние поверхности. Измеренные коэффициенты тепло- проводности колеблются в интервале от 40 до 110 британских тепловых единиц в час на 1°Р и на 1 κв.фут, в зависимости от размера и плотности частиц движущегося слоя.

Размер частиц регулировался изменением расхода воздуха для распыления, что является главным фактором, определяющим измельчение частиц; количество этого эффект зависит от подвижности слоя, температура которого образующейся окиси алюминия. Различные технологические факторы влияют в значительной степени на скорость превращения кальцинируемой аморфной окиси алюминия в кристаллическую форму альфа (или в гамма- или йота-форму). Измельчение частиц возрастает по мере увеличения содержания окиси алюминия в альфа-форме; поэтому средний размер частиц слоя уменьшается, а скорость оседания частиц увеличивается по мере увеличения содержания альфа-формы. Слой, содержащий больше окиси алюминия в альфа-форме, обладает большей плотностью и содержит меньше нитратов. Оба эти качества являются положительными. Для образования альфа-формы в качестве составной части загрузочного материала необходимо вводить натрий; однако влияние натрия может быть скомпенсовано добавлением в загрузочный материал борной кислоты. Для получения продукта в желательном виде рекомендуется добавлять одну из этих составных частей в загрузочный материал.

Пористость частиц изменяется от 5 до 60% и зависит непосредственно от температуры движущегося слоя (изменяющейся от 250° до 550°C) и от концентрации загрузочного массы (от 0,8 до 2,0 М алюминия) и лишь в малой степени зависит от каких-либо других переменных. Были использованы скорости движения слоя от 0,15 до 0,76 м/сек; наилучшие результаты получаются при скоростях менее 0,3 м/сек.

Исследования были проведены как с конденсацией выходящих газов, так и без конденсации и с почти полным возвращением в цикл не поддающихся конденсации выходящих газов для придания массе подвижности. Этот последний метод представляется перспективным для уменьшения загрязнения атмосферы до минимума.

Сообщаются результаты предварительных работ на показательной установке по кальцинированию отходов в емкости диаметром 1,2 м.

ESTUDIOS EN PLANTA PILOTO DEL PROCESO DE CALCINACIÓN DE DESECHOS EN LECHO FLUIDIFICADO.
Les autores han realizado estudios en lechos fluidificados de 6 y 12 pulg de diámetro, calentados eléctricamente, y en un lecho de 24 pulg, calentado por NaK; también los están efectuando en dos instalaciones más grandes. Aunque los primeros estudios demostraron la posibilidad de aplicar este proceso a los desechos de elementos combustibles revestidos de acero inoxidable y de circonio, la mayor parte del trabajo se ha llevado a cabo con desechos de elementos combustibles revestidos de aluminio.
FLUIDIZED-BED WASTE CALCINATION PROCESS

INTRODUCTION

The fluidized-bed calcination process is a totally continuous process for the conversion of high-level aqueous radioactive waste solutions, resulting from fuel reprocessing, into compact granular solids. The continuous nature of the process permits its application to a wide range of processing capacities without need for installation of multiple units. The production of a free-flowing, readily transported, granular product is an important and unique advantage of this process; the granular product may conveniently and economically be transported pneumatically to almost any type of storage container, and may be subsequently retrieved very readily if some additional processing or treatment is desired, or if permanent storage in less elaborate facilities is desired following interim storage in small, cooled vaults. Primarily, because of these two important process characteristics, the fluidized-bed calcination process was the initial process selected for early development in the United States for conversion to solids of high-level waste solutions.

The fluidized-bed calcination process has been found adaptable to a wide variety of aqueous waste solutions, including Purex process wastes, stainless-steel nitrate wastes, and zirconium fluoride wastes. By and large, however, nearly all of the work to date on this process has been directed toward its application to aluminium nitrate wastes resulting from the reprocessing of aluminium-uranium alloy fuels such as those used in many test reactors in the United States. The process is described in this paper primarily as applies to aluminium-nitrate waste solutions.

The fluidized-bed calcination process was conceived at the Argonne National Laboratory [1], and has been under development by the Atomic
Energy Division of Phillips Petroleum Company since 1955 [2] as a means of converting to solids the high-level aluminium nitrate wastes stored at the Idaho Chemical Processing Plant (ICPP). Fairly extensive studies directed at applying the process to Purex waste solutions have been conducted at the Argonne National Laboratory [3] and at the Hanford Atomic Power Operation [4], while preliminary studies directed at its application to stainless-steel nitrate wastes have been conducted at the Idaho Chemical Processing Plant [5]. Laboratory and brief pilot-plant tests have been conducted at ICPP [5, 20], which indicate a potential application of the process to zirconium-fluoride waste solutions upon completion of additional development work to circumvent the potentially severe condensate corrosion problem.

After promising results were obtained with aluminium nitrate waste solutions by both Argonne [3] and Phillips [5] in 6-in-diam. pilot-plant calciners, design and construction of a Demonstrational Waste Calcining Facility (DWCF) at the ICPP was started [6]. Cold testing of the DWCF was initiated in February, 1961, and is still under way. As would be expected for the first large-scale unit of its kind, a number of mechanical problems were detected and corrected during the early stages of cold testing.

To provide design and operating data in support of the DWCF, a two-feet-square pilot-plant calciner was constructed and has been operated intermittently over a 3-yr period [7, 8]. Special studies have been conducted under subcontract at the Battelle Memorial Institute on a modified feed-introduction system [9], and at the Stanford Research Institute on alumina phase transformation [13]. Advanced process studies are being conducted in a 12-in-diam. pilot-plant calciner which was constructed in 1961 [10].

Process development is essentially complete for aluminium nitrate aqueous wastes, except for demonstration of the process in the DWCF with full-level radioactive waste which is anticipated within a year. Process improvements are being studied in both pilot-plant calciner units on means of improving current methods of operation and on additional steps which may be employed to produce an impervious product. Detailed process studies are being extended on a pilot-plant scale to other high-level waste solutions such as stainless-steel nitrate-waste solutions and zirconium-fluoride waste solutions.

THE BASIC FLUIDIZED-BED CALCINATION PROCESS

Briefly, the fluidized-bed calcination process consists of spraying feed solution into a well-fluidized bed of granular solids into which sufficient heat for the calcination reactions is also introduced. Figure 1 shows a schematic diagram of a fluidized-bed calciner. There are two effluent streams from the calciner, the granular solid product and the effluent gas containing entrained fine solids. The product has been removed from the bed both by means of overflow from a point above the normal bed level, and by means of pneumatic transport from a position near the bottom of the bed. The latter method employs the hydrostatic head of the fluidized bed for transport of solids to storage. The many possible methods of removing the fine solids from the effluent gas, for returning the fines to the bed, and for ultimate treatment of the off-gas are discussed in subsequent sections.
Feed introduction has generally been accomplished by means of pneumatic atomizing nozzles beneath the bed level [11]. Several sizes of commercial nozzles of conventional design have been used to give a fine horizontal spray with a solid conical angle of approximately 20 deg. Brief tests have also been made with single-fluid pressure nozzles and with a coarse spray directed onto the top of the bed. All of these methods of feed introduction appear workable. The optimum of feed introduction and specific conditions of operation employed are necessarily dependent upon the particle growth and attrition characteristics of the bed as discussed in a subsequent section. Feed rates ranging from 5 to 1501/hr per nozzle have been employed without any tendency to cake because of the density of feed introduction. Higher feed-rates per nozzle could apparently be employed, since heat transfer into the bed appears to be the limiting capacity factor.

Heat transfer to the calciner bed by means of heated internal surfaces is the preferred method of heat introduction because it permits the highest capacity for a given size of bed. Alternate methods employed on occasion include heat input through the wall and the use of high-temperature fluidizing gas. Measured heat-transfer coefficients between inserted heating surfaces and the bed range from 40-100 BTU/(hr)(°F)(ft²) in the two-feet-square pilot-plant calciner [7]. This heat-transfer coefficient has been found to be a function of the cube of the mass median particle diameter divided by the square of the fluidized-bed density in accordance with the method of correlation advanced by MICKLEY and TRILLING [12]. Three methods of heating inserted surfaces have been employed in pilot-plant test equipment. These are the use of circulating NaK heated in an external oil-fired furnace, sheathed electric resistance heaters, and direct-fired tubes in which combustion occurs in the inserted heating coil. Heat fluxes of approximately the same magnitude can be achieved with each of these methods, but certain operating advantages and disadvantages exist with each method. Foremost
among these is the possibility of localized burnout with electric resistance heaters when even a small section of the bed is momentarily poorly fluidized. For this reason, this method of heating is not recommended for a radioactive unit. The choice between the other two methods - or between other similar methods - must be made primarily on economic grounds which would differ under various situations. Circulating NaK is employed in the DWCF and in the two-feet-square pilot-plant calciner, and these systems have proven to be highly satisfactory.

Although the rate of heat transfer from one portion to another within the fluidized beds used in these studies has not been quantitatively determined, it has been found to be so rapid that it does not limit the capacity of any existing unit. Significant temperature gradients have not been detected in fluidized beds used in these studies. Therefore, the capacity of a fluidized-bed calciner for any given feed composition is dependent upon the heat-transfer area, the bed temperature, the temperature of the heating medium, the particle size and the fluidized bed-density, the latter two being those that influence the controlling heat-transfer coefficient. The quantitative relationship between these capacity factors is shown in Fig. 2 for calcining in a well-insulated vessel a typical waste solution containing 1.72 M aluminium-nitrate. Unit heat-transfer surface area was selected as the basis for the correlation in Fig. 2, rather than calciner diameter or volume, because heat introduc-
of calciner capacity on bed temperature, as shown in Fig. 2 is an important economic factor influencing operation at relatively low bed temperatures. Heat introduction through the wall of a fluidized-bed calciner has been found satisfactory in small test units, but is not recommended for larger units because of the limited area available per unit bed volume. Similarly, pre-heating of the fluidizing medium can be employed only at a significant reduction in capacity for given sized fluidized bed operating at the usual fluidizing velocity. Fluidizing velocities four to five times those ordinarily employed would be required to obtain the same capacity for a bed heated by hot fluidizing gas as for one heated from internal surfaces.

Fluidization velocities varying from 0.5 to 2.5 ft/sec, based upon the superficial cross-sectional area inside the bed, have been employed in the pilot plant and DWCF calciners. Best results have been obtained at superficial fluidizing velocities between 0.5 and 1.0 ft/sec. Temperature uniformity and adequate mixing without caking are achieved at these velocities; the use of higher fluidization velocities leads to unnecessary increases in bed material attrition and fine solids carryover. At the fluidization velocities employed, bed temperatures have been uniform within the 5° C accuracy of measurement. Samples of the bed material taken from numerous locations in the bed after shutdown have agreed closely with each other with respect to particle-size distribution and other material properties. Also, the analyses of such samples agree closely with the immediately preceding product-sample analyses, thus indicating that the product is a representative sample of the material in the well-mixed bed.

NATURE OF ALUMINA PRODUCT

The principle reaction product, alumina, is produced primarily in two different physical forms in a fluidized-bed calciner. Both amorphous alumina and alpha-crystalline alumina have been produced, generally as mixtures of the two forms in various proportions. In isolated cases, the gamma and iota-crystalline forms have also been observed. Satisfactory operation of a fluidized-bed calciner with either the alpha or amorphous form of alumina product appears possible, although a balance of the various factors involved is required for any given installation to select the optimum form for operation. Factors favouring operation with the alpha form are its higher absolute density and the need for less atomizing air to achieve a desirable, stable particle size, the result of the higher fractureability of the alpha form. Factors favouring the amorphous form are a lower rate of solids carry-over from the bed, and its solubility in dilute acid solutions such as are used in scrub systems for off-gas clean-up.

Although the extent and rate of formation of alpha alumina is a complex function of temperature and time factors and of other variables, satisfactory promotion and inhibition of the formation of alpha alumina in the product have been found possible by addition of nominal quantities of inexpensive chemicals to the feed. As suggested by work done under subcontract at the Stanford Research Institute [13], boric acid added to the feed in concentrations as low as 0.01 M has been found an effective inhibitor of the formation of the alpha form. Alpha alumina formation has been found to require the
presence of sodium ion in the feed at concentrations in excess of about 0.01M; addition of sodium nitrate to the feed in excess of the 0.04 - 0.08M level now in the stored ICPP waste solutions promotes the formation of the alpha phase.

Bulk density is perhaps the most important factor affecting the economics of calciner product storage. The bulk density of a granular product such as is produced in the fluidized-bed calciner depends upon three factors, inter-particle voids, absolute material density, and intra-particle porosity. Inter-particle void fraction for as-poured granular alumina product has been remarkably constant at about 41%. The absolute density of pure alpha alumina is 3.96 g/cm³, while that of the amorphous form is approximately 2.60 g/cm³. The absolute density of mixtures of these two forms of alumina has been found to vary in an essentially linear manner with alpha alumina content. Thus, the bulk density of stored material is significantly affected by the alpha alumina content of the material produced. The third factor, intra-particle porosity, also can make a significant difference in the bulk density of the stored product. The intra-particle porosity of calcined alumina has been found to range from 5 to 60%, and to depend primarily on bed temperature and feed-aluminium concentration. A thorough study [8] of factors affecting the intra-particle porosity of amorphous alumina showed that only these two factors had a significant effect. Low-porosity amorphous alumina is produced by the use of an appropriate combination of low bed temperature and dilute feed aluminium concentration in accordance with the quantitative relationship shown graphically in Fig.3. Minor effects on the intra-particle porosity were exhibited by feed-sodium concentration and by alpha alumina content of the product. The use of a sodium concentration three-to-four-fold higher than usual has generally resulted in a decrease
in the intra-particle porosity to about three-fours its usual value. The presence of alpha alumina in the product, if not created by the use of a higher-than-normal feed-sodium concentration, generally results in a slight increase in intra-particle porosity. No other process or equipment variable was found to have a significant effect on the intra-particle porosity of the alumina produced in a fluidized-bed calciner.

Another factor of considerable importance with respect to the economics of solids storage is the thermal conductivity of the stored material. This property is important because the solids in storage must be maintained below some maximum temperature to prevent fission-product volatilization, and the heat released from fission-product decay must be removed by thermal conduction through the calcine. The thermal conductivity of bulk amorphous alumina having a high intra-particle porosity has been found to vary in a linear manner from 0.08 BTU/(hr)(ft)(°F) at 40°C to approximately 0.025 BTU/(hr)(ft)(°F) at 800°C. Studies of the thermal conductivity of the alpha alumina form and of low-porosity amorphous alumina have not been completed; it is expected, however, that the thermal conductivity of each of these materials will be higher than that of the porous amorphous form.

A third important product attribute is its median size and its size distribution. Particle size has been found to vary over a fairly wide range and to be influenced by a complex particle growth and break-up mechanism, as discussed in the following section.

PARTICLE GROWTH AND ATTRITION IN FLUIDIZED-BED CALCINERS

While it is possible to produce product particles in a wide variety of sizes, the desirable range of the mass-median particle diameter has been established at approximately 0.25 to 0.6 mm. If the mass-median particle diameter of the product, and hence of the bed, is below this size range, excessive solids carry-over from the bed is incurred. If the mass-median particle diameter is significantly above this range, the capacity of the fluidized-bed calciner is seriously curtailed since it depends upon the rate of heat transfer from a heated surface to the bed. Therefore, studies have generally been directed towards the determination of factors required to obtain a product particle size within this range.

Particle growth has been found to occur on bed particles at a relatively uniform linear rate, at least for particles of any given size. The photomicrograph in Fig. 4A shows the growth of alumina calcine around sand particles used as a starting bed in some pilot-plant studies. Note that the depth of alumina around each sand kernel is rather uniform, and also that the particles tend to assume a spherical shape, regardless of the shape of the seed particle. In Fig. 4B the uniformity of growth of particles is shown in a different manner. The particles shown in that Figure contain growth rings created by periodic addition to the solution fed to the calciner of a material having a coloured oxide visible in the sectioned particles. Detailed studies are being conducted of particle growth by both of the illustrated techniques and also by the use of radioactive tracers. To date, no quantitative correlations have been evolved, although indications are that the linear growth-rate of particles increases as the particle size increases, a finding contra-
ry to the usual simplifying assumption of independence of growth rate and particle size.

Since the product removed from a bed has been found to be a representative sample of the material in the bed (with the exception of a very small percentage of fine bed material which does not always appear in the product), the removal from the bed of product particles of any given size must follow a simple exponential decay law. Thus, under steady-state conditions, as
many new seed particles are required as are removed as product. This means
that, for a given production rate, the greater the number of effective seeds
introduced into the fluidized bed, the greater will be the number of particles
in the product, and hence the smaller will be the average product-particle
size.

Seed-particle introduction into the bed has been accomplished in most
of the studies to date by creation of small particles by attrition caused by
the impingement of the nozzle atomizing air on the bed. As the nozzle air-
rate is increased, the attrition rate of bed particles is increased, and, as
a consequence, the mass-median particle diameter of the bed decreases.
Alternative means of seed formation have been tested only briefly during
pilot-plant studies, but they appear to be effective. One of these alternate
means is the use of a separate air blast as a jet grinder; this has the ad-

tage of permitting separate control over atomization of the liquid feed
and over seed formation. Another method of providing the necessary seeds
is direct introduction into the bed of inert material of suitable size; this
method also permits the separation of the feed introduction and seed creation
operations.

Attrition of fluidized-bed particles occurs continuously during fluidized-
bed calcination. Such attrition is desirable when it results in the formation
of needed seed-sized material. However, the attrition is undesirable when
it results in the formation of material too small to function as seeds, and
which is rapidly elutriated from the bed. The quantitative attrition rate of
bed material is significantly influenced by the physical nature of the material
as well as by the rate of introduction of nozzle atomizing air and of fluidizing
air. A standard empirical attrition-resistance index test has been developed,
based on a method advanced by FORSYTHE and HERTWIG [14]. The test
measured the resistance to breakup of calcine by a sonic velocity air stream
impinging through a 1/64-in orifice on a 50-g sample of 28-35 Tyler-mesh
solids for a period of an hour; results are reported as the percentage of
the original material remaining unchanged in size, and hence represent the
resistance of the material to attrition. Although significant data scatter is
evident when comparing the results of this test with the alpha alumina content
of the product, the attrition-resistance index has been found to be consider-
ably lower for high-alpha-content alumina than for low-alpha-content alu-
mina. Typical values of this index for amorphous alumina created by the
addition of boric acid to the feed are from 92 to 98% unchanged in size; ma-
terial having an alpha alumina content under 10% has an attrition-resistance
index in the 80 to 96% range, whereas material having an alpha content greater
than 30% has an attrition-resistance index in the 5 to 75% range.

Attrition has been found to occur mostly as a breaking off of small ir-
regularly shaped particles from the outer portion of the bed particles. This
has been observed both directly and indirectly. Direct observations have
been made by examination of growth rings such as those shown in Fig. 4B.
The growth rings often show clear indentations at points where small
particles were broken out before ring formation; breaks in the rings are
believed due to attrition occurring after the formation of the ring. One ex-
ample of indirect evidence as to the nature of attrition is the fact that chemi-
cal tracers added to or removed from the feed in step-like fashion appear
or disappear gradually rather than immediately in the solids being carried from the bed. This shows that the elutriated solids are not created solely by spray drying or by mere rubbing off of the outside layer, but that they do include significant portions of older material. This conclusion is supported also by the observations that the average alpha alumina content of the fines carried over from the bed is generally less than that of the bed, and that the alpha alumina content of bed particles is generally greater at the centre than at the outside.

Attrition rates of calcine have been measured indirectly by determining the rate of elutriation of fine solids from pilot-plant calciners under varying conditions of operations. All such tests clearly indicate that most of the attrition is related to the introduction of the feed spray. When neither the aqueous feed solution nor nozzle air are being introduced to a bed, the resulting attrition of old material by the fluidizing action is observed to be generally less than 10 to 20% of that incurred during normal operation. When nozzle atomizing air alone is introduced, the bed attrition rate generally ranges from 30 to 80% of normal values.

An indeterminate factor is the break-up of particles which can occur during normal operation with both the aqueous feed and atomizing air, as a result of weakening of the particles by the thermal shock resulting from contact with the cold spray. Such break-up might occur away from the feed zone; quantitative separation of this effect from that of direct break-up of particles by means of the high-energy atomizing air blast has not been accomplished. Reduction in nozzle air-rate under any given condition does result, as expected, in a reduced attrition rate. The effect of variation in liquid-feed introduction rate per nozzle is not always consistent.

Solids carry-over from fluidized beds has been found to be considerably reduced by the introduction of louvered baffles in the top of the calciner vessels. Table I shows typical solids elutriation rates for amorphous and high alpha alumina beds for both the two-foot-square pilot-plant calciner and for the DWCF when louvered baffles are used and when dry fines are not returned to the bed. Minimization of the solids carry-over rate and development of satisfactory methods for removing the solids from the effluent gas and returning them to the bed has required a major development effort.

**TABLE I**

**SOLIDS ELUTRIATION RATES FROM FLUIDIZED-BED CALCINERS**

<table>
<thead>
<tr>
<th>Calciner</th>
<th>Solids elutriation rate* (Percent of product rate)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Amorphous alumina bed (Under 10% alpha)</td>
</tr>
<tr>
<td>DWCF Two-foot-square</td>
<td>30</td>
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<tr>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

* Test Conditions: 1. Louvered baffles installed below off-gas outlet. 2. Dry fines not returned to bed. 3. Operating conditions comparable between units and at usual values.
FINES REMOVAL AND DISPOSAL

Removal of most of the solids from the calciner effluent gas has generally been performed as a two-step process wherein solids are removed in a dry state in a primary cyclone and as a solution or slurry in a downstream venturi scrubber and its accompanying cyclone. Figure 5 shows in solid lines the normal fines removal and disposal system employed in the DWCF. Alternate systems for fines removal and disposal are shown in the same Figure in dotted lines.

Primary cyclones employed in studies to date have been designed to remove all particles larger than 10 to 40 μ from the calciner effluent gas. This has been accomplished by using gas-inlet velocities resulting in pressure drops in the range of 1 to 10 in of water. Measured collection efficiencies of these cyclones have varied from 50 to 98%, depending on gas velocities employed and on the size and density of the entering solids.

Disposal of the fines collected in the primary cyclone is one of the most vital and difficult steps in the fluidized-bed calcination process. These fines may either be returned to the bed or sent to solids storage. Return to the bed results in more desirable product properties because these light fines cannot then lower the bulk density of stored solids nor create a fines-handling problem if the product is later removed for additional processing or for storage in a different container. However, as long as the rate of production of dry fines is considerably below the product rate, consideration can be given to directing these fines to the solids storage bins. Return of dry fines to the bed has been attempted with gravity flow dip-legs, with air jet-pumps, and with mechanical contrivances such as screw conveyors. The
use of an air jet-pump on the bottom of a vertical leg leading from the primary cyclone to the upper part of the bed is a reliable and simple method which also improves the collection efficiency of the primary cyclone because of the gas downflow created. It is desirable that fines returned to the calciner bed be incorporated into product-sized particles either as seeds for new particle formation or by being incorporated in the crust of particles through contact with wet particles or spray droplets. When the dry fines are merely returned to a single position in the bed, their probability of forming in product particles on a given pass is relatively small, and they must therefore make many circuits through the primary cyclone loop before they are so incorporated. A combined dry-fines return and feed-introduction system is being studied in which the feed is sprayed from the bottom of the primary cyclone dip-leg, and a single air stream is used for both atomizing and jet-pump motivation. This system shows considerable promise for greatly increasing the probability of incorporating dry fines into product-sized particles.

If a sufficiently high capture rate for returned dry fines cannot be established, the use of a secondary cyclone for collection of the finest particles carried from the bed might be employed. In that case, the primary cyclone would return seed-sized particles to the bed and the smaller particles collected in the secondary cyclone would be sent to product storage.

Most of the particles escaping the cyclone are removed from the effluent gas in a venturi scrubber in which the gas is contacted by a spray of scrubber solution. Solid particles are occluded in the scrubber by the larger spray particles and are removed from the gas stream by the scrubber cyclone. The venturi scrubber is generally operated at a higher pressure drop than that incurred across the primary cyclone. The collection efficiency increases as this pressure drop increases, but under almost all conditions of operation, particles escaping the venturi scrubber are submicron in size [15]. A spray quench tower is employed in the DWCF ahead of the venturi scrubber to provide precooling; while such a unit may be needed for very high fluidizing velocities, it is probably not necessary under usual operating conditions.

The scrubber solution consists of an acidic solution recycled from previous contacts and containing aluminium oxide as a slurry, aluminium nitrate in solution, or some of each. The alpha alumina material in the solids collected does not dissolve in the dilute acid scrub solution, whereas the amorphous alumina does. The rate of recycle of scrubber solution to the feed can be varied. As this recycle rate is increased, the capacity of the calciner for fresh feed solution is correspondingly decreased. However, since this also decreases the concentration of aluminium nitrate in the feed entering the calciner, and hence decreases the intra-particle porosity of the product, the storage costs are simultaneously reduced. The aluminium in the scrubber solution, whether in the form of an alumina slurry or an aluminium nitrate solution, has a high probability of being incorporated in new crust material when sprayed into the calciner along with fresh feed. Pumps of special design are required to resist erosion when handling the recycled slurry. Metering this slurry also requires the use of special flow-rate measuring equipment in the feed system; electromagnetic flow meters have been found to be highly satisfactory in this respect.
After passing through a primary cyclone and a venturi scrubber and its associated cyclone, the effluent gas is freed from the bulk of the solid material it contained when it left the calciner. Solids removed up to this point have been present in sufficient quantities to require facilities to return them to the calciner. However, the quantity of solids remaining in the off-gas downstream from the venturi scrubber cyclone is very small, and the problem from this point on is one of clean-up of the off-gas stream for disposal rather than of collecting the solids for recycle.

OFF-GAS CLEAN-UP AND RELEASE

The off-gas from which most of the entrained solids have been removed must be further decontaminated before release. Depending on weather conditions, reduction in solids loading of the gas released from the DWCF to \(2\times10^{-5}\) grains/ft\(^8\) is required to meet United States requirements for strontium-90 release [16]. Four different methods have been evolved for accomplishing this decontamination; these methods differ from each other in whether or not the condensible components of the off-gas are condensed, and in the nature of the gas used for fluidization in the calciner. These four methods are:

1. Using air for fluidization, the entire stream may be released as a gas if it is maintained above its dew point. This method is employed in the DWCF, and is shown schematically in Part A of Fig. 6.

2. With air fluidization, the condensible components of the gas stream can be condensed and the remaining components can be released as a gas. A two-step system is required for decontamination of the condensate and for rectification into water and concentrated acid for disposal or possible reuse. This method is illustrated in Part B of Fig. 6.

3. Using superheated steam for fluidization, the same off-gas treatment steps as in the second case could be employed. In this case, nearly all of the gas would be condensed and the gas released to the atmosphere would consist of the non-condensible gases used for pneumatic instrumentation and for solids transport and the small quantity of non-condensibles generated by the reaction. This method is also illustrated in Part B of Fig. 6.

4. To achieve a minimum release of both gases and liquids to the surroundings, fluidization can be accomplished by recycling the non-condensible off-gases as is shown in Part C of Fig. 6. This method is similar to the two previous methods except that minimum gas-and water-stream rates are achieved at the expense of employing a blower to recycle the nearly decontaminated gas. The same blower or a second blower in series is used to pressurize the gas for use in atomization, in the jet-pump for return of fines, and in the pneumatic transport of product.

Estimated rates of release of gas and liquids for each of these methods are shown in Table II for a fluidized-bed calciner operating at the design throughput of the DWCF, 60 gal/hr. The solids transport gas-rate shown for the first case is approximately that employed in the DWCF; transport gas-rates shown for the other cases are based on widely demonstrated operations [22] for dilute-phase pneumatic transport. Considerably less transport gas could be used if it is desired to employ dense-phase gas transport [22].
Table II clearly shows the wide variation possible in gas and liquid release rates from fluidized-bed waste calcination. Selection of the optimum method of operation would be dependent upon whether or not the slightly contaminated nitric acid and water streams could be reused in a processing plant. Other factors involved in the choice of operating method are atmospheric and geological conditions in the area and economic considerations.

Significant differences between these four methods of off-gas decontamination exist in the behaviour of ruthenium, a fission product whose tetroxide has a normal boiling point of about 135°C and hence can be vaporized during the calcination process. Ruthenium tetroxide can be converted to ruthenium dioxide, a compound not volatile at temperatures employed in the fluidized-bed calcination process. Since it is desired that all fission products end up in the granular solid product, conversion of all ruthenium to the dioxide, and retention in or return of this compound to the bed is necessary. When calcining at a 500°C bed temperature, little or no ruthenium is found in the effluent gas from the calciner [3]. However, when employing a calciner-bed temperature of 400°C, about 95% of the ruthenium present is volatilized initially from the calciner [3]. Much of the ruthenium is converted to the dioxide in the initial fines-removal operations and is returned to the
### Table II

GAS AND LIQUID EFFLUENT PRODUCTION FOR VARIOUS METHODS OF OFF-GAS TREATMENT

Bases: 60 gal/hr fresh feed rate  
20 gal/hr recycled scrubber solution flow-rate  
6.4 M nitrate in combined feed  
0.75 ft/sec superficial fluidizing velocity  
Nozzle gas-to-liquid volume ratio of 300

<table>
<thead>
<tr>
<th>No.</th>
<th>Fluidization and atomization gas</th>
<th>Solids transport gas</th>
<th>Off-gas condenser</th>
<th>Release rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>gas ft³/min (STP)</td>
<td>Water (gal/hr)</td>
</tr>
<tr>
<td>1.</td>
<td>Air</td>
<td>72 ft³/min (STP)</td>
<td>No</td>
<td>475</td>
</tr>
<tr>
<td>2.</td>
<td>Air</td>
<td>10 ft³/min (STP)</td>
<td>Yes</td>
<td>240</td>
</tr>
<tr>
<td>3.</td>
<td>Steam</td>
<td>10 ft³/min (STP)</td>
<td>Yes</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>Recycled off-gas</td>
<td>Recycled off-gas</td>
<td>Yes</td>
<td>2</td>
</tr>
</tbody>
</table>

FLUIDIZED-BED WASTE CALCINATION PROCESS
bed as the dioxide either along with the dry fines or with the scrubber solution recycle. An extended pilot-plant test [5] indicated that only one-third of the ruthenium present in the feed would appear in the off-gas downstream from the venturi scrubber at a bed temperature of 400°C. This ruthenium can be adsorbed on silica gel in essentially a quantitative manner [17], or it can be essentially quantitatively removed from the gas stream by condensation [3]. If the ruthenium is adsorbed on silica gel, the gas must be maintained above its dew point throughout the process; the adsorbers are regenerated at periodic intervals and the regenerating solution is returned to the feed for recycle to the calciner. If the ruthenium is removed from the gas by condensation, it can be concentrated in the bottoms product of an evaporator and returned to the feed. In operating such an evaporator, it is necessary to maintain the acidity of the contents of the evaporator below about six molar in order to prevent significant revolatilization of the ruthenium [19]. This can probably be best accomplished by recycle of water to the evaporator for acid stripping.

Removal of ruthenium by either method removes incidentally a large fraction of the remaining particulate material; the remaining off-gas is then filtered before release to the atmosphere. High-efficiency glass-asbestos filters are employed with all of the methods shown in Fig. 6 to effect this final removal of particulate matter.

Solids loading in the gas leading to the final filters during cold operations of the DWCF has been sufficiently low that no significant increase in pressure drop across these filters has been observed after successive periods of operation totalling in excess of 60 d. It, therefore, appears that this train of effluent clean-up devices will function satisfactorily. An electrostatic precipitator could be employed as an additional off-gas cleaning step before the absolute filters; the capability of a wetted-wall electrostatic precipitator to remove solids from such a gas stream has been studied in pilot-plant equipment [19].

Determination of the residual activity in the gas released from the DWCF is one of the major objectives of radioactive operation of that unit. Preliminary information will be obtained at an early date through employment of a sodium-24 spike in the feed solution. Tracer activity will be determined on appropriate samples taken at all key points in the off-gas clean-up system. These tests should give reliable information on the effectiveness of removal of particulate material from the off-gas.

CONCLUSIONS AND FUTURE STUDIES

The fluidized-bed calcination process has been developed to the point where satisfactory operation is obtained for aluminium nitrate wastes. The following specific conclusions can be drawn from these studies:

(1) Fluidized-bed calciners employing this process can be constructed in almost any desired size in excess of 6 in diam. Calciner capacity ranges from 3 to 12 l/hr-ft² of internal heating surface, depending upon the bed temperature, heating-surface temperature, and feed concentration employed.

(2) The crystalline form of alumina produced can be controlled by addition of moderate amounts of inexpensive chemicals to the feed. The process
can be operated with either a predominantly amorphous or a predominantly alpha bed by addition of boric acid or sodium nitrate, respectively, to the feed. Operation with an alpha alumina bed results in a product with a higher material density and lower nitrate content. Operation with an amorphous bed minimizes solids carry-over problems.

(3) A variety of methods for introduction of feed and control of product size are available. Each of these operations has a considerable influence on the other, and they must be carefully matched.

(4) Dry fines removed from the gas after elutriation from the bed can either be combined with the product or returned to the bed. The latter results in the most desirable stored solids properties.

(5) Four different methods of off-gas clean-up and effluent disposal are available. The choice of which method to employ would depend upon the possibility of reuse of liquid effluents, upon atmospheric and geological conditions in the area, and upon economic considerations.

Pilot-plant and laboratory studies are underway to extend the fluidized-bed calcination process to other waste solutions. The first two additional wastes to be studied in detail at the ICPP are stainless-steel nitrate wastes and zirconium fluoride wastes. Initial studies with the latter solutions will employ calcium ion addition to the feed to tie up the fluoride as non-volatile calcium fluoride. By this means, the serious potential condensate corrosion problem may be avoided. Additional studies are planned to adapt the fluidized-bed calcination process to a variety of blended wastes, and, eventually to new types of high-level waste solutions.

It is recognized that the direct application of the fluidized-bed calcination process does not result in a product having ultimate safe storage properties because water-soluble fission products can be leached out. Therefore, development of a post-calcination operation to convert the product to an impervious form is being considered. Employment of suitable feed additives together with high-temperature post-calcination treatment can produce either a granular material with a glazed coating of low permeability or, alternatively, a non-porous glass-like mass.

REFERENCES

DISCUSSION

D. S. WEBSTER: Is there an obvious explanation for the fact that much more ruthenium volatilized at 300°C than at 500°C?

J. A. McBRI'DE: There are two competing processes: RuO₄ is volatilized at 135°C, but as the temperature increases the RuO₄ breaks down to a non-volatile oxide, which is returned to the calciner feed with the scrub solution. The latter process becomes dominant at temperatures between 400°C and 500°C.

N. BREZHNEVA: During the drying process, do you obtain a medium with equal-sized particles? Secondly, if particles are of different sizes, what cyclone systems are used for trapping them?

J. A. McBRI'DE: The answer to your first question is no. In a typical calcine product of, say, 0.5 mm Mass Median Particle Diameter (MMPD), particle sizes range from submicron to ~1.0 mm. A typical distribution curve might be as follows:
As regards the system used, conventional cyclones, with tangential gas inlet and internal baffle, were used in pilot-plant work. The cyclone used in the Demonstrational Waste Calcining Facility consisted of multiple units of generally similar construction. At the gas velocities and solid loadings existing in the process, the cut-off (separation point) of these cyclones is generally in the range of 10-40μ.

J. C. MARILLIER: What materials are used for the reactor and the blower? Have you solved the problems of corrosion, erosion or blockage of the blowers or the bed support plate?

J. A. McBRIDE: Stainless steel, Type 304, is used throughout the primary process system. No corrosion problems have been encountered. No particular maintenance problems have been encountered with the bed support plate or with the blower, used to provide the motive power for off-gas, which receive only clean gas. Some minor mechanical problems not associated specifically with the process have been encountered with this blower. Erosion has been found with the secondary cyclone, following the venturi scrubber, in pilot-plant units, but no such observations have been made in over 100-d operation of the DWCF (diam. 4 ft).

S. LINDHE: Are any hazards associated with the NaK heating medium? Would it not be possible to improve heat-transfer characteristics by burning oil or gas directly in the bed?

J. A. McBRIDE: A detailed analysis of the hazards possible with NaK indicates that no conceivable set of circumstances can result in a catastrophic situation. Fire is a certain result of leaks in the NaK system outside the calciner vessel. Inside the calciner vessel, the heat-exchange tubes are jacketed with a helium annulus incorporated in a pressure alarm system, which warns of leaks in the calciner NaK system.

The use of preheated air to convey process heat to the calciner results in a marked decrease in the unit's capacity, due to the limitation on the heat which can be introduced, resulting from the upper limit on fluidizing gas velocity. High-temperature gas could, however, be used in place of NaK to supply heat to the internal heat-transfer surfaces. This would no doubt permit considerably higher surfaces temperatures than can be attained with NaK.

W. H. HARDWICK: Is the ruthenium problem completely solved? When you calcine at lower temperatures there is a fairly high percentage of nitrate in the product. Perhaps, when you go on to make glass, this ruthenium will come off as RuO₄ and you will have to decontaminate the off-gas.

Secondly, since the caesium and strontium in the products from the fluid bed and spray calciners presumably are leachable, could this not form a simpler process than those described earlier for separating these two potentially valuable fission products?

J. A. McBRIDE: As regards your first question this contingency has not been investigated. It may well be that a problem such as described will arise in subsequent thermal treatment of high-nitrate calcine. As regards your second question, it is true that caesium and strontium are both very readily leached, caesium being obtained very nearly quantitatively with little difficulty. The strontium could presumably also be leached nearly quantitatively, but preliminary work on this indicates that it will require a greater
number of contacting stages. We agree this would in fact offer a simpler, and quite likely more economical, way of accomplishing caesium and strontium removal from the waste than the processes described earlier.
POT-CALCINATION PROCESS FOR CONVERTING HIGHLY RADIOACTIVE WASTES TO SOLIDS

OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN.

Abstract — Résumé — Аннотация — Resumen

POT-CALCINATION PROCESS FOR CONVERTING HIGHLY RADIOACTIVE WASTES TO SOLIDS. The pot-calcination process has successfully converted synthetic non-radioactive Purex, TBP-25 (aluminium, HNO₃) and Darex (stainless steel, HNO₃) wastes to solids in both bench-scale (24 x 4 in diam.) and engineering-scale (82 x 8 in diam.) pots. The process includes feed evaporation, calcination to 900°C in the pot and recycle of the calciner vapour to the evaporator in a closed loop. Vapour from the evaporator is fractionated to produce water for disposal and nitric acid for re-use. The stainless-steel pot would be sealed after being filled and would serve as both the shipping and ultimate containment vessel.

The nitrate content of the calcined solids varied between 60 and 500 ppm. Sulphate volatility during calcination of Purex waste was reduced to less than 0.8% by conversion to thermally stable sodium, magnesium, or calcium salts. Ruthenium volatility from the pot was reduced to less than 20% of the feed by the addition of phosphate or nitric oxide gas to the calciner. Steam stripping to avoid excessive acid build-up in the evaporator limited the volatility of ruthenium from the evaporator to approximately 2% of the feed. Addition of up to 1 ml/l each of monobutyl and dibutyl phosphate to the feed to simulate solvent degradation products reduced the ruthenium volatility to < 1%. The mercury in TBP wastes was completely volatilized during calcination.

Control of a 25-l hold-up continuous evaporator close-coupled to the engineering-scale pot calciner was demonstrated and a batch evaporation system was developed during 25 experimental tests. Average feed rates for both systems varied between 8 and 30 l/hr. Small-scale equipment (24 x 4 in diam. pots) for studying fission-product volatilities from actual wastes is installed in a hot cell at Oak Ridge National Laboratory. A 20-l/hr pilot plant for calcination of radioactive Purex, Darex, and TBP-25 wastes in 82 x 6-12-in-diam. pots is being designed for installation at the Idaho Chemical Processing Plant. Provisions will also be included for production of glassy solids in the calciner pots. A programme on mechanical aspects is in progress to develop methods for remotely connecting the calciner pots to the pilot-plant system and sealing them for permanent storage.

CALCINATION EN POT POUR LA CONVERSION EN SOLIDES DE DÉCHETS DE HAUTE ACTIVITÉ. Par la méthode de calcination en pot (à l'échelle expérimentale: pots de 60 cm de haut et 10 cm de diamètre, et à l'échelle industrielle: 205 cm x 20 cm de diamètre), les auteurs ont transformé en solides les déchets inactifs synthétiques des procédés Purex, TBP-25 (aluminium, HNO₃) et Darex (acier inoxydable, HNO₃). La méthode comporte l'évaporation de la matière première, la calcination en pot à 900°C, et le recyclage de la vapeur du calcinateur à l'évaporateur, en circuit fermé. La vapeur provenant de l'évaporateur est dissociée en eau que l'on évacue et en acide nitrique que l'on utilise à nouveau. Une fois rempli, le pot en acier inoxydable est fermé hermétiquement: il servira ainsi de récipient pour le transport et pour le stockage définitif des déchets.

La teneur en nitrate des solides calcinés variait entre 60 et 500 ppm. On a réduit à moins de 0,8% la volatilité du sulfate pendant la calcination des déchets Purex en le convertissant en sel de sodium, de magnésium ou de calcium thermiquement stables. En ajoutant au calcinateur du phosphite ou de l'oxyde nitrique gazeux, on a réduit la volatilité du ruthénium contenu dans le pot à moins de 20% de celle de la charge. L'extraction de la vapeur, pour éviter une accumulation excessive d'acide dans l'évaporateur, a permis de réduire la volatilité du ruthénium à environ 2% de celle de la charge. En ajoutant jusqu'à 1 ml/l de phosphate de monobutyle et de phosphate de dibutyle à la charge, afin de simuler les produits de dégradation du solvant, on a réduit la volatilité du ruthénium à moins de 1%. Le mercure présent dans les déchets du procédé TBP s'est complètement volatilisé au cours de la calcination.
Les auteurs ont démontré la possibilité de contrôler le fonctionnement en continu d'un évaporateur de 25 l en communication directe avec un pot de calcination de dimension industrielle, et ils ont mis au point, au cours d'une série de 25 essais, un système d'évaporation par charge. Les quantités chargées dans l'un et l'autre système variaient entre 8 et 30 l/h. Dans une cellule de haute activité du Laboratoire national d'Oak Ridge, on a installé des appareils de dimensions réduites (pots de 60 cm x 10 cm de diamètre) pour étudier la volatilité des produits de fission contenus dans des déchets réels. On étudie les plans d'une installation pilote, d'une capacité de 20 l/h, où les déchets radioactifs des procédés Purex. Daredex et TBP 25 seraient calcinés dans des pots de 206 cm x 15 à 30 cm de diamètre. L'installation, qui serait destinée à l'Ideho Chemical Processing Plant, permettrait aussi de produire, dans les pots de calcination, des solides vitreux. On poursuit l'étude de méthodes qui permettraient de connecter par télécommande les pots de calcination à l'installation pilote et de les sceller hermétiquement en vue du stockage définitif.

Le processus de calcination dans une cellule de haute activité du Laboratoire national d'Oak Ridge, on a installé des appareils de dimensions réduites (pots de 60 cm x 10 cm de diamètre) pour étudier la volatilité des produits de fission contenus dans des déchets réels. On étudie les plans d'une installation pilote, d'une capacité de 20 l/h, où les déchets radioactifs des procédés Purex, Daredex et TBP 25 seraient calcinés dans des pots de 206 cm x 15 à 30 cm de diamètre. L'installation, qui serait destinée à l'Ideho Chemical Processing Plant, permettrait aussi de produire, dans les pots de calcination, des solides vitreux. On poursuit l'étude de méthodes qui permettraient de connecter par télécommande les pots de calcination à l'installation pilote et de les sceller hermétiquement en vue du stockage définitif.

**Procédé de calcination dans une cellule de haute activité**

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**Étude de méthodes de calcination**

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**Évaporation et calcination**

Les auteurs ont démontré la possibilité de contrôler le fonctionnement en continu d'un évaporateur de 25 l en communication directe avec un pot de calcination de dimension industrielle, et ils ont mis au point, au cours d'une série de 25 essais, un système d'évaporation par charge. Les quantités chargées dans l'un et l'autre système variaient entre 8 et 30 l/h. Dans une cellule de haute activité du Laboratoire national d'Oak Ridge, on a installé des appareils de dimensions réduites (pots de 60 cm x 10 cm de diamètre) pour étudier la volatilité des produits de fission contenus dans des déchets réels. On étudie les plans d'une installation pilote, d'une capacité de 20 l/h, où les déchets radioactifs des procédés Purex, Daredex et TBP 25 seraient calcinés dans des pots de 206 cm x 15 à 30 cm de diamètre. L'installation, qui serait destinée à l'Ideho Chemical Processing Plant, permettrait aussi de produire, dans les pots de calcination, des solides vitreux. On poursuit l'étude de méthodes qui permettraient de connecter par télécommande les pots de calcination à l'installation pilote et de les sceller hermétiquement en vue du stockage définitif.

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1 ml/1 de fosfato de monobutilo y de fosfato de dibutilo a la carga, a fin de simular los productos de degrada-
ción del disolvente, redujo a menos de 1% la volatilidad del rutenio. El mercurio presente en los desechos
de TBP se volatilizó por completo durante la calcinación.

Se demostró la posibilidad de controlar un evaporador de marcha continua de 25 l de capacidad, conec-
tado directamente al crisol de calcinación de tamaño industrial y se perfeccionó un sistema de evaporación
por cargas en una serie de 25 ensayos. Las cantidades cargadas en ambos sistemas varían entre 8 y 30 l/h.
En una celda de gran actividad, del Oak Ridge National Laboratory, se instaló un equipo en pequeña escala
(críosoles de 24 x 4 pulg de diámetro) para estudiar las volatilidades de los productos de fisión en desechos reales.
Con el propósito de instalarla en la Idaho Chemical Processing Plant, se está proyectando una planta piloto
de 20 l/h para calcinar desechos radiactivos de los procesos Purex, Darex y TBP-25 en crisoles de 82 x 6 a
12 pulg de diámetro. La instalación permitirá también obtener materiales vitreos en los crisoles de calcinación.
Se viene aplicando un programa de estudio de métodos mecánicos para conectar a distancia los crisoles de
calcinación con el circuito de la planta piloto y para cerrarlos herméticamente antes de proceder a su almacena-
miento definitivo.

1. INTRODUCTION

The production of large quantities of liquid radioactive wastes by reactor
fuel-processing plants has provided incentive for developing a safe, econom-
ic method for ultimate waste disposal. Conversion to a solid is attractive
since it decreases the volume and potential hazard of the wastes and makes
feasible the shipment to a permanent dry environment such as a salt mine.
A pot-calcination process has been developed at Oak Ridge National Labo-
ratory for evaporation and calcination of wastes in cylindrical stainless-
steel pots which, when sealed by welding, serve as the final storage con-
tainers. The process is suitable for calcination of a variety of wastes con-
taining nitrate and sulphate salts and can also be used to incorporate wastes
in glassy solids [1] of very low solubility. Objectives of the pot-calcination
programme include complete retention of salts and fission products in the
pot with the evolution of only nitric acid (for recycle) and a minimum amount
of non-condensible off-gas; solidification in the final storage container to
minimize production of contaminated dust; adequate solid thermal conductivi-
ty to prevent heating to higher than the original calcination temperatures
by fission product-heat during storage; decrease of the volatile content of
the solids so that excessive pressure or corrosion will not occur in the
sealed pot as the result of radiation or thermal decomposition during stor-
age; and economical processing costs.

Non-radioactive studies of pot calcination have been made at Oak Ridge
National Laboratory in both laboratory- and engineering-scale equipment
[2-13] . Small-scale tests were made initially with radioactive wastes to
determine fission product volatility [14] . A small-scale test unit (24 by
4-in-diam. pots) is currently being installed at ORNL [13] , and a pilot plant
(99 by 6 or 12-in-diam. pots) is being designed [9-13] for installation at
Hanford, Washington, for tests on highly radioactive wastes.

2. PROCESS DESCRIPTION

In the pot-calcination process, radioactive waste is evaporated to de-
crease its volume as much as possible without precipitation of solids and
is then fed to the calcination vessel for thermal decomposition of the dis-
solved solids to metal oxides and sulphates at temperatures up to 900°C (Fig. 1). The vapours and non-condensible off-gas from the calciner are condensed and recycled to the evaporator. The evaporator off-gas, containing all the nitric acid in the original waste, is sent to the fractionator where the nitric acid is concentrated and recycled to the fuel-processing plant while the distillate, very dilute nitric acid of low activity, is discharged to the environment or recycled to strip nitric acid in the evaporator. Off-gas from the fractionator condenser includes the non-condensibles from the calciner and air from instrument bubblers and system in-leakage. Its volume is small, about 28-100 \( \ell/\ell \) of liquid feed in the engineering-scale equipment.

The calciner off-gas stream is decontaminated primarily by condensing the acid vapours and absorbing the nitrogen oxides in the calciner condenser. The acid condensate is re-evaporated in the evaporator and passed through a de-entrainer along with the non-condensible nitrogen oxides from the calciner. This removes entrained solids and liquids from the vapour feed to the fractionator and returns them to the evaporator, where they are recycled to the pot calciner. Scrubbing of the off-gases as they pass through the fractionator provides additional decontamination before final filtration and disposal to the stack [15].

Ruthenium volatilized in the pot calciner is absorbed in the calciner condenser and returned to the evaporator, where further volatilization is prevented by maintaining a low acidity in the liquid. Condensate from the fractionator overhead is recycled to the evaporator to strip nitric acid and control the evaporator acidity.

In pilot-plant tests, after completion of calcination at 900°C, the pots will be disconnected from the system, sealed, pressure-tested, and observed for radiation or temperature variation and pressure build-up. Final storage will probably be in a dry, geologically isolated environment such as a salt mine.
The system illustrated in Fig. 1 is proposed for demonstrating pot calcination as a separate unit in a fuel-processing plant. However, the pot calciner alone could be integrated into a fuel-processing plant that had an evaporator and fractionator in the acid recovery system.

3. TYPES OF WASTE

Three major types of waste - Purex, TBP-25 and Darex - have been successfully pot calcined in non-radioactive experiments. All three types (Table I) are produced during the solvent extraction of nitrate solutions containing dissolved nuclear fuel. In acidic Purex wastes, the iron and sulphate ions are added as ferrous sulphamate, which is used as a reductant for plutonium in solvent extraction; the aluminium and sodium ions result from the decladding of the aluminium fuel. The TBP-25 waste is produced by total dissolution of aluminium-uranium alloy fuels with mercury as a catalyst. Darex wastes contain iron, chromium and nickel from the complete dissolution of stainless-steel-containing fuels in dilute aqua regia or by electrolytic dissolution in nitric acid. The chloride ion in Darex wastes is low because it has been stripped from solution with nitric acid before solvent extraction. The low acidity shown for Darex waste is based on the assumption that steam stripping has been used to decrease the nitric acid in

<table>
<thead>
<tr>
<th>Component</th>
<th>Purex (40 gal/t U)</th>
<th>TBP-25 (112 gal/kg U²³⁵)</th>
<th>Darex (35 gal/kg U²³⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.1</td>
<td>1.72</td>
<td>---</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.5</td>
<td>0.003</td>
<td>1.3</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.01</td>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.01</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.6</td>
<td>0.10</td>
<td>---</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt;</td>
<td>5.6</td>
<td>1.26</td>
<td>0.9</td>
</tr>
<tr>
<td>Hg&lt;sup&gt;++&lt;/sup&gt;</td>
<td>---</td>
<td>0.020</td>
<td>---</td>
</tr>
<tr>
<td>NH₄&lt;sup&gt;+&lt;/sup&gt;</td>
<td>---</td>
<td>&lt; 0.05</td>
<td>---</td>
</tr>
<tr>
<td>NO₃&lt;sup&gt;-&lt;/sup&gt;</td>
<td>6.1</td>
<td>6.6</td>
<td>6.4</td>
</tr>
<tr>
<td>SO₄&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>1.0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>---</td>
<td>&lt; 0.001</td>
<td>0.003</td>
</tr>
</tbody>
</table>
order to enhance the solubility of iron, nickel and chromium nitrates for concentrated liquid storage. To date, no radioactive Darex waste has been generated.

In addition to the components shown, all the wastes contain hydrated SiO₂ formed from silicon in the original fuel element. During processing this silica increases extensively in volume by acquiring water of hydration. For example, in Darex processing, a flocculent material consisting of 3% silica and 97% water is formed during dissolution and chloride stripping. The presence of hydrated SiO₂ may be a problem in pumping radioactive waste streams from present waste-storage tanks and feeding evaporated wastes to the pot calciner.

The presence of organic material such as tributyl phosphate (TBP), dibutyl phosphate (DBP), monobutyl phosphates (MBP) and other solvent degradation products may also present problems such as foaming and violent reactions with the nitrate salts. However, in non-radioactive tests where TBP, DBP and MBP were added to the simulated waste feed, no violent reactions were observed.

**Fig. 2**

Diagram of apparatus for evaporating, calcining and melting wastes and scrubbing volatile ruthenium from off-gas

4. LABORATORY-SCALE STUDIES

Bench-scale studies with synthetic wastes have been made with both batch and semicontinuous evaporation and calcination of the three waste types.
In the batch experiments waste volumes of 200, 1500, 4000 cm$^3$ were used, while in semicontinuous operation stainless-steel pots 18 to 24 in long and 2 to 4 in diam. were used. In addition to the pot calciner, the semicontinuous equipment (Fig. 2) included a de-entrainment section, downdraft condenser, packed scrubber and gas expansion bag. Provision was also made to add nitric oxide gas to the calciner in order to control ruthenium volatility. Feed was pumped continuously to the pot at a rate approximately equal to the boil-off rate, which dropped off as the pot filled with solids.

In a typical semicontinuous test, Purex waste (40 gal/t of uranium processed) was evaporated and calcined at an average rate of 3 l/hr to a solids volume of 5.7 gal/t. The product contained in the 15 by 4-in-diam. pot had a bulk density of 1.32 g/ml, a residual NO$_3$ content of 0.18 wt.% and a calculated porosity of 58%. Nitric oxide gas introduced at a rate of 0.40 M/l of waste in order to decrease ruthenium volatility reacted with the excess gas produced by the calcination, so that the net production of off-gas from the system was zero.

4.1 Nitrate volatility

The nitrate content of the batch-evaporated and -calcined cakes is shown in Fig. 3 as a function of the final calcination temperature. The lower nitrate content of the Darex waste may have been due to ease of denitrification of stainless-steel nitrates or its longer calcination time since the denitrification is dependent not only on the temperature but on the time at calcination temperature. These data indicate that nitrate concentrations can be decreased to less than 0.3% at 900°C.

4.2 Sulphate volatility

Volatilization of sulphuric acid during calcination results in a build-up in concentration in recycled process streams, excessive corrosion of equipment and an additional disposal problem. Batch studies on Purex waste without additives indicated that only about 30% of the sulphate remained in the cake after calcination. Addition of sodium, calcium and magnesium compounds to the waste in concentrations to maintain the stoichiometric ratio of Na + Ca or Mg to SO$_4$ $\geq$ 1, prevented sulphate loss beyond that caused by entrainment in the off-gas. In semi-continuous operation with Purex waste, addition of 1.2 M of NaOH and 0.2 M/l of Ca(OH)$_2$ or 0.2 M of MgO substituted for the Ca(OH)$_2$ decreased the sulphate in the off-gas to less than 0.51% of that originally present.

4.3 Ruthenium volatility

Retention of ruthenium in the pot is desirable since ruthenium in the calciner off-gas would be recycled to the evaporator and gradually increase the inventory in the system. Batch evaporation and calcination of Purex waste in a nitric oxide reducing atmosphere decreased the ruthenium in the condensate to 0.9-1.5% from the 72% obtained with an air atmosphere. In the absence of NO sweep gas, the presence of about 2 ml of TBP per litre
of waste decreased ruthenium volatilization to 4-15%, depending on the other additives in the waste. Ruthenium volatilization was significantly decreased by the addition of phosphite ion before batch evaporation and calcination; 2.0 moles of phosphite per liter of TBP-25 waste decreased the volatility to 0.1% (Fig. 4) during evaporation and calcination to 1000°C.

In semicontinuous bench-scale experiments (see Fig. 2 for flow-sheet) addition of NO gas to the calciner did not produce an equivalent decrease in ruthenium volatility. In a Purex test in which magnesium and sodium were added and an NO atmosphere was used in the pot, ruthenium in the condensate was 32% of the original amount. Contacting of the NO gas with the feed upstream of the calciner decreased the volatility to 18-20%. In semicontinuous tests in which phosphorus acid or sodium hypophosphite were added to TBP-25 wastes to form glassy solids in the calciner, ruthenium volatilities were 12 to 16%.
The problem of ruthenium volatilization during evaporation alone was investigated with a Gillespie equilibrium still. The data (Fig. 5) for pure nitric acid and simulated TBP-25 waste solutions containing 0.002 M ruthenium indicate that ruthenium volatility increases with increasing acidity in the vapour phase. Above 0.2 M HNO₃ in the vapour, the ruthenium is more volatile in the TBP system at 748 mm Hg pressure. This effect was probably
due to an increase in the solution boiling point caused by the dissolved aluminium salts. At a lower pressure (570 mm Hg) the TBP-25 solution had about the same ruthenium volatility as the nitric acid solution boiling at 748 mm Hg pressure at comparable vapour acidities.

4.4 Thermal conductivity of calcined solids

In the storage of calcined wastes in which heat is internally generated by fission products, cake thermal conductivities of at least 0.1 BTU/hr-ft-°F [16] are desirable for efficient heat dissipation to prevent attainment of temperatures higher than the original calcination temperature. The conductivities of calcined wastes measured in situ were all greater than 0.1 BTU/hr-ft-°F and the values increased almost linearly with increasing temperature (Figs. 6 and 7). This variation of thermal conductivity with temperature is typical of a powder rather than a cellular material even though the calcined wastes had the physical appearance of a cellular material.

4.5 Corrosion

Corrosion of the pot-calciner condenser, off-gas system and evaporator as well as the calciner itself must be considered for all the waste types to be processed. The permanent equipment presents a more difficult corrosion problem than the calciner pot since the former will be operated over a period of years while the latter will be subjected to corrosion over only one calcination cycle.
Figure 6

Variation of thermal conductivity with temperature for calcined TBP-25 and Darex wastes.

Figure 7

Variation of thermal conductivity with temperature for calcined Purex waste.
Type-304L stainless steel appears to be a satisfactory material of construction for the calcination pots. Stainless steel exposed in simulated waste solutions subjected to a single-batch evaporation-fixation cycle underwent a brief period of fairly aggressive corrosion during expulsion of the last amounts of acid, water and nitrate from the system. With longer high-temperature exposures, the overall corrosion rate continued to decrease. For example, average penetrations of type-304L stainless steel exposed to a single TBP evaporation-calcination cycle followed by "soaking" at 900°C for total times of 24 and 168 hr were 0.17 and 0.37 mil, respectively (Table II). In the design of calcination pots for a radioactive pilot plant, a conservative overall corrosion allowance of 0.125 in was used for type-304L stainless steel, based on a maximum pot-wall temperature of 900°C during calcination and 300°C during 100 yr storage.

**TABLE II**

<table>
<thead>
<tr>
<th>Stainless steel</th>
<th>Environment</th>
<th>Exposure time, (hr)</th>
<th>Overall corrosion rate, (mil/month)</th>
<th>Avg. total penetration (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>Air</td>
<td>24</td>
<td>1.4</td>
<td>0.05</td>
</tr>
<tr>
<td>304L</td>
<td>Purex, formaldehyde treated</td>
<td>24</td>
<td>6.7</td>
<td>0.22</td>
</tr>
<tr>
<td>304L</td>
<td>Purex, formaldehyde treated</td>
<td>24</td>
<td>7.9</td>
<td>0.26</td>
</tr>
<tr>
<td>304L</td>
<td>Purex solids after calcination to ~1000°C</td>
<td>123</td>
<td>3.6</td>
<td>0.61</td>
</tr>
<tr>
<td>304L</td>
<td>TBP-25</td>
<td>24</td>
<td>5.10</td>
<td>0.17</td>
</tr>
<tr>
<td>304L</td>
<td>TBP-25</td>
<td>168</td>
<td>1.59</td>
<td>0.37</td>
</tr>
<tr>
<td>347</td>
<td>TBP-25</td>
<td>24</td>
<td>10.5</td>
<td>0.35</td>
</tr>
<tr>
<td>347</td>
<td>TBP-25</td>
<td>168</td>
<td>1.9</td>
<td>0.45</td>
</tr>
</tbody>
</table>

* Time at maximum temperature.

Under conditions in the condenser for the overhead vapours from the pot calciner, titanium 45A was much more satisfactory than Hastelloy F or type-347 stainless steel in resistance to the condensate from Purex waste solutions. Maximum rates for titanium for 100-hr exposures in refluxing initial- and average-composition Purex condensate were 0.04 and 1.47 mil/month, respectively, with little or no local attack. Hastelloy F and type-347
5. ENGINEERING-SCALE STUDIES

Engineering-scale studies were made on the evaporation and calcination steps of the pot-calcination flow-sheet with a small continuous evaporator and a larger batch evaporator to feed an 8-in-diam, by 90-in-high stainless-steel calciner. A schematic process flow-sheet for both systems is shown in Fig. 8. The experimental equipment did not contain a fractionator.

In the continuous evaporator system, feed is added to the evaporator and is continuously evaporated and transferred by pump to the calciner. Overhead vapour from the calciner is condensed and recycled to the evaporator. Nitric acid is continuously stripped from the evaporator by added water, which in a complete process would originate from the overhead of the fractionator column. The average rate of water addition is normally about four times the rate of waste feed to the evaporator. In the batch evaporator system, a complete batch of feed is added to the evaporator at the start of a run and evaporated while condensate from the calciner is recycled continuously to the batch evaporator and stripped of nitric acid by water. The feed for the calciner is the prior evaporator batch, which has been transferred to the feed hold tank from which it is pumped to the calciner.

The two types of evaporator systems have distinct advantages and both will be tested in the pilot plant for comparison on operating-economic bases. The batch evaporator, with a simpler control system, allows more precise control of calciner feed composition and density, and, because of its long hold-up time, affords an opportunity for decomposition of any organic solvent degradation products that might be present before they are fed to the calciner. It also provides a feed hold-up tank between the evaporator and the calciner which could, if desired, be used as a gravity feed tank or a feed tank for the addition of glass-making additives before calcination. The continuous evaporator combines the advantages of small size and low hold-up and permits a somewhat more compact and efficient process, which could be coupled to several pot calciners operating in parallel.

5.1 Equipment

The continuous evaporator system includes a 25 to 301 hold-up natural-circulation evaporator equipped with a 22 ft² area heat exchanger which produces a boil-up rate of 4 to 6 1/min. A bottom draw-off from the evaporator to a pump loop flows past the calciner and returns to the evaporator. A 230-l/hr flow is maintained in the loop by a canned-rotor pump to decrease the probability of plugging; the feed to the calciner is a small side stream, ranging from 10 to 70 l/hr and average about 20 l/hr drawn off close to the pot calciner and regulated by a control valve. Water purge metered into the feed stream downstream of the control valve at approximately 1 l/hr decreased the frequency of plugging.
Waste-calcination schematic flow-sheet
The pot-calciner vapour is condensed in a 30-ft$^2$ area downdraft condenser and returned directly to the evaporator. Excess area in the condenser supercools the condensate, which promotes the absorption of 85 to 95% of the nitrogen oxides from the vapour stream and decreases the volume of gas for better decontamination. Vapour from the continuous evaporator passes through a de-entraining section consisting of 24 in of Yorkmesh packing and then to a 34-ft$^2$ area downdraft condenser. The condensible fraction of the vapour goes to a condensate receiver while the non-condensible fraction goes to the off-gas system where it is filtered and metered.

The batch-evaporator system includes a submerged coil evaporator and feed hold-up tank capable of processing a 150-gal batch of waste solution. Waste from the hold-up tank is fed to the calciner through the pump loop by either a canned-rotor pump or a submerged cantiliver-shaft centrifugal pump. Gravity feeding has also been demonstrated with a head tank. Vapour from the batch evaporator passes through an impingement de-entrainer based on the work of SCHLEG and WALSH [17] (Fig. 9). Of the
two impingement plates provided, the first removes the bulk of the liquid at velocities of up to 33 ft/sec and the second is designed to remove particulates in the 3 to 10-μ range at velocities up to 90 ft/sec. At higher velocities re-entrainment will occur.

Calcination pots used in this study were fabricated of 8-in-diam schedule 5 stainless-steel pipe (0.109-in wall thickness) with an overall length of 90 in, a heated length of 72 in, and a solids capacity of about 60 l. A 3-in flange or Grayloc coupling permitted simultaneous connection of the feed, additive and off-gas lines (Fig. 10). The pots were suspended in a 54-kW electric resistance furnace divided into six independently controlled zones, each about 13 in high. Twenty-five thermocouples in four sets were positioned inside the pot along the centre line and 1 in from the wall, outside the pot along the wall and in the furnace sections. Two other thermocouples were used for the differential liquid-level controller. This system consists of a stainless-steel sheathed copper rod extending down the centre of the calciner pot 9 to 12 in below the desired liquid level (Fig. 11). The temperature at the thermocouple in the rod is a function of the height of liquid along the rod. When the liquid level is below the lower end of the rod, the rod is heated by radiation from the 900°C pot wall. However, as the liquid level rises along the rod, heat is transferred to the liquid and the rod temperature decreases as a function of the liquid level. By maintaining a temperature...
differential of 100°C between the rod and the liquid thermocouples, it is possible to maintain a liquid level 4 in below the thermocouple point in the rod.

5.2 Operation

In a typical experiment in the continuous evaporator, Purex waste was fed to it at a maximum rate of 70 l/hr during the first part of the run. After concentration by a factor of about 1.4 in the evaporator, 50 l/hr was fed to the pot calciner and at the same time 3.0 M Ca(NO₃)₂ was fed to the calciner through a separate nozzle at a constant rate, the pot having been initially filled with Ca(NO₃)₂ solution to prevent volatilization of SO₃.

The solids were deposited radially on the vessel walls maintained at a temperature of 900°C and the heat input to the liquid decreased due to the increased thermal resistance and the feed rate decreased proportionately. The average feed rate for the entire feeding period to the evaporator was about 40 l/hr and to the calciner about 29 l/hr. Average feed rates for other types of waste have varied between 8 and 30 l/hr, depending on the waste type and the presence of organic materials which cause foaming.

The nitric acid concentration in the calciner vapour varied between 3 and 10 M, and approximately 0.8% of the sulphate, 7% of the iron and 8% of the ruthenium fed to the pot appeared in the vapour. The overhead vapour down-stream of the evaporator de-entrainer contained less than 0.1% of
the iron and sulphate and approximately 2% of the ruthenium fed to the system.

The evaporators and the pot calciner were controlled as follows (Fig. 8):

(1) **Evaporator acidity (batch and continuous)**

The evaporator acidity was indirectly controlled by maintaining the water addition rate to give the desired overhead vapour acidity as measured by a conductivity cell or the vapour temperature. Since the vapour acidity and temperature and the liquid acidity are related, control of the evaporator acidity was satisfactory.

(2) **Evaporator metal-ion concentration (batch and continuous)**

The metal-ion concentration in the evaporator was maintained by controlling the density, which in turn was controlled by the boil-up rate. This is effective only because the acidity has less effect on density and is itself independently controlled.

(3) **Evaporator liquid level (continuous evaporator)**

The evaporator feed was controlled to maintain the desired liquid level.

(4) **Evaporator pressure (batch and continuous evaporator)**

Regulation of the off-gas vacuum pump maintained the pressure at 700 mm Hg.

(5) **Calciner-pot level (batch and continuous)**

The liquid level in the pot calciner as measured by the differential thermocouple was maintained by controlling the feed from the pump loop to the calciner feed inlet. A proportional control valve positioned by a controller operating on a very long reset time (approximately 3 hr) and a very wide proportional band (approximately 200%) gave stable level control and lessened the possibility of feed settling or solidifying in the feed line because a constant flow was maintained. A 1 to 3-1/hr water purge was added continuously downstream of the control valve to prevent plugging of the feed tube.

During deposition of the solids from the feed and subsequent calcination, the temperatures at the centre of the calciner and 1 in from the wall were measured in each of six control zones along the length of the vessel. Radial deposition of the solids in the centre four zones was believed to have occurred during feeding as indicated by the approximately equal times required to reach 200°C on the centre thermocouples. The data for radial deposition of the solids along the vessel wall were correlated by [18]

\[
t = \frac{\varepsilon \rho L R^2}{4K(\Delta t)} \left[ 2 \left( \frac{r}{R} \right)^2 \ln \left( \frac{r}{R} \right) + 1 - \left( \frac{r}{R} \right)^2 \right],
\]
where $t =$ time, hr,

$\alpha =$ volume of condensate per volume of deposited solids,

$\rho =$ condensate density, lb/ft$^3$,

$\lambda =$ condensate latent heat, BTU/lb,

$R =$ vessel radius, ft,

$K =$ cake thermal conductivity, BTU/hr-ft-°F,

$\Delta t =$ temperature difference between wall and boiling liquid, °F,

$r =$ distance from axis of vessel to surface of deposited solid, ft.

However, in the calcined cakes from many tests a V-shaped core extended one third to half the length of the pot and the bottom portion of the cake was solid, indicating that radial deposition was not uniform. The solid cake resulting from a typical Purex run had an average bulk density of about 1.2 g/cm$^3$ (based on the cake-plus-core volume) and its indicated thermal conductivity during feeding was 0.4 to 0.6 BTU/hr-ft-°F. Its appearance was that of a hard-brown cellular material and its volume was approximately 12% of the liquid-feed volume (based on 40 gal/t of U).

The off-gas averaged about 1100 l/hr (STP) and included the air added to the instruments, air inleakage to the equipment (the system operated under 1 lb/in$^2$ vacuum) and non-condensible gases from the pot calciner. The latter off-gas rate was about 110 l/hr (STP) and its main constituent was oxygen from the decomposition of NO$_3$ to NO and NO$_2$. This small amount of off-gas could be easily decontaminated and discharged to the atmosphere.

5.3 Experimental results

Twenty-eight tests were made with synthetic Purex, TBP-25, and Darex wastes (Table III). Of these, seven were made with the batch evaporator. In four runs, 1 ml each of monobutyl phosphate (MBP) and dibutyl phosphate (DBP) were added to the feed to simulate solvent degradation products possibly present in some high-activity wastes. In all Purex runs but four, calcium nitrate solution (3 M) was added directly to the calciner to restrict sulphate volatilization. Feed rates averaged about 30 l/hr for Purex, 15-20 l/hr for TBP-25 and 10-15 l/hr for Darex wastes.

The presence of organic in the feed (MBP and DBP) resulted in severe foaming in the pot, lower feed rates and calcined solids of lower bulk density. The volume of water required to strip nitric acid from the evaporator solution varied from factors of 2 to almost 6 times the volume of the feed and the concentration of the major non-volatile salts in the waste was maintained within acceptable ranges. Residual nitrate in the calcined solids ranged from a few hundredths to several weight percent, the higher values representing samples taken near the top of the pot when calcination temperatures of 900°C had not been reached. Bulk densities of the solids averaged 1.3 g/cm$^3$ for Darex waste, 0.64 for TBP-25 and 1.2 for Purex. Typical calcined cakes for the three waste types are shown in Figs. 12, 13, and 14. Volume reduction factors (volume of evaporator feed/volume of cake) averaged 8/1 for Purex, 8/1 for TBP-25 and 10/1 for Darex.

Efficiencies for the batch evaporator impingement de-entrainer and the continuous evaporator Yorkmesh de-entrainer were indicated by the
### TABLE III

SUMMARY OF ENGINEERING-SCALE TESTS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed</th>
<th>Avg. System feed rate (1/hr)</th>
<th>Feed vol. (l)</th>
<th>water to feed-vol. ratio</th>
<th>Evap. Fe or Al Conc, b (g/l)</th>
<th>Sulphate in solids, (% of feed)</th>
<th>Off-Gas c to feed-vol. ratio, (ft³/l)</th>
<th>NO ind d solids (wt.%)</th>
<th>Solids e density (g/cm³)</th>
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<td>-</td>
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<td>93</td>
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<td>Avg. System feed rate, (1/hr)</td>
<td>Feed vol. (1)</td>
<td>Water-to-feed vol. ratio</td>
<td>Evap. Fe or Al Conc. b (g/l)</td>
<td>Sulphate in solids, (% of feed)</td>
<td>Off-Gas c to feed-vol. ratio, (ft^3/l)</td>
<td>NO₃ in d solids, (wt.%)</td>
<td>Solids e density, (g/cm^3)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------------------------------</td>
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<td>8.9</td>
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<td>1.4</td>
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<td>28&quot;a&quot;</td>
<td>Darex</td>
<td>10.6</td>
<td>307</td>
<td>2.0</td>
<td>112-93</td>
<td>1.4</td>
<td></td>
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</table>

a Continuous evaporator except those marked "a," which were made with the batch evaporator.
b Range of concentration during calciner feeding.
c Includes 10 to 20-ft^3/hr system leakage.
d Nitrate range from top to bottom of pot.
e Density based on full pot volume of 60 l.
f No additive for sulphate.
g Magnesium added to feed such that Na⁺ + Mg²⁺ were 10% in excess of SO₄²⁻.
h Calcium nitrate solution added directly to calciner in excess of free SO₄²⁻.
i One milliliter each of MBP and DBP added to each liter of feed before processing.
concentration of nonvolatile Fe$^{3+}$ and Al$^{3+}$ in the overhead condensate (Table IV). The data confirm that the impingment de-entrainer decreases in efficiency at superficial velocities above 90 ft/sec (boil-up rates above 400 lb/hr). Both de-entrainers limited the maximum entrainment to below 10 ppm, while the average entrainment in the evaporator condensate was less than 2 ppm.
The dependence of ruthenium volatility on the evaporator condensate acidity was confirmed in engineering scale tests on Purex waste containing stable ruthenium (Fig. 15). The ruthenium volatility from TBP-25 feed was decreased by adding monobutyl and dibutyl phosphate, simulating the presence of solvent degradation products. At the desired evaporator vapour concentration of 1.5 N HNO₃ for Purex waste, the ruthenium concentration was
Ruthenium volatility during evaporation of Purex and TBP-25 wastes

about 0.6 mg/l, which corresponds to approximately 2% of the ruthenium fed to the system. This was decreased to approximately 0.7% by the presence of organics at the concentration studied.

In processing of TBP-25 waste, the mercury volatilized as the solids reached a temperature of 300-400°C. The resulting yellow oxide of mercury deposited in and tended to plug the off-gas line to the condenser unless the line was heated to at least 300°C. A condensation trap for mercury compounds is being studied for removing the mercury as it leaves the calciner in order to prevent its recycle to the evaporator.

6. RADIOACTIVE PILOT-PLANT DESIGN

A proposal [19] for the demonstration of a pot-calcination pilot plant on radioactive wastes has been accepted and design is under way for its installation at the Hanford Laboratories Operation, Richland, Wash., in 1964. Acidic Purex wastes that have been treated with formaldehyde to reduce the nitrate concentration will probably be used for the demonstration along with acidic aluminium-bearing Redox wastes to simulate TBP-25 waste. Darex wastes could be simulated by adding dissolved stainless steel to non-sulphate-bearing Purex waste.
6.1 Process flow-sheet

A design has been prepared that will permit either batch or continuous processing of Purex, TBP-25, or Darex waste in 6-, 8-, or 12-in-diam. by 6-ft-high calcination pots. The nominal feed rate will be about 5 gal/hr. A simplified process flow-sheet showing the major equipment items and capacities based on maximum flow rates is given in Fig. 16. The rates will be maximum when feeding 12-in-diam. pots. However, solids-deposition-rate studies have shown that the average rate will be independent of the pot diameter and therefore will be the same for the three pots, and the total filling time will be proportional to the pot cross-sectional area. Average filling plus calcination times (neglecting the effect of internal heat generation) of approximately 27 hr for 8-in-diam. pots filled with Purex waste are expected. TBP-25 waste processed in a 12-in-diam. pot will require approximately 47 hr for filling and calcination. The choice of pot diameter for a particular waste will be dependent on the internal heat-generation rate and the rate of heat dissipation from the pot wall during storage [16]. For a pot full of solids with a maximum centre temperature of 900°C and a maximum wall temperature of 300°C (specified from heat dissipation and corrosion considerations), the maximum pot radius may be determined from

\[ R = (4320 \frac{K}{Q})^{1/2} \]

where \( R \) = pot radius, ft, 
\( Q \) = internal heat-generation rate, BTU/hr-ft\(^3\), 
\( K \) = solids thermal conductivity, BTU/hr-ft-\(^°\)F,

Optimum fill volumes for various diameter pots were estimated to range from 99.8% for 6-in-diam. to 92.5% for 24-in-diam. vessels [20]. However, for practical purposes, 90% fill volumes are considered acceptable.

The proposed pilot-plant flow-sheet (Fig. 16) will permit operation as a continuous evaporation system with a pump for feeding the calciner or a batch-evaporation system with gravity or pump feeding. Provision will also be made for feeding additives along with the wastes to form glassy solids in the pot.

The material of construction for the pilot-plant equipment will be type-304L stainless steel except for the evaporator, calciner condenser and fractionator which will be of titanium. The selection of titanium for these vessels was based on its resistance to chloride and Cr(VI) attack from Darex solutions and the absence of grain boundary corrosion, which occurs in stainless steel contracted with Purex solutions.

6.2 Mechanical equipment

A mechanical development programme is in progress to develop a permanent seal for the pots by remote heliarc welding or a mechanical closure and to develop remote mechanical equipment to demonstrate positioning of the pot and connecting it to its off-gas and feed lines. A gasketed connector (Fig. 17), used to seal the off-gas and feed lines during pot filling and calcination, incorporates a screwed cap which can be seal-welded for ultimate
Fig. 16

ICPP pot-calcination pilot plant. Maximum flow rates and liquid volumes based on use of a 12-in-diam. pot.
storage or transportation to a permanent site. A Grayloc connector (Fig. 18) has also been studied which would use a stainless-steel ring for both the filling operation and storage period. The welded seals have shown leak rates less than 0.2 (STP) cubic centimeters of helium gas per year under cyclic temperature conditions (25 to 300°C) at 150 lb/in² internal pressure. Under the same conditions, the Grayloc seal had a maximum leak rate of 70 cm³/yr. Welding is preferred for final sealing of pot calciners before shipment to permanent storage.

A cell mock-up of the mechanical equipment installed at the Lockheed Nuclear Products facility at Georgia Nuclear Laboratories will demonstrate the positioning of a pot plus connecting it to and disconnecting it from its off-gas and feed lines. The pot will be lowered into its furnace mounted on a dolly (Fig. 19) positioned beneath its filling cap, lifted along with the furnace by jacks mounted on the dolly, and clamped to its off-gas line by a screw clamp operated by a shaft extending through the cell wall. After the pot is filled, the clamp will be opened and the pot and furnace lowered slightly. A temporary metal plate cap will then be dropped on top of the pot by a slide mechanism. The pot and furnace will be lowered to the mobile position and moved to the sealing station, where the permanent seal will be attached; the pot will then be removed from the furnace to a storage facility for observation of temperature and pressure build-up. A vent on the pots will permit relief of any excess pressure that may build up.

6.3 Internal heat-generation considerations

The average feed times calculated for the pilot plant will be decreased significantly for wastes with high internal heat-generation rates [18]. For
example, the time required to fill a 12-in-diam. pot with Purex waste (assumed thermal diffusivity = 0.010 ft$^2$/hr) would be decreased from 78 to 55 hr as the heat-generation rate increased from 0 to 5000 BTU/hr-ft$^3$ (Fig. 20). However, if this type of operation should be attempted, the solids temperature during the filling process would exceed the wall temperature by about 200°C due to the cake thickness and internal heat-generation rate. This is undesirable from the standpoint of excessive sulphate, sodium and fission product volatilities and excessive pot wall corrosion. To correct this situation, it has been proposed that the pots be filled until the slope of the temperature gradient at the pot wall is zero, indicating that no heat is being added to or removed from the wall. If feed is continued beyond this point, it will be necessary to cool the pot wall in such a way as to cause to move through the cake a thermal wave with a maximum always of 900°C [21].
Under this condition, the thermal heat generated in that position of the cake between the pot wall and the temperature maximum must be removed by cooling the wall and the internal heat generated in the remainder of the cake will evaporate the liquid filling the internal cavity. A programme for the pot-wall temperature has been determined as a function of the radius of the internal cavity (Fig. 21).
The problem of cooling and calcining the cake upon completion of the feeding has also been studied [22] for the case where cake deposition is discontinued when the temperature maximum is at the wall and the temperature gradient at the wall is zero. A pot-wall temperature programme is required in order to ensure calcination of the entire cake in the range 900 to 980°C and then cool it to its equilibrium temperature profile. A linear
approximation to a pot-wall temperature programme which involves holding the pot wall at 900°C for 0.8 hr and then cooling the wall for 2 hr to an equilibrium temperature corresponding to a 900°C temperature at the radius of the cake cavity will accomplish the desired effect for a cake with a 4000 BTU/hr-ft³ internal heat-generation rate and thermal diffusivities of 0.0046 and 0.0092 ft²/hr.

7. CONCLUSIONS

Development of the pot-calcination process for reducing Purex, TBP-25, and Darex wastes to solids has progressed through non-radioactive laboratory and engineering-scale study and is now ready for testing on radioactive wastes. A pilot plant currently under design will establish the operability of the process and the degree of decontamination that can be obtained on actual Purex and aluminium wastes that vary from day to day in composition and suspended solids content. The demonstration will also provide data to be used for comparing the cost of pot calcination with tank storage [23, 24] and different types of calciners such as the fluidized bed [25] the radiant spray system [26], and the rotary kiln [27].

Outstanding problems that remain in non-radioactive work include the development of a suitable mercury trap for removing mercury compounds from the calciner off-gas, demonstration of the mechanical equipment and the testing of pumps under simulated operating conditions to determine their reliability for remote service.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made of the contributions of R. M. Beckers, E. J. Frederick, and L. Rice of ORNL and E. W. Miller and C. E. Vivian of Lockheed Nuclear Products to this project.

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N. BREZHNUEVA: How do you explain the influence exerted by tributyl phosphate on the volatility of ruthenium?

J. M. HOLMES: We believe that the decomposition of tributyl phosphate creates a reducing atmosphere which prevents ruthenium volatilization. This is also true for the monobutyl phosphate and dibutyl phosphate.
DESIGN OF A HOT PILOT-PLANT FACILITY FOR DEMONSTRATING THE POT-CALCINATION PROCESS

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Abstract — Résumé — Аннотация — Resumen

DESIGN OF A HOT PILOT-PLANT FACILITY FOR DEMONSTRATING THE POT-CALCINATION PROCESS.

A facility has been designed for demonstrating the pot-calcination process with full-level wastes from processing aluminum alloy fuels, from Darex or electrolytic processing of stainless-steel fuels and from Purex processes. This facility will also permit the determination of procedures required for economical production of low-porosity, relatively non-leachable materials by the addition of suitable reagents to the wastes fed to the calciner. The pot-calcination process, consisting of concentration by evaporation and thermal decomposition in situ in pots which also serve as the final disposal containers, was evolved at the Oak Ridge National Laboratory and developed there in radioactive bench-scale and non-radioactive pilot-plant scale studies.

The radioactive demonstration unit will permit identification and solution of operational and control problems connected with the calciner or its closely associated feed preparation and condensate clean-up systems; many of these problems are associated with self-heating and the volatility of fission products. This unit will permit determination of pot loading and density, leachability, melting point, volatile material content, heat release and thermal conductivity of the calcine. Also to be determined are transient calcine temperature distributions, fission-product behavior during calcination, de-entrainment obtained in the various parts of the system, decontamination achieved on all liquid and gaseous effluent streams, need for venting of stored pots, optimum means of remotely sealing the pots, and methods required for production of a minimum volume of non-condensable off-gas.

This facility will employ nominal full-scale pots 8 and 12 inches in diameter and 8 feet long. A unique evaporator design was evolved to permit operation either with close-coupled continuous feed preparation or with bath feed preparation. Provisions were made to circumvent possible explosions due to organic material in feed solutions and other suspected hazards.

INSTALLATION PILOTE DE HAUTE ACTIVITÉ POUR LA DÉMONSTRATION DU PROCÉDÉ DE CALCI-NATION EN POT. On a mis au point une installation pour la démonstration du procédé de calcination en pot avec des déchets de haute activité provenant du traitement de combustibles gainés avec des alliages d'aluminium, du traitement Darex ou électrolytique de combustibles à gain en acier inoxydable et du procédé Purex. Cette installation permettra aussi de déterminer les méthodes à suivre pour une production économique de matières de faible porosité et relativement non lixiviables, par l'addition des réactifs appropriés aux déchets introduits dans le calcinateur. Le procédé de calcination en pot, qui consiste en une concentration par évaporation et une décomposition thermique dans le pot qui servira de récipient de stockage définitif, a été élaboré au Laboratoire national d'Oak Ridge; il a été mis au point: en laboratoire, avec des substances radioactives; dans une installation pilote avec des substances inactives.

L'appareillage de démonstration avec des substances radioactives permettra de précéder et de résoudre les problèmes de fonctionnement et de contrôle que posent le calcinateur ou les appareils annexes de préparation de la charge et d'épuration des condensats; beaucoup de ces problèmes sont liés à l'auto-échauffement et à la volatilité des produits de fission. Cet appareillage permettra de déterminer la charge et la densité dans le pot, la capacité d'lixiviation, le point de fusion, la teneur en substances volatiles, le dégagement de chaleur et la conductibilité thermique du produit calciné. Il faut déterminer en outre: les fluctuations transitoires de température du produit calciné, le comportement des produits de fission pendant la calcination, la décontamination de tous les effluents liquides et gazeux, le besoin de ventilation des pots stockés, la meilleure méthode de scellage à distance des pots et les méthodes à suivre pour réduire au minimum le volume des gaz d'échappement non condensables.

On utilisera des pots de 20 à 30 cm de diamètre et de 2,40 m de haut. On a mis au point un évaporateur d'un type entièrement nouveau, qui pourrait fonctionner avec un chargement en continu ou un chargement...
Конструкция горячей опытной установки для демонстрации процесса кальцинирования в тиглях.

Была сконструирована установка для демонстрации процесса кальцинирования в тиглях отходов, получаемых при переработке топлива с оболочками из алюминиевого сплава, отходов "Дарекс-процесса" и отходов от электролитической переработки топлива с оболочками из нержавеющей стали, а также отходов "Пурекс-процесса". Эта установка дает также возможность определить технологические приемы, необходимые для экономичного производства малопористых, относительно невыщелачиваемых материалов посредством добавления к отходам, загруженным в охлаждающую печь, подходящих реагентов. Процесс кальцинирования в чанах, состоящий в концентрировании путем упаривания и термического разложения в тиглях, которое вместе с тем служит контейнером для окончательного удаления отходов, был разработан в Окридской национальной лаборатории с радиоактивными отходами в лабораторных масштабах и в масштабе опытной установки с нерадиоактивными отходами.

Аппарат для демонстрации процесса переработки радиоактивных отходов дает возможность определить и разрешить эксплуатационные вопросы и вопросы управления процессом при кальцинировании, подготовке исходного раствора и системе очистки конденсата; многие из этих проблем возникают из-за самопроизвольного нагрева и летучести продуктов деления. Этот аппарат позволяет определить загрузку тигля, а также плотность, выщелачиваемость, точку плавления, содержание летучих веществ, теплополучение и теплопроводность конечного продукта. Необходимо также установить распределение температуры во времени в кальцинируемой массе, поведение продуктов деления во время кальцинирования, их концентрацию в различных частях системы, дезактивацию, достигаемую во всех видах и газообразных потоках эффективных, необходимость приготовления тиглей при хранении, какие способы дистанционной герметизации тиглей и методы, необходимые для достижения минимального объема неподдающихся конденсации выходящих газов.

На этой установке будут использованы тигли высотой 2,43 м и диаметром 2,43 и 3,66 м, считающиеся пригодными для промышленной переработки отходов. Была разработана особая конструкция испарителя, дающая возможность вести непрерывную подачу загрузочной массы, либо загружать ее партиями. Были приняты меры для предотвращения опасности возможных взрывов из-за наличия органических веществ в исходном растворе и для предотвращения других возможных аварийных случаев.

СТРУКТУРА ИССЛЕДОВАТЕЛЬСКОЙ УСТАНОВКИ ДЛЯ ДЕМОНСТРАЦИИ ПРОЦЕССА КАЛЬЦИНИРОВАНИЯ В ЧАНАХ. SE ha construido una instalación para demostrar la posibilidad de aplicar el proceso de calcinación en crisol a desechos de elevada radioactividad procedentes del tratamiento de combustibles de aleaciones de aluminio, del tratamiento Darex o electrolítico de combustibles de acero inoxidable y del proceso Purex. La instalación permitirá también determinar los procedimientos necesarios para la producción económica de materiales de baja porosidad, relativamente no lixiviables por adición de reactivos adecuados a los desechos que se introducen en el crisol de calcinación. La calcinación en crisol, que consiste en la concentración por evaporation y descomposición térmica in situ en crisoles que también sirven de recipientes para el almacenamiento definitivo de los desechos, fue elaborada en el Oak Ridge National Laboratory and perfeccionada en escala de laboratorio con sustancias radiactivas y en planta piloto con sustancias inactivas.

La instalación radiactiva con fines de demostración permitirá identificar y resolver los problemas de funcionamiento y control que plantea el crisol de calcinación y los sistemas extendidamente asociados de preparación del producto de alimentación y depuración del condensado; muchos de estos problemas guardan una relación con el autoencalentamiento y la volatilidad de los productos de fisión. Permitirá determinar la carga y densidad en el crisol, la capacidad de lixiviación, el punto de fusión, el contenido de sustancias volátiles, el desprendimiento de calor, y la conductividad térmica del producto calcinado. Igualmente se determinarán las distribuciones de las fluctuaciones transitorias de temperatura del producto calcinado, el comportamiento de los productos de fisión durante la calcinación, la segregación en diversas partes del sistema, la descontaminación de los efluentes líquidos y gaseosos, la necesidad de ventilar los crisoles almacenados, los medios más adecuados para sellar a distancia los crisoles, y los métodos necesarios para reducir al mínimo el volumen de los gases de escape no condensables.

En esta instalación se emplearán crisoles en escala normal de 8 y 12 pulg. de diámetro y 8 pies de longitud. Se ha ideado un evaporador que podrá funcionar con una preparación continua o intermitente del producto de alimentación. Se han adoptado las medidas necesarias para impedir las explosiones debidas a sustancias orgánicas en las soluciones de alimentación, y para evitar otros riesgos pasibles.
SUMMARY

A facility has been designed for demonstration of the pot-calcination process with full-level wastes from processing aluminium alloy fuels, from Darex or electrolytic processing of stainless-steel fuels and from Purex processes. This facility will also permit determination of procedures required for economical production of low-porosity, relatively non-leachable materials by addition of suitable reagents to the wastes fed to the calciner. The pot-calcination process, consisting of concentration by evaporation and thermal decomposition in situ in pots which also serve as the final disposal containers, was evolved at the Oak Ridge National Laboratory and developed there in radioactive bench-scale and non-radioactive pilot-plant scale studies.

The radioactive demonstration unit will permit identification and solution of operational and control problems connected with the calciner or its closely associated feed preparation and condensate clean-up systems; many of these problems are associated with self-heating and volatilization of fission products. This unit will permit determination of pot loading and density, leachability, melting point, volatile material content, heat release and thermal conductivity of the calcine. Also to be determined are transient calcine temperature distributions, fission-product behaviour during calcination, de-entrainment obtained in the various parts of the system, decontamination achieved on all liquid and gaseous effluent streams, need for venting of stored pots, optimum means of remotely sealing the pots and methods required for production of a minimum volume of non-condensible off-gas.

A unique evaporator design was evolved to permit operation either with close-coupled continuous feed preparation or with batch-feed preparation. Provisions were made to circumvent possible explosions due to organic material in feed solutions and other suspected hazards.

This facility will employ cylindrical pots, 6, 8, and 12 in in diam. and about 8 ft long. Minimum requirements of the cell for installation of the designed facility are 4½-ft thick shielding walls, a 20-ft cell height, viewing windows located about 9 ft above the cell floor and a track and dolly for movement of the pots. A small crane, heavy-duty manipulators and light-duty manipulators are required for various remote handling operations.

INTRODUCTION

The pot-calcination process is one of the more promising processes for the conversion to solids of radioactive waste solutions resulting from the reprocessing of spent nuclear-fuel elements, particularly for the extremely high-activity level waste solutions. This process has been under extensive development for several years in the United States at the Oak Ridge National Laboratory [1, 2, 3, 4, 5] and has also been studied at the Hanford Atomic Products Operation [6, 7, 8, 9, 10]. A similar process has been studied extensively at Harwell in the United Kingdom [14]. The pot-calcination process consists of evaporating aqueous wastes to dryness and then calcining the resulting solids at a temperature level of approximately 900°C in portable stainless-
steel cylindrical pots which also serve as final storage containers. Preparation of feed and decontamination of both condensed and non-condensible portions of the overhead stream from the calciner are associated process steps. Development of this process in laboratory and cold pilot-plant equipment has proceeded to the point where pilot-plant scale testing with full-level radioactive wastes is required to obtain additional design data and to permit economic comparison with other contending calcination processes.

Operation of a pilot-plant facility with full-level radioactive material will permit identification and solution of operational and control problems in connection with the pot calciner and its closely associated feed preparation and off-gas and condensate decontamination systems. Many of the problems are associated with self-heating and volatilization of fission products and cannot be resolved fully in the absence of these materials. A demonstration with radioactive material will also indicate whether such factors as foaming or entrainment are limiting capacity factors. In addition, the demonstration will serve to develop equipment and handling techniques required to make and break calciner vessel process lines, to seal the vessel and to remove it from the operating area for permanent disposal.

A pilot-plant facility for the demonstration of the pot-calcination process with full-level activity wastes has been designed by the Atomic Energy Division of the Phillips Petroleum Company in co-operation with the Chemical Technology Division of the Oak Ridge National Laboratory. This facility was designed as part of a joint co-operative programme between these two organizations with the intention of installing the equipment in the Hot Pilot Plant at the Idaho Chemical Processing Plant. In April 1962, when the design was nearly completed, the USAEC decided that the facility should be installed instead at the Hanford Atomic Products Operation where Purex waste solutions would be more readily available. While certain details of the design will undoubtedly have to be changed to conform to the new location, most of the design features are applicable to the facility installation at Hanford.

SCOPE OF PROCESS DEMONSTRATION

The radioactive demonstration facility for the pot-calcination process is intended to demonstrate and provide design data on an integrated process including, in addition to the calcination step itself, feed preparation, off-gas decontamination and liquid-effluent decontamination systems. Use of the facility for demonstration of the process with several types of aqueous high-level radioactive wastes is intended. Waste solutions to be employed during initial demonstration runs include aluminium nitrate waste solutions, Darex or electrolytic dissolution process wastes, high-sulphate Purex process wastes and perhaps sulphate-free Purex process wastes, all of which would be studied at several composition and activity levels. Table I shows typical compositions for the first three of these waste solutions; a typical composition for sulphate-free Purex waste solutions has not been established. Pot-calcination of a stainless-steel sulphate wastes and fluoride-bearing wastes from processing of zirconium alloy fuels is a desirable goal and may be accomplished at a later date depending on the state of technology. Calci-
nation of the latter type of waste, however, depends on finding a suitable additive to prevent equipment corrosion from fluorine-containing compounds.

**TABLE I**

**AVERAGE COMPOSITION OF TYPICAL RAW WASTE SOLUTIONS FOR POT-CALCINATION PROCESS DEMONSTRATION**

<table>
<thead>
<tr>
<th>Component</th>
<th>Aluminium nitrate</th>
<th>High-sulphate Purex</th>
<th>Stainless-steel nitrate (Darex or electrolytic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sup&gt;+++&lt;/sup&gt;, M</td>
<td>1.72</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;+++&lt;/sup&gt;, M</td>
<td>0.003</td>
<td>0.5</td>
<td>1.25</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;+++&lt;/sup&gt;, M</td>
<td>0.01</td>
<td>0.91</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;++&lt;/sup&gt;, M</td>
<td>0.01</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;, M</td>
<td>0.10</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;++&lt;/sup&gt;, M</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt;, M</td>
<td>1.26</td>
<td>5.6</td>
<td>0.90</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;, M</td>
<td>6.60</td>
<td>6.1</td>
<td>6.15</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;, M</td>
<td>6.15</td>
<td>6.15</td>
<td></td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;, M</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Raw waste vol/run**

| 8-in diam. pot, 1 | 482 | 420 | 555 |
| 12-in diam. pot, 1 | 1077 | 941 | 1252 |

**Solids per "filled" pot**

| 8-in diam. pot, kg | 44 | 88 | 82 |
| 12-in diam. pot, kg | 99 | 198 | 185 |

or on the replacement of certain key items of equipment with special corrosion-resistant equipment.

In a second phase of the radioactive demonstration of this process, appropriate additives will be used in various wastes to form impermeable, glass-like, calcined materials. Modification of the process in this manner appears attractive as a means of reducing liquid-waste solutions to low-porosity, low-leachability solids having a high thermal conductivity. Such material could be stored in larger diameter pots because of the improved heat-dissipating capability, with an attendant reduction in process costs.

Provisions were made in the design of this facility for eventual parallel demonstration of other types of calculiners. The feed preparation, off-gas decontamination and process liquid-decontamination systems of the potcalcination process demonstration facility can also be used for the recycled-gas fluidized-bed calcination process, the rotary ball-mill calcination process and the radiant-spray calcination process. The maximum size of the other calculiners will be necessarily governed by the capacity of the auxiliary
equipment designed primarily for demonstration of the pot-calcination process. Space is to be left in the cells in which this pilot-plant facility is installed for simultaneous installation of a second type of calciner.

SPECIFIC OBJECTIVES OF THE RADIOACTIVE DEMONSTRATION FACILITY

The primary objective of operation of this radioactive demonstration facility will be the procurement of process data for the purpose of ultimate design of a production unit and for comparison of the pot-calcination process with other contending calcination processes. Therefore, the attainment of complete and meaningful data was an overriding consideration throughout the design of the facility. Every effort was made to insure that each run in the facility could be essentially independent of all others, thereby permitting the procurement of a maximum amount of useful data from a minimum number of runs. The following specific objectives have been established for the pot-calcination demonstration facility:

1. Demonstration of processing rates

Operating conditions which influence calcining costs through their effects on processing rates are to be thoroughly explored during this demonstration. The processing rate is affected by average feed rates attained, by down-time required to change pots and by the pot volume effectively used. All of these factors will be examined in the radioactive demonstration, but the latter factor is the one most likely to be influenced by operation with radioactive material since foaming and self-heating by fission products could influence the characteristics of the deposited calcine.

2. Demonstration of suitable feed preparation

Preparation of suitable waste feed for the pot calciner is a key step in the demonstration of an integrated process in which concentration of the feed is conducted simultaneously with decontamination of the acidic condensate from the calciner. To minimize ruthenium volatility problems during feed preparation, nitric acid is stripped from the blended solution by the addition of process water to the evaporator. Preparation of a highly concentrated calciner feed solution in the presence of full-level radioactive material is to be demonstrated.

3. Determination of calcine properties

The leachability, porosity, melting point and volatile constituents of the calcine are to be determined on samples of calcine. Such factors as heat-release rate, calcine thermal conductivity, radiolytic decay rate of residual nitrate compounds and creation of localized hot spots in the calcine are to be determined by appropriate temperature and pressure measurement during interim storage of the pot.
4. Establishment of optimum pot size for various waste solutions

The upper limit on pot diameter is determined by the heat-generating characteristics of the waste solids and by the maximum allowable centreline temperature of the stored product [12]. The ability of the pot-calcined solids system to reject the generated heat and maintain this maximum centreline temperature, is highly dependent upon the calcine thermal conductivity, which in turn is dependent upon the nature and porosity of the calcine. Such factors as waste composition, geometrical configuration of the pots, additives and operating conditions employed should have a significant effect on the calcine porosity and, hence, upon the optimum pot size. A variety of modes of operation may be employed in order to determine optimum operating methods. Differences in possible operating methods involve the manner of introducing liquid feed to the pot (continuous or intermittent) and the use of a variety of temperature-time control combinations.

5. Determination of the effects of using additives

The effect of various additives to the feed on suppression of ruthenium volatilization, on suppression of volatilization of corrosive sulphur compounds and upon the formation of glass-like calcine will be determined in the radioactive demonstration. Adverse or desirable effects, if any, on fission-product behaviour as the result of the use of additives are to be determined.

6. Determination of the effects of fission-product heat release

The release of heat by fission products may create a serious operating problem near the end of a run. If overshooting of the normal calcination temperature is to be avoided, this heat must be removed from those portions of the calcine in which the residual heat requirements for decomposition are exceeded. This must be done, however, at a time when portions of the calcine still require additional heat to complete the calcination reactions. Overheating may release corrosive sulphur compounds from some wastes or result in volatilization of fission products from others. It also endangers the structural integrity of the pot itself. In the case of underheating, excessive residual nitrate may create a problem if the pots are eventually sealed. The development of suitable operating procedures to detect and control addition and removal of heat from various portions of the pot is a necessary objective of the radioactive demonstration facility.

7. Demonstration of adequate de-entrainment of gas streams

Effective de-entrainment of mists from the gas streams is required if effluents from the process are to be disposed to the surroundings. This is of especial importance in the feed evaporator since it handles not only the raw waste, but also the volatile products from the pot. Equipment in the process is designed to minimize entrainment and the effectiveness of de-entrainment is to be determined during operation with high-level waste solutions.
8. Demonstration of adequate decontamination of effluent streams

The integrated pot-calcination process produces four effluents - calcine, off-gas, decontaminated water and decontaminated concentrated nitric acid. Reduction of the activity level of the last three of these effluents to a point permitting disposal to the surroundings is to be demonstrated.

9. Development of suitable pot-closure techniques

For interim storage, the pots are to be closed with a temporary, reliable, mechanical seal which will permit re-opening the pot for sampling or venting, if necessary. Before the pots are moved to a repository for permanent disposal, a high-integrity permanent pot closure, possibly a welded closure, might be necessary. Determination of the suitability of a closure without a vent is to be based on observations made during interim storage and the proper closure is to be demonstrated during remote operation.

10. Observation of pots during storage

All filled pots are to be stored for an interim period for observation of temperature and pressure transient behaviour. Should a pot develop an excessive internal pressure, that pot will be connected to a manifold for pressure relief and for analysis of the off-gas. The extent of pot corrosion occurring during or following calcination is to be determined. Data obtained during interim storage of pots will be used to establish requirements for permanent storage of the pots.

GENERAL PROCESS FLOW-SHEET CONSIDERATIONS

Calcination is to be demonstrated in pots of three sizes - 6, 8, and 12 in in diameter, each with an over-all length of 7\(\frac{1}{2}\) ft and an active pot length of 6 ft. During most runs, 8-in-diam. pots will be used; 6-in-diam. pots will be used for extremely high-activity level wastes, while the 12-in-diam. pots will be tested to determine the effect of pot diameter on such factors as solids deposition rate, bridging and porosity.

The design basis, a maximum pot feed-rate of about 100 l/hr, sets in turn the capacity of all auxiliary equipment. It would be possible to exceed this feed-rate somewhat for a short initial period of operation with the 12-in-diam. pots; however, the basis selected will permit maximum throughput rates under all other intended conditions of operation. The pot demand for feed tapers off rapidly after the first hour of processing, when solids start to deposite on the pot walls. The minimum or final feed-rate at which a batch run is terminated must necessarily be established on an economic basis but it is estimated to be around 2 l/hr.

With three exceptions, all equipment in this facility is to be constructed of stainless steel. The three pieces of equipment subject to high-temperature contact with feed and condensate streams are to be constructed from unalloyed titanium. The use of this material will impart satisfactory corrosion resistance to the feed evaporator, the calciner condenser and the fractionator even when processing aluminium nitrate and Darex process
wastes. These solutions are excessively corrosive to stainless steel at the expected contact temperatures.

The pot-calcination process as designed for the hot demonstration consists of the following four functions: (1) the calcination operation itself, including connecting and disconnecting the pot from the process equipment; (2) feed preparation, including initial treatment of the calciner condensate; (3) decontamination of the non-condensible off-gas for discharge to the atmosphere; (4) decontamination of the liquid effluents for reuse in other plant operations or for disposal to the ground. A simplified flow-sheet integrating these four functions is shown in Fig. 1 and the four process systems required are discussed in the following sections.

**Fig. 1**

Simplified pot-calcination process flow-sheet

**BASIC POT-CALCINATION SYSTEM**

Remote filling of the pots on the batch basis required by the process involves a considerable number of mechanical operations, which must be carried out under direct view of the operator. The pot-handling system is therefore located in a cell fitted with several viewing windows, manipulators and a crane. A remotely operated dolly serves to transport the pot and induction furnace to and from the calcining station. Figure 2 shows some of the more important details of the calciner, the stationary feed head, the induction furnace and the dolly.
To prepare for a run, an empty cylindrical pot is placed inside the water-cooled induction furnace mounted on a moveable mechanical dolly, and the dolly is then centred below the stationary pot feed head. The pot and furnace are mechanically jacked upward and connected to the feed head by means of a special connector and a special clamp actuated from outside the cell. Liquid waste is usually introduced continuously to the pot calciner and evaporated to dryness and calcined at temperatures in the 900°C range. The feed-rate to the calciner is controlled by means of a thermocouple located in a vertical well protruding just below the intended liquid level. The feed line is jacketed where it passes through the stationary feed head, which permits close temperature control to avoid plugging as a result of either overcooling or overheating. A separate water-cooled inlet line is provided for admitting process additives directly to the pot, if this becomes desirable in advanced processes.

Decomposition gases from the calciner pass through a mercury-trap for removal of volatile mercury compounds, if any are present and then to the calciner condenser. A seal-pot is provided in an alternate off-gas line between the pot calciner and the calciner condenser, as a safety meas-
DEMONSTRATION OF THE POT-CALCINATION PROCESS

ure to prevent over-pressurizing of the pot should the primary off-gas line between these two units plug.

Thermocouples placed in the centre of the pot and one inch from the inside wall of the pot at elevations corresponding to six outer-wall thermocouples will be used to determine the temperature of the solids in the pot. On a typical calcination run, liquid waste will be introduced to the pot until the feed rate drops to under 2 l/hr. The solids will then be heated to drive off volatile components, mainly nitrates, until the temperature in all parts of the pot approaches 900°C. Heat released from fission products near the end of a run may cause some auto-calcination. Because of fission product heating, internal temperatures in the pot would reach excessive values if heat introduction were not stopped at the appropriate stage of the run [13]. Excessive temperatures are to be avoided because they might cause undesired volatilization of certain fission products or of corrosive sulphur compounds. On the other hand, failure to reach a sufficiently high temperature in all portions of the pot will result in retention of excessive quantities of volatile material and introduce pot-sealing problems. Therefore, internal pot temperatures must be carefully monitored near the end of a run.

The furnace is designed for individual temperature control in six equally spaced, vertically oriented zones of the pot. This makes it possible to create steep, vertical temperature gradients during specialized runs such as might be employed for forming glass-like products. The heat input from each zone of the furnace is controlled by a skin thermocouple located at the centre of each zone of the pot surface. An induction furnace is specified for use in this facility because it permits instantaneous control of external heat input and provides automatically for removal of heat from the pot by the water-cooled induction coils. Both of these features are expected to be very necessary at the end of a calcination run for removal of fission-product heat. Furnace specifications call for a total heat-introduction rate to the pot of 300 000 BTU/hr, and a net heat loss of 30 000 BTU/hr to the cooling coils, when the pot vessel walls are at 900°C. Additional advantages of an induction furnace over a resistance furnace in this application are felt to be longer life expectancy at the high operating temperatures employed and less susceptibility to fracture from abuse during remote insertion and removal of heavy pots. A small nitrogen purge is introduced at the bottom of the furnace to curtail pot scaling during a run. Additional emergency cooling can be provided by introducing approximately 100 ft³/min (STP) of air to the furnace through the nitrogen purge lines.

After the pot is filled with solids, it is remotely disconnected from the feed-head. During the disconnecting operation, air is drawn through a shroud surrounding the pot-head to catch any dust that may be dislodged as the pot is lowered. The shroud is connected to a process off-gas line so that this dust is collected on a final off-gas filter. The pot and furnace, after being lowered to their original position by means of the mechanical jacks, are moved by the dolly from under the feed-head to a special station for sampling of the calcine and for temporary pot closure.

Following temporary closure of a pot at the end of a run, the pot is removed from the furnace and stored in racks in an adjacent cell for observation of corrosion, internal pressure and temperature and evidence of
products of decomposition. If no unusual corrosion, pressures, or temperatures are observed during this interim storage, which is expected to be for at least a one-year period, the pots will be permanently sealed, decontaminated, placed in a cask and transported to permanent storage. Remote welding is the preferred method at this time for permanent pot sealing. Contamination of the outside of the shipping cask will be prevented by pulling the pots directly into a shielded cask through an opening in the ceiling of the cell. Data obtained during observation of pots in interim storage will be used to establish requirements for design of permanent pot-storage facilities.

FEED-PREPARATION SYSTEM

Maximum processing rates are achieved by preconcentrating the calciner feed to a point just short of saturation. Since liquid wastes in storage are generally somewhat more dilute than this, partially, at least, due to jet dilution during transfer, the use of a feed evaporator is necessary to achieve a high unit throughput.

The feed evaporator, in addition to concentrating the waste feed solution, removes ruthenium and entrained solids from the calciner condensate for recycle. In order to avoid volatilization of significant quantities of ruthenium while evaporating the feed solution, it is necessary to maintain the nitric acid concentration of the boiling liquid below about six molar [11]. This is accomplished by recycling low-activity level water (resulting from further rectification of the overhead vapours) to the evaporator to strip nitric acid from the evaporator solution. The bottoms product from the evaporator is fed to the pot calciner. The overhead stream from the evaporator goes to a fractionator for separation into appropriate streams for recycle or disposal. It is important to note that any fission products vaporized in the evaporator or entrained in the vapour leaving the evaporator will be contained in one of the streams intended for disposal. Therefore, a very high decontamination factor must be achieved in this evaporator.

Two methods of evaporator operation have been evolved for this process: close-coupled continuous operation and batch operation. The former method of operation employs a low-holdup evaporator to concentrate waste solution and to decontaminate the calciner acid condensate at the same time that the calciner is being fed directly and continuously from the evaporator. Continuous operation in this manner provides the means for recycling the maximum quantity of ruthenium and solids escaping from a pot back to the same pot on the same run. The latter method, batch operation, employs an evaporator having a large holdup to concentrate an entire batch of feed for a succeeding run while decontaminating the calciner condensate from the current run; this, therefore, requires that ruthenium and solids escaping from the calciner be recycled to the calciner on the succeeding run. Close-coupled continuous operation is preferred so that undesirable interactions between runs might be avoided. However, because of possible control problems with a close-coupled continuous evaporator, special design provisions were employed so that operation by either method could be used during radioactive demonstration.
Figure 3 shows principal details of the evaporator designed for use in this facility with either method of operation. The evaporator is constructed of titanium to provide satisfactory corrosion resistance when processing aluminium-nitrate and Darex-type waste solutions. For close-coupled continuous operation, the evaporator functions as a standard thermosyphon evaporator and has a holdup of only 65 l. The enlarged vapour head, while not needed for continuous operation, permits operation of the same unit as a batch evaporator. The impact type de-entrainment device provides two stages of separation with maximum impact velocities of 35 and 100 ft/sec.

During continuous operation, the flow by gravity to the evaporator of calciner condensate is unregulated, that of raw waste solution is controlled by the liquid level in the evaporator and that of process water is controlled by the acidity of the evaporator vapour. Provisions have been made to determine overhead vapour acidity either by dew point or by electrical conductivity of a totally-condensed side stream. The heat flux or boilup rate is controlled by the density of the blended solution in the evaporator. Control of the continuous evaporator is complicated by the necessity to concentrate feed solutions to narrow specifications; since the holdup in a continuous evaporator is low, small changes in the composition or rates of the input streams will cause large changes in the boilup rate and evaporator liquid composition. Use of a combination predictive control system employing both feed-forward and feed-back principles is being considered to improve evaporator control during continuous operation.

Control of the evaporator during batch operation will be less difficult, since the total volume of raw waste required for the succeeding run is added before operation; the effect of small changes in the composition or inlet
rates of condensate and process water will, therefore, be diminished due to the large volume of liquid in the evaporator. During batch operation, as in continuous operation, addition of process water will be controlled by the acidity of the overhead vapour and the heat flux will be controlled by the density of the blended solution in the evaporator. The calciner condensate flow is again unregulated.

The versatility achieved by providing for both continuous and batch operation of the evaporator requires the installation of much additional piping and of an additional tank. A concentrated feed tank, not shown on the simplified flow-sheet in Fig. 1, is required to store concentrated waste solution during batch operation but is not needed during continuous operation. The concentrated feed tank can also be used for the admission and mixing of additives to the feed system. Important features of the two feed storage tanks are given in Table II along with similar information on other in-cell storage tanks.

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Position</th>
<th>Diam. (in)</th>
<th>Over-all length (in)</th>
<th>Capacity (l)</th>
<th>Jacketed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste feed-storage tank</td>
<td>Vertical</td>
<td>36</td>
<td>82</td>
<td>1200</td>
<td>Yes</td>
</tr>
<tr>
<td>Concentrated feed tank</td>
<td>Horizontal</td>
<td>36</td>
<td>82</td>
<td>1200</td>
<td>Yes</td>
</tr>
<tr>
<td>Condensate hold tank</td>
<td>Vertical</td>
<td>36</td>
<td>82</td>
<td>1200</td>
<td>Yes</td>
</tr>
<tr>
<td>Water-storage tank</td>
<td>Horizontal</td>
<td>36</td>
<td>82</td>
<td>1200</td>
<td>No</td>
</tr>
</tbody>
</table>

Waste solution from the evaporator can be transferred directly to the calciner during continuous operation, or to the concentrated feed tank during batch operation, by either a pump or a steam jet operating on a recycle loop. During batch operation, the solution in the concentrated feed tank may be fed to the calciner by gravity, by the steam jet, or by the pump. A feed cooler is required when using the steam jet for concentrated feed transfer, since steam jets do not function satisfactorily when the inlet liquid temperature is above 60°C. Important details of this cooler are shown in Table III, along with similar details for the other heat exchange equipment designed for the pilot-plant facility.

All feed lines are jacketed to prevent cooling of feed solutions and possible precipitation of salt during transfer. Plugging from insoluble material (originating from entrainment in the pot and contained in the condensate fed to the evaporator) is avoided by maintaining continuous solution flow through feed lines and, in some cases, by continuously bleeding a small quantity of water into the lines and the pot calciner head.

Consideration has been given to the possible hazard of introducing organic compounds into the feed evaporator. Existing data [15] indicate no
<table>
<thead>
<tr>
<th>Component</th>
<th>Maximum process stream throughput (1/hr)</th>
<th>Maximum heat duty (BTU/hr)</th>
<th>Heat transfer area (ft²)</th>
<th>Approx. shell diam. (in)</th>
<th>No.</th>
<th>Diam.</th>
<th>Length (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Evaporator reboiler</td>
<td>600*</td>
<td>1 280 000</td>
<td>98</td>
<td>12</td>
<td>111</td>
<td>3/4</td>
<td>54</td>
</tr>
<tr>
<td>2. Feed-storage tank reflux condenser</td>
<td>35</td>
<td>75 000</td>
<td>5</td>
<td>4</td>
<td>10</td>
<td>3/4</td>
<td>32</td>
</tr>
<tr>
<td>3. Feed cooler</td>
<td>200</td>
<td>60 000</td>
<td>32</td>
<td>8</td>
<td>74</td>
<td>1/2</td>
<td>40</td>
</tr>
<tr>
<td>4. Calciner furnace</td>
<td>---</td>
<td>300 000</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Calciner condenser</td>
<td>100</td>
<td>240 000</td>
<td>148</td>
<td>12</td>
<td>111</td>
<td>3/4</td>
<td>82</td>
</tr>
<tr>
<td>6. Fractionator reboiler</td>
<td>53</td>
<td>380 000</td>
<td>33</td>
<td>**</td>
<td>*</td>
<td>3/4</td>
<td>56</td>
</tr>
<tr>
<td>7. Fractionator partial condenser</td>
<td>154</td>
<td>345 000</td>
<td>12</td>
<td>**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Fractionator condenser</td>
<td>473</td>
<td>1 110 000</td>
<td>149</td>
<td>12</td>
<td>115</td>
<td>3/4</td>
<td>81</td>
</tr>
<tr>
<td>9. Off-gas heater</td>
<td>175 ft³/hr(STP)</td>
<td>2 500</td>
<td>10</td>
<td>6</td>
<td>22</td>
<td>3/4</td>
<td>28</td>
</tr>
<tr>
<td>10. Final off-gas condenser</td>
<td>90*</td>
<td>208 000</td>
<td>33</td>
<td>6</td>
<td>31</td>
<td>3/4</td>
<td>66</td>
</tr>
</tbody>
</table>

* Includes 100 l/hr feed, 100 l/hr condensate and 400 l/hr water.


*** Condensed jet-motivation steam.
hazard from tributyl phosphate or its usual diluent (kerosene) up to the limit of their solubility in water. However, the addition of a separate phase of these organic compounds might lead to a safety hazard [15]. To avoid this hazard in experimental operations, raw wastes should not be taken from the top or bottom layers of storage tanks, but rather from the central portion where a single phase aqueous solution is known to exist.

PROCESS OFF-GAS DECONTAMINATION SYSTEM

Gases are evolved from the pot calciner at temperatures varying between 100°C and 900°C, and they consist of nitric acid, water vapour, nitrogen oxides, nitrogen, oxygen, ruthenium tetroxide and perhaps volatile mercury compounds; solids may also be entrained in this stream. The gases are first introduced to a cooler to trap mercury compounds and then to a 148 ft² titanium shell-and-tube condenser in which nitric acid and water vapour are condensed and where partial absorption of nitrogen dioxide occurs. Details of this condenser are given in Table III. A large percentage of the solids entrained from the calciner are removed with the condensate from this condenser. This condenser was designed to be an effective absorber of nitrogen dioxide as well as to condense nearly all of the water vapour, in line with the intent to operate the experimental unit with a minimum production of off-gas.

The effluent gas from the calciner condenser is routed through the feed evaporator to take advantage of any additional decontamination of this stream which may be obtained by scrubbing in the evaporator or by passing through its overhead de-entrainment device. The overhead stream from the evaporator, after passing through the de-entrainment device, will undergo slight partial condensation because of heat loss to the surroundings; since the condensate might contain additional particulate matter, the line leading from the evaporator to the fractionator is sloped back towards the evaporator. The same off-gas, along with the vapours from the evaporator, is then introduced into a fractionating column where the dilute nitric acid is separated into water and concentrated nitric acid, and where the non-condensible gases are further decontaminated. Separation of additional particulate matter from the off-gas in the fractionator occurs by a mechanism similar to that which occurs in a condenser; during repeated condensation, solid particles act as nuclei for condensation until they grow in size sufficiently to impinge on the column packing and be collected in the liquid phase [3].

The overhead stream from the fractionator is introduced to a 149-ft² stainless-steel condenser where condensation, additional nitrogen dioxide absorption and further decontamination of the gas stream occur; additional details of this condenser are given in Table III. The non-condensible gases leaving the fractionator condenser pass through a small heat-exchanger to vaporize any residual liquid droplets, and finally through one of a pair of absolute filters to which are attached silica-gel cartridges for adsorption of any residual ruthenium.

Off-gas motivation is accomplished by means of a steam-jet located downstream of the absolute filters. The rate of gas recycle to the suction
side of the jet is used to control the negative pressure in the pot, or alternatively that in the evaporator.

The quantity of non-condensible gas leaving the process will be accurately determined before discharge, as will the quantity of instrument and purge air introduced to the process. By material balance, the net quantity of off-gas generated in the pot-calcination process can be calculated.

**LIQUID-EFFLUENT DECONTAMINATION SYSTEM**

The vapour leaving the evaporator is rectified to produce a water stream and a concentrated nitric acid stream, both of which are expected to be sufficiently free from radioactivity that they may be safely discharged to the ground or reused in a chemical processing plant. The relative quantities of water and concentrated nitric acid resulting from pot calcination are dependent upon the composition of the waste solution fed to the process; for many wastes, approximately equal quantities of these solutions are generated.

If any radioactive material enters the fractionator along with the vapour from the evaporator, it is most likely to end up in the bottoms product from the fractionator, the concentrated nitric acid stream. For this reason, the activity level of the concentrated nitric acid effluent might be greater than that of the water. There will, therefore, be a greater incentive to reuse that stream than the water stream in a chemical processing plant.

The fractionating column was designed to separate 1.0M nitric acid, fed as a vapour, into an essentially water-overhead stream consisting of 0.02M nitric acid and a bottoms product consisting of 13M nitric acid. Five theoretical plates are required for the separation and a reflux ratio of twice the minimum value was selected. Pertinent details of the fractionating column and its reboiler are shown in Fig. 4. A packed column was selected, rather than a bubble-cap plate column, in order to increase aerosol attenuation [3]. Product quality from the fractionating column is controlled by adjusting both the boil-up rate in the reboiler and the reflux rate. The boil-up rate is controlled by the density of the acid in the reboiler, while the reflux rate is controlled by the vapour temperature at the top of the column which regulates the flow of cooling water to the reflux condenser. With this mode of operation, rates of all streams are variable, but product quality is maintained constant.

Concentrated nitric acid accumulates in the reboiler until run termination, at which time it is jetted to disposal facilities. Vapour from the top of the fractionating column is condensed and transferred to a storage tank by a two-stage airlift. This stream, except that portion recycled by gravity flow to the evaporator, is accumulated in the water-storage tank until run termination when it is sampled and jetted to disposal facilities.

When calcining aluminium nitrate wastes, which contain significant quantities of mercuric nitrate, an additional effluent stream is produced, namely the mercuric nitrate solution obtained from dissolving mercury and mercury oxides collected in the mercury trap. This stream is not returned to the calciner because mercury cannot be retained in the calcine at the temperatures employed in this process. It is, therefore, stored as a contaminated liquid stream.
REQUIRED HOT-CELL FACILITIES

Special features are required for the cells in which the designed equipment is installed. External shielding equivalent to at least 4.5 ft of concrete is necessary. Viewing windows are required on at least two walls to permit observation of the many required remote operations; the windows in the vicinity of the pot-feeding head and the capping stations must be about 9 ft above the floor on which the dolly rides. A vertical distance of at least 16 ft between the crane hook and the dolly platform is required for removing the pot from the furnace, unless a clam-shell furnace design is employed. In addition to the crane, heavy-duty and light-duty manipulators are needed to perform the required remote operations.

At least a 20-ft cell height is required if gravity flow of most streams is to be retained. The use of a cell with a lower height would require employment of additional pumps or multi-stage air-lifts.

To make maximum use of the auxiliary equipment in this facility, space should be reserved for installation of a second type of calciner which could use the same feed-preparation system and the same off-gas and liquid-effluent decontamination systems.

Isolation of interim storage facilities would be desirable to facilitate direct maintenance. While some of the equipment could be repaired remotely, cell entrance for direct maintenance is an eventual necessity. All equipment has been designed to permit external and internal decontamination by standard remote techniques.
CONCLUSIONS

A pilot-plant facility has been designed for radioactive demonstration of an integrated pot-calcination process with a wide variety of high-level radioactive waste solutions. Extensive exploratory work in the chemical laboratory and Unit Operations laboratory, essentially all of which was with non-radioactive simulated wastes, formed the basis of the approach to design of the hot pilot-plant facility. During the course of the design effort, the need for additional definitive paper and experimental studies was indicated; as a result, significant simplification and improvement of the process was effected.

Several of the equipment choices selected as a result of these studies are believed to provide for significantly improved operability of the radioactive demonstration facility. Among these are:

1. Use of an induction furnace rather than a resistance furnace provides the means for adequate calcine temperature control and permits operation with a wider variety of control methods;
2. Selection of a temperature-measurement device for sensing liquid level in the pot eliminates reliance on bubbler probes which are prone to plugging;
3. Temperature control of pot-feed solutions by jacketing the lines adjacent to and in the pot-feed head should minimize plugging of these lines;
4. The use of a shroud on the pot-feed head to minimize dusting during pot-changing operations should ease decontamination problems;
5. Employment of a low-holdup evaporator for continuous feed preparation will minimize undesirable interactions between runs.

In addition, design studies permitted a reduction in the system complexity. Extensive off-gas holdup and recycle facilities were eliminated, as were other non-essential process components. Equipment was arranged to permit minimum use of pumps and maximum use of gravity flow for solution transfer. Safety hazards were evaluated throughout the course of the design effort, and possible hazards were circumvented by employing appropriate design features.

A target date for radioactive operation of the pilot-plant facility has been established as early in 1965. Data from radioactive operation of this facility are expected to provide a basis for design of a production facility employing the pot-calcination process.

REFERENCES

DISCUSSION

W. H. HARDWICK: Do you not think it might be very difficult to remove a calciner vessel from the furnace in the event of vessel failure, since you do not have vertical access, but rely on horizontal movement beneath the furnace?

J. A. BUCKHAM: A vessel failure, e.g. by accidental over-pressurization, would be very unpleasant and we have done all we can in the facility design to avoid such an occurrence. For example, a seal loop has been provided in case the principal off-gas line to the condenser becomes plugged. (Incidentally, this has happened only once in non-radioactive pilot-plant tests). The dolly is a device which moves the pot and furnace horizontally between stations. Vertical access is then available (by means of in-cell cranes and manipulators) for removal of the pot from the furnace. A clamshell type of furnace is being considered, which would give an additional degree of freedom for remote operations such as the one you mention.

E. MESTRE: At what temperature does the evaporation condensate circulate between the evaporator and the calciner and is there any risk of crystallization during transfer?

J. A. BUCKHAM: The concentrated feed solution is maintained at any desired temperature between 20° and 100°C by means of jackets placed around all feed system lines; the jackets are connected to both the steam and cold water systems. Under circumstances where this solution is transferred by steam jet, the concentrated feed solution must be kept below about 60°C for satisfactory jet operation, but higher feed solution temperatures may be used when a pump or gravity feed is used. It is believed that this system will prevent crystallization in the feed system if properly used. In the event of faulty operation, the ability to heat these lines may provide a means of unplugging the lines. Since an evaporator is a far more effective...
heat-transfer device than a pot calciner, there is considerable incentive
to concentrate the feed to a high degree. Only extensive operating experience
can determine how close one can safely approach saturation of the feed solu­
tion without getting into difficulty.

J. R. GROVER: You pointed out in your oral presentation that as the
pot is filled, decay heat becomes a major factor. Under these conditions,
how is the heat input controlled to prevent overheating of the vessel?

J. A. BUCKHAM: Determination of satisfactory operating procedures
to avoid over- or underheating of the calciner in the presence of fission-
product heat release will be one of the major objectives in operating the
radioactive demonstration facility. Several provisions for control of this
temperature have been made in the design of the facility. The use of an in­
duction furnace gives practically instantaneous control of the heat input,
whereas a resistance furnace would have had an inherent time-lag. The di­
vision of the furnace into six vertical zones should provide sufficient flexi­
bility over the vertical temperature gradient. Moreover, the cooling coils
of the induction furnace are designed to remove heat continuously at a rate
exceeding the highest expected rate of release of heat by fission products.
These provisions, combined with appropriate alarm systems, should ensure
that effective operating procedures can be devised to prevent over—or under-
heating of the calciner.

W. H. HARDWICK: Would you expect to have any solids present in
the feed solution as a result of radiolysis products of tributyl phosphate,
and might these cause trouble?

J. A. BUCKHAM: I think that most wastes leave a slight sludge in the
tanks. One thing we would intend to do, initially in a pilot plant is to avoid
drawing feed solutions from the very bottom or even the very top of a tank,
until we have learnt how far we can safely approach the top or bottom. We
shall have to obtain some operating experience before we can answer that
question.
ECONOMIC EVALUATION OF TANK STORAGE AND POT CALCINATION OF POWER-REACTOR FUEL-REPROCESSING WASTES

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OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENN.

Abstract — Résumé — Аннотация — Resumen

ECONOMIC EVALUATION OF TANK STORAGE AND POT CALCINATION OF POWER-REACTOR FUEL-REPROCESSING WASTES. As part of a comprehensive study undertaken to evaluate the economics and hazards associated with methods for ultimate disposal of highly radioactive liquid and solid wastes, costs have been estimated for interim storage of the wastes in tanks and conversion to solids by pot calcination. A 6-t(metric)/d capacity fuel-processing plant was assumed, processing 1500 t/yr of uranium fuel of 10 000-MWd/t burn-up and 270 t/yr of thorium fuel of 20 000-MWd/t burn-up, which would process all the fuel from a 15 000-MWe nuclear economy.

Costs for storage of acidic and neutralized Purex and Thorex wastes were estimated for storage in stainless-steel tanks for acidic wastes and mild steel for neutralized wastes. With interim storage time defined as filling time plus full time, tank costs were minimum when the full time was roughly 40 to 75% of the interim storage time. For 0.5 - 30 yr storage, costs ranged from 2.0 x 10^-3 to 9.3 x 10^-3 mill/kWhe for acid wastes and from 1.5 x 10^-3 to 4.7 x 10^-3 mill/kWhe for alkaline wastes.

Costs were estimated for converting acidic and reacidified Purex and Thorex wastes to solids by pot calcination and for producing glass from acidic Thorex wastes. The vessels studied were made of 6-, 12-, and 24-in-diam. stainless-steel pipe, 10 ft high, with estimated costs of $500, $855 and $2515. Aging had negligible effect on costs for processing in a vessel of a given size, because capital costs were only about 10% of vessel and operating costs, but permitted larger vessels to be used; costs for processing in 6-in-diam. vessels were two to three times those in 24-in-diam. vessels. The lowest cost was 0.87 x 10^-2 mill/kWhe for processing acidic Purex and Thorex wastes in 24-in-diam. vessels and the highest was 5.0 x 10^-2 mill/kWhe for processing reacidified Purex and Thorex wastes in 6-in-diam. vessels.

ASPECTS ÉCONOMIQUES DU STOCKAGE EN RÉSERVOIRS ET DE LA CALCINATION EN POT DES DÉCHETS DU TRAITEMENT DU COMBUSTIBLE IRADIÉ DANS DES REACTEURS DE PUISSANCE. Dans le cadre d'une vaste étude des aspects économiques et des risques de diverses méthodes d'élimination de déchets liquides et solides de haute activité, les auteurs évaluent le coût du stockage provisoire de ces déchets dans des réservoirs et de leur calcination en pot. Ils prennent comme base de calcul le cas d'une installation de traitement du combustible d'une capacité de 6 t/j, où sont traitées annuellement 1500 t de combustible d'uranium, ayant un taux de combustion de 10 000 MWj/t, et 270 t de combustible de thorium, ayant un taux de combustion de 20 000 MWj/t, et où tout le combustible provenant d'une centrale nucléaire de 15 000 MWe serait régénéré.

Les auteurs ont évalué le coût du stockage des déchets résultant du traitement par les procédés Purex et Thorex, en admettant que les déchets acides sont stockés dans des réservoirs d'acier inoxydable et les déchets neutralisés dans des réservoirs d'acier doux. Le temps de stockage provisoire étant défini comme la somme du temps de remplissage et du temps pendant lequel les réservoirs sont pleins, le coût du stockage est minimum lorsque le temps pendant lequel les réservoirs demeurent remplis est de l'ordre de 40 à 75% du temps de stockage provisoire. Pour un temps de stockage allant de six mois à 30 ans, les coûts varient de 2.0 x 10^-3 à 9.3 x 10^-3 mill/kWhe pour les déchets acides et de 1.5 x 10^-3 à 4.7 x 10^-3 mill/kWhe pour les déchets alcalins.

Les auteurs ont évalué le coût de la solidification, par calcination en pot, des déchets acides et reacidifiés résultant des procédés Purex et Thorex ainsi que celui de la fabrication de produits vitrifiés à partir des déchets acides provenant du procédé Thorex. Le coût des récipients considérés, qui consistaient en tubes d'acier inoxydable de 15,30 et 60 cm de diamètre et 3 m de hauteur, a été évalué à 500, 855 et 2 515 dollars, respectivement.

Le vieillissemment est un facteur négligeable du coût du traitement dans un récipient de dimensions donnés, du fait que les immobilisations ne représentent qu'environ 10% du total du prix des récipients et des frais d'exploitation, mais il permet d'utiliser des récipients de grande dimension. Le coût du traitement dans des récipients de 15 cm de diamètre est deux ou trois fois plus élevé que celui du traitement des récipients de 60 cm de diamètre. Le coût minimum - 0.87 x 10^-2 mill/kWhe - est celui du traitement des déchets acides provenant
EVALUACIÓN ECONÓMICA DE LAS OPERACIONES DE ALMACENAMIENTO EN TANQUES Y CALCINACIÓN EN CRISOLES DE LOS DESECHOS DE LA REGENERACIÓN DEL COMBUSTIBLE DE REACTORES DE POTENCIA. Como parte de un amplio estudio emprendido con miras a evaluar los aspectos económicos y los riesgos que entrañan los métodos de evacuación definitiva de desechos líquidos y sólidos de elevada actividad, se han calculado los costos del almacenamiento provisional de los desechos en tanques y su transformación en sólidos por calcinación en crisoles. Como base para el cálculo, se adoptó una planta de tratamiento de combustibles con una capacidad de 6 t diarias, en la que se tratan 1 500 t/a de combustible de uranio con un grado de combustión de 10 000 MWd/t y 270 t/a de combustible de torio con un grado de combustión de 20 000 MWd/t, y donde se regeneraría todo el combustible procedente de una central nucleoeléctrica de 15 000 MW(e).

Se calculó el costo del almacenamiento de los desechos de los procesos Purex y Thorex, ácidos y neutralizados, suponiendo que los desechos ácidos se almacenan en tanques de acero inoxidable y los desechos, neutralizados, en tanques de acero dulce. Llamando tiempo de almacenamiento provisional a la suma del tiempo de carga más el tiempo durante el cual los tanques permanecen llenos, se comprobó que el costo de los tanques es mínimo cuando el tiempo que permanecen cargados es del orden del 40 al 75% del tiempo de almacenamiento provisional. Para un almacenamiento de 6 meses a 30 años, los costos varían entre 2,0 \cdot 10^{-3} y 9,3 \cdot 10^{-3} mill/kWh(e) en el caso de los residuos ácidos y entre 1,5 \cdot 10^{-3} y 4,7 \cdot 10^{-3} mill/kWh(e), en el caso de los desechos alcalinos.

Se calculó el costo de la solidificación de los desechos de los procesos Purex y Thorex, ácidos y reacidificados, suponiendo que los desechos ácidos se almacenan en tanques de acero inoxidable y los desechos, neutralizados, en tanques de acero dulce. Llamando tiempo de almacenamiento provisional a la suma del tiempo de carga más el tiempo durante el cual los tanques permanecen llenos, se comprobó que el costo de los tanques es mínimo cuando el tiempo que permanecen cargados es del orden del 40 al 75% del tiempo de almacenamiento provisional. Para un almacenamiento de 6 meses a 30 años, los costos varían entre 2,0 \cdot 10^{-3} y 9,3 \cdot 10^{-3} mill/kWh(e) en el caso de los residuos ácidos y entre 1,5 \cdot 10^{-3} y 4,7 \cdot 10^{-3} mill/kWh(e), en el caso de los desechos alcalinos.

Se calculó el costo del almacenamiento de los desechos de los procesos Purex y Thorex, ácidos y reacidificados, por calcinación en crisoles, así como el costo de obtención de vidrios a partir de los desechos ácidos del proceso Thorex. El costo de los recipientes estudiados, que consistían en tubos de acero inoxidable de 6, 12 y 24 pulg de diámetro por 10 pies de altura, se calculó en 500, 855 y 2 515 dólares, respectivamente.

El envejecimiento influye poco en el costo de tratamiento en un recipiente de dimensiones dadas, debido a que los gastos de capital sólo representan alrededor del 10% del costo del recipiente y de explotación, pero permite utilizar recipientes de mayor tamaño; el costo del tratamiento en recipientes de 6 pulg de diámetro es dos o tres veces mayor que el del tratamiento en recipientes de 24 pulg de diámetro. El costo mínimo es de 0,87 \cdot 10^{-2} mill/kWh(e) y corresponde al tratamiento de los desechos ácidos procedentes de los procesos Purex y Thorex en recipientes de 24 pulg de diámetro; el costo máximo asciende a 5,0 \cdot 10^{-2} mill/kWh(e) y corresponde al tratamiento de los desechos Purex y Thorex reacidificados, en recipientes de 6 pulg de diámetro.
INTRODUCTION

A study has been undertaken to evaluate from economics and hazards standpoints the various methods of highly radioactive liquid and solid waste disposal being developed at Oak Ridge National Laboratory and to evaluate the various operations leading to those ultimate storage methods. It is expected that this study will indicate the optimum combination of preliminary operations and final storage methods out of the large number of combinations possible. Such an evaluation is a necessary prerequisite to the most meaningful experimental study of radioactive waste disposal.

A 6-t (metric)/d plant is assumed, processing 1500 t/yr of uranium converter fuel at a burnup of 10 000 MWe/d and 270 t/yr of thorium converter fuel at a burnup of 20 000 MWe/t. This hypothetical plant would be processing all the fuel from a 15 000-MWe nuclear economy, which may be in existence in the USA by 1975. The preliminary operations to be evaluated are: (1) interim liquid storage; (2) conversion to solids by pot calcination; (3) interim storage of calcined solids; (4) shipment, and (5) removal of significant fission products. The ultimate disposal methods to be evaluated are: (1) calcined solids in salt deposits; (2) calcined solids in vaults; (3) calcined solids in vertical shafts; (4) liquids in salt deposits; (5) liquids by hydrofracture; and (6) liquids in tanks.

Cost estimates of interim liquid storage, conversion to solids by calcination and shipping were completed [1, 2, 3]. Tentative costs for ultimate disposal of calcined solids in salt deposits are given in this symposium by BRADSHAW et al. [4].

HEAT-GENERATION RATE IN PROCESSING-PLANT EFFLUENT

If a stream of radioactive material is accumulated, the change in the number of atoms of any nuclide i in the accumulated stream is given by

\[
\frac{dN_i}{dt} = FC_i - \lambda_i N_i \tag{1}
\]

where \( N_i \) = number of atoms of nuclide \( i \),
\( t \) = time since start of accumulation, hr,
\( F \) = flow-rate of stream, gal/hr,
\( C_i \) = concentration of nuclide \( i \) in stream, atoms/gal,
\( \lambda_i \) = radioactive decay constant, hr\(^{-1}\).

If \( F \) and \( C_i \) are constant with time, eq 1 may be integrated:

\[
\int_0^t dt = \int_0^{N_i} \frac{dN_i}{FC_i - \lambda_i N_i} , \tag{2}
\]

\[
t = \frac{1}{\lambda_i} \ln \frac{FC_i}{FC_i - \lambda_i N_i} \tag{3}
\]
The heat-generation rate in the accumulated stream at any time $t$ may be obtained from

$$N_i = \sum_{i=1}^{n} \frac{F C_i}{\lambda_i} (1 - e^{-\lambda_i t}).$$

(4)

In the calculations, 120 d was assumed to have elapsed between reactor discharge and processing-plant discharge. The uranium-converter fuel was assumed to have been irradiated for $3 \times 10^7$ sec ($\sim 1$ yr) at a flux of $3 \times 10^{13}$ and to have initially $5.1 \times 10^{25}$ atoms of U$^{235}$/t of fuel (2% enriched). The specific waste volumes for the uranium-converter were assumed to be 50 gal/t of fuel for acidic waste and 60 gal/t for neutralized waste.

The correlations of BLOMEKE and TODD [5] were used to calculate the concentrations of 15 nuclides in the 120-day-old waste stream. However, nuclides contributing less than 0.5%, were eliminated, leaving eight nuclides for subsequent calculations. The total heat-generation rate as a function of accumulation time and decay curves following the cessation of accumulation after 0.5 to 30 yr was calculated and plotted (Fig. 1a). The thorium-converter fuel was assumed to have been irradiated for $3 \times 10^7$ sec at a flux of $3 \times 10^{13}$ n/sec-cm$^2$ and to have initially $1.05 \times 10^{26}$ atoms of U$^{233}$/t of fuel [95% ThO$_2$ -5% enriched (93%) UO$_2$]. The specific volumes for the thorium-converter waste were assumed to be 400 gal/t of fuel for acid waste and 642 gal/t for neutralized waste (Table I). The correlations of Blomeke and Todd were again used because a similar comprehensive work for U$^{233}$ has not yet been done and the fission yield curves for U$^{233}$ and U$^{235}$ are not too dissimilar. Heat-generation rates in thorium-converter waste are shown in Fig. 1b.

**TANK-FARM DESIGN AND COSTS**

For purposes of cost estimation, a conceptual design of a tank farm was used and the major items were size estimated. The tanks were assumed to contain cooling coils that would hold the radioactive waste solutions at 140°F. Experience with alkaline waste storage in mild steel and acidic aluminum waste storage in stainless steel has shown that corrosion rates in either system can be expected to average a few tenths of a mil per year at temperatures near 150°F. Pumps would circulate cooling water through the coils and through a heat exchanger, where the primary cooling water would be cooled by exchange with a secondary loop including a cooling tower.

Pumps in the primary loop and heat exchangers would be housed in modular cells with concrete walls 2 ft thick, each cell containing two 2000-ft$^2$ heat exchangers and a 1000-gal/min pump. Thus, in the event of contamination of one primary cooling coil loop, maintenance could be carried
Heat-generation rate in (a) Uranium converter waste from 1500 t/yr of fuel irradiated to 10 000 MWD/t and (b) Thorium converter waste from 270 t/yr of fuel irradiated to 20 000 MWD/t as a function of accumulation and decay time.

**Fig. 1**

- Decay After Accumulation Time of 0.5 y
- Decay After Accumulation Time of 1 y
- Decay After Accumulation Time of 3 y
- Decay After Accumulation Time of 10 y
- Decay After Accumulation Time of 30 y
<table>
<thead>
<tr>
<th>Component</th>
<th>Purex</th>
<th></th>
<th></th>
<th>Thorex</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acidic</td>
<td>Neutralized</td>
<td>Reacidified</td>
<td>Acidic</td>
<td>Neutralized</td>
<td>Reacidified</td>
</tr>
<tr>
<td>Volume, gal/t</td>
<td>50</td>
<td>60</td>
<td>80</td>
<td>400</td>
<td>642</td>
<td>770</td>
</tr>
<tr>
<td>H+, N</td>
<td>7.3</td>
<td>-</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na+, N</td>
<td>0.7</td>
<td>8.4</td>
<td>6.3</td>
<td>-</td>
<td>7.1</td>
<td>5.9</td>
</tr>
<tr>
<td>Fe3+, N</td>
<td>1.1</td>
<td>0.9*</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NO3-, N</td>
<td>8.4</td>
<td>7.0</td>
<td>5.2</td>
<td>6.7</td>
<td>4.2</td>
<td>3.5</td>
</tr>
<tr>
<td>OH-, N</td>
<td>-</td>
<td>1.7*</td>
<td>-</td>
<td>0.5**</td>
<td>1.4</td>
<td>0.2**</td>
</tr>
<tr>
<td>SO4²-, N</td>
<td>0.7</td>
<td>0.6</td>
<td>6.3</td>
<td>-</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>Al3+, N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.2</td>
<td>-</td>
<td>3.7</td>
</tr>
<tr>
<td>AIO2³-, N</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Solids vol., gal/t</td>
<td>7.1</td>
<td>-</td>
<td>13.5</td>
<td>60</td>
<td>-</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>(porous)</td>
<td>(melted)</td>
<td>(porous)</td>
<td>(melted)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NaSO4 + FeO3</td>
<td>NaSO4 + FeO3</td>
<td>A12O3</td>
<td>Na2SO4 + AlO3</td>
<td>Na2SO4 + AlO3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 0.9 of the OH⁻ is precipitated with the Fe³⁺ as Fe(OH)₂.

** Acid deficient: OH⁻ actually present as A(KOH)(NO₃)₂.
out with minimum exposure and with no release of activity to the secondary loop.

Tanks of the Savannah River type were chosen because their design would be more nearly acceptable over a wide range of environments and the resultant cost figure would be more conservative (higher). The tank has internal columns for support and is equipped with cooling coils arranged in both horizontal and vertical banks. A water-cooled reflux condenser and filter are supplied to take care of the heat load in the event of a cooling-system breakdown. Additional facilities include level indicators, sampling and monitoring devices and means for evacuating the tank when the occasion demands. The tops of tanks would lie 6 to 9 ft below grade.

Acidic wastes were assumed stored in stainless-steel tanks with stainless-steel cooling coils and neutralized wastes in mild steel tanks with mild steel coils. In order to estimate the costs of stainless-steel tanks of Savannah River design, a breakdown of Savannah River costs was inspected and those attributable to the cost of the metal were adjusted. Cooling-coil lengths were calculated to take care of the peak heat flux in each tank and coil costs were added to costs for empty tanks.

Costs of mild steel tanks of Savannah River design as a function of tank size were reported by STOCKDALE et al. [6]. A breakdown of costs for installed 750 000-gal tanks shows that about 50% of the total costs were due directly to the metal liners. The costs directly attributable to fabricated metal were assumed to be 5 times as high for stainless steel as for mild steel. If x represents the cost of a mild steel tank of Savannah River design without cooling coils, the cost of a similar stainless-steel tank is given by

\[ x(0.5)(5) + x(0.5) = 3.0x \]  

In the calculations for cooling coil lengths, five waste volumes were chosen in the range 100 000 to 3 000 000 gal and the times required for the accumulation of these volumes were calculated. Corresponding maximum heat-generation rates were obtained from Fig. 1. The cooling coil tubing was chosen to be 3 in internal diam. with a 6 B.W.G. wall. A heat-transfer coefficient for the cooling water inside the tube was estimated at 1000 BTU/hr-ft²-°F from the Dittus-Boelter equation (Reynolds number \(1.88 \times 10^6\), Prandtl number 4.1). A coefficient of 85 BTU/hr-ft²-°F was estimated for the outer surface of the tube from a nomograph in McADAMS' book, assuming waste with the properties of water [7]. The resultant overall coefficient was calculated to be 83 BTU/hr-ft²-°F, but a value of 60 was used in order to be conservative. The log mean temperature difference was calculated to be 27.3°F. Although the required lengths of cooling coils are of the order of several miles in the larger tanks (Table II), the highest ratio of coil volume to tank volume is only about 1/10.

Cooling coil costs were based on a cost of $2.50/ft for fabricated and installed mild steel coils, including valves and fittings, and $15.00/ft for stainless-steel coils. These costs assume that labour plus indirect costs are equal to 1.15 times the material costs.

In calculating the yearly costs for tanks that must be charged to the yearly electricity production, the following were assumed: (1) tanks costs
### TOTAL INSTALLED COSTS OF TANKS WITH COOLING COILS

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Tank size, gal</th>
<th>Cost of tank without coils</th>
<th>Length of coil, (ft)</th>
<th>Cost of coil</th>
<th>Total tank cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Purex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>110 000</td>
<td>$5.65 \times 10^5</td>
<td>20 400</td>
<td>3.93</td>
<td>$8.71 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>212 000</td>
<td>9.46</td>
<td>26 720</td>
<td>4.79</td>
<td>13.39</td>
</tr>
<tr>
<td></td>
<td>415 000</td>
<td>15.30</td>
<td>31 900</td>
<td>5.83</td>
<td>20.13</td>
</tr>
<tr>
<td></td>
<td>1 018 000</td>
<td>30.50</td>
<td>39 200</td>
<td>8.10</td>
<td>38.60</td>
</tr>
<tr>
<td></td>
<td>2 274 000</td>
<td>53.40</td>
<td>54 000</td>
<td>13.39</td>
<td>61.50</td>
</tr>
<tr>
<td>Neutralized Purex</td>
<td>109 000</td>
<td>1.85 \times 10^5</td>
<td>18 700</td>
<td>0.47 \times 10^5</td>
<td>2.32 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>212 000</td>
<td>3.10</td>
<td>24 700</td>
<td>0.62</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>414 000</td>
<td>5.00</td>
<td>30 600</td>
<td>0.76</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>1 018 000</td>
<td>10.00</td>
<td>37 700</td>
<td>0.94</td>
<td>10.94</td>
</tr>
<tr>
<td></td>
<td>3 026 000</td>
<td>21.50</td>
<td>55 200</td>
<td>1.38</td>
<td>22.88</td>
</tr>
<tr>
<td>Acid Thorex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>103 000</td>
<td>5.34 \times 10^5</td>
<td>6 500</td>
<td>0.97 \times 10^5</td>
<td>6.31 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>204 000</td>
<td>8.84</td>
<td>8 500</td>
<td>1.27</td>
<td>10.11</td>
</tr>
<tr>
<td></td>
<td>405 000</td>
<td>14.95</td>
<td>10 500</td>
<td>1.57</td>
<td>16.52</td>
</tr>
<tr>
<td></td>
<td>1 006 000</td>
<td>30.50</td>
<td>13 500</td>
<td>2.02</td>
<td>32.52</td>
</tr>
<tr>
<td></td>
<td>3 009 000</td>
<td>65.60</td>
<td>18 600</td>
<td>2.79</td>
<td>68.39</td>
</tr>
<tr>
<td>Neutralized Thorex</td>
<td>102 000</td>
<td>1.75 \times 10^5</td>
<td>5 000</td>
<td>0.12 \times 10^5</td>
<td>1.87 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>203 000</td>
<td>2.90</td>
<td>7 000</td>
<td>0.17</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>404 000</td>
<td>4.90</td>
<td>9 000</td>
<td>0.22</td>
<td>5.12</td>
</tr>
<tr>
<td></td>
<td>1 006 000</td>
<td>9.80</td>
<td>12 000</td>
<td>0.30</td>
<td>10.10</td>
</tr>
<tr>
<td></td>
<td>3 008 000</td>
<td>21.40</td>
<td>16 000</td>
<td>0.40</td>
<td>21.80</td>
</tr>
</tbody>
</table>

are amortized over a period of 60 yr; (2) capital invested in tanks will be charged an interest rate of 4%/yr; (3) present worth capital can be invested at 4%/yr to accumulate the required funds for building tanks as they become needed; (4) one spare tank (for each waste type) will be built initially; (5) the number of operating tanks, exclusive of the spare, is such that there will always be a total freeboard equivalent to one tank volume; (6) after the initial filling cycle, waste will be removed from the farm at the same rate it enters. Based on the above assumptions the required number of tanks for each waste type, including the spare, is

\[ N = 1 + 2(2F + D)/2F = 3 + D/F \]  

where \( F \) and \( D \) are the filling and dead storage times, respectively, and the emptying time is assumed equal to the filling time. However, for each waste, only two tanks are built initially, the spare and one operating tank, and the remainder are built as needed.

Repayment costs calculations included a fixed sum of $125 000 per tank to cover three items which are proportional to the number of tanks: $85 000
for piping, ventilating and waste-line encasement; $ 15 000 for sampling facilities; and $ 25 000 for electrics and instruments. As an example, the waste volume of an acidic Purex tank with a filling time of one year and a dead storage time of one year will be 75 000 gal and the volume including coils will be 83 000 gal. The cost is found to be $ 730 000. To this is added the fixed sum of $ 125 000, giving a total of $ 855 000. This value times the annuity factor 0.0442 give a repayment cost per year of $ 37 800.

The total number of tanks required is \( N = 3 + \frac{1}{1} = 4 \). Two of these tanks will be built immediately (the initial tank plus the spare) and their present worth factor will be 2 (unity for each tank). At the end of the first year the first tank will be full and another tank must be built, but the present worth, at 4% interest, of this tank is only 0.9615. At the end of the second year the second tank will be full and a fourth tank, which has a present worth of 0.9246, must be built. At the end of the third year the initial tank will have been filled for one year, set in dead storage for one year, and emptied for one year so that now the cycle can be repeated. Thus, the total present worth factor is 3.8861. This factor times the $ 37 800/yr per tank gives a total tank cost per year of $ 147 000.

In Fig. 2 a family of curves of tank capital cost per year for different dead storage times is plotted against the interim liquid-storage time, where interim storage is defined as filling time plus dead-storage time. Each curve, for a fixed dead-storage time, has a minimum value at some value of interim liquid-storage time. The rise in the curve at the low end is due to the fact that, as the interim storage time approaches the dead-storage time, the number of required tanks becomes large, the volume of an individual tank becomes small and the cost per gallon of capacity increases with decreasing tank size. The rise in the curve for longer storage times is due to the increasing total capacity requirements.

The dashed curves in Fig. 2a and b are the loci of minimum tank capital costs per year as a function of the interim liquid-storage time. Tangency of these curves is along relatively flat sections of the fixed dead-storage curves, indicating a more or less broad optimum relation between dead time and interim storage time.

Items other than tanks which were cost estimated are: (1) cooling towers; (2) heat exchangers; (3) pumps for primary and secondary circuits; (4) electric motors for pumps; and (5) cells and secondary containment for housing heat exchangers and primary loop pumps.

Tank-farm costs as a function of storage time for acidic Purex and Thorex wastes are summarized in Table III. Items 1 through 5 were amortized over a 20-yr period and the remaining item over 60 yr. Tank-farm costs are the same for neutralized Purex as for acidic Purex and the same for neutralized Thorex as for acidic Thorex.

**TOTAL COSTS FOR INTERIM LIQUID STORAGE**

Electric power costs were based on the following assumptions: (1) cost of electric power is 1¢/kWh; (2) cooling tower and heat-exchanger pump motors are 90% efficient; (3) all pumps (excluding spares) operate continuously; (4) all other power consumptions are negligible.
Fig. 2
Tank capital cost per year as a function of interim storage time with parameters of dead time for (a) Purex waste and (b) Thorex waste. --- indicates locus of optimum dead times
### TABLE III

**TANK-FARM CAPITAL COSTS**

<table>
<thead>
<tr>
<th>Item No.</th>
<th>0.5 yr</th>
<th>1 yr</th>
<th>3 yr</th>
<th>10 yr</th>
<th>30 yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6 x 10^7</td>
<td>2.3 x 10^7</td>
<td>3.5 x 10^7</td>
<td>4.75 x 10^7</td>
<td>6.8 x 10^8</td>
</tr>
<tr>
<td>Cooling-tower cost</td>
<td>$32,000</td>
<td>$46,000</td>
<td>$70,000</td>
<td>$95,000</td>
<td>$136,000</td>
</tr>
<tr>
<td>2</td>
<td>5,300</td>
<td>7,700</td>
<td>11,600</td>
<td>15,800</td>
<td>22,700</td>
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<tr>
<td>Heat-exchanger surface, ft²</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Number of 2000-ft² units</td>
<td>$21,000</td>
<td>$28,000</td>
<td>$42,000</td>
<td>$56,000</td>
<td>$84,000</td>
</tr>
<tr>
<td>Cost ($7,000 ea.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling-tower pump duty, gal/min</td>
<td>3,200</td>
<td>4,600</td>
<td>7,000</td>
<td>9,500</td>
<td>13,600</td>
</tr>
<tr>
<td>Number of 1000-gal/min units</td>
<td>8</td>
<td>10</td>
<td>14</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>Cost ($3,750 ea.)</td>
<td>$30,000</td>
<td>$37,500</td>
<td>$52,500</td>
<td>$75,000</td>
<td>$105,000</td>
</tr>
<tr>
<td>Tank-coil pump duty, gal/min</td>
<td>1,000</td>
<td>1,500</td>
<td>2,300</td>
<td>3,200</td>
<td>4,500</td>
</tr>
<tr>
<td>Number of 1000-gal/min units</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Cost ($12,500 ea.)</td>
<td>$7,500</td>
<td>$15,000</td>
<td>$22,500</td>
<td>$30,000</td>
<td>$37,500</td>
</tr>
<tr>
<td>Electric pump motors, 40-HP</td>
<td>10</td>
<td>14</td>
<td>20</td>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>(1 spare ea.)</td>
<td>$12,500</td>
<td>$17,500</td>
<td>$25,000</td>
<td>$35,000</td>
<td>$47,500</td>
</tr>
<tr>
<td>Pump and heat-exchanger cell and secondary containment</td>
<td>$76,000</td>
<td>$76,000</td>
<td>$99,000</td>
<td>$121,000</td>
<td>$162,000</td>
</tr>
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</table>

**Acid Thorex, 108,000 gal/yr**

<table>
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<tr>
<th>Item No.</th>
<th>0.63 x 10^7</th>
<th>0.87 x 10^7</th>
<th>1.3 x 10^7</th>
<th>1.80 x 10^7</th>
<th>2.5 x 10^8</th>
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<tbody>
<tr>
<td>1</td>
<td>12,600</td>
<td>17,400</td>
<td>26,000</td>
<td>36,000</td>
<td>50,000</td>
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<tr>
<td>Cooling-tower cost</td>
<td>$2,100</td>
<td>$2,900</td>
<td>$4,330</td>
<td>$6,000</td>
<td>$8,330</td>
</tr>
<tr>
<td>Heat-exchanger surface, ft²</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Number of 2000-ft² units</td>
<td>$14,000</td>
<td>$14,000</td>
<td>$21,000</td>
<td>$21,000</td>
<td>$35,000</td>
</tr>
<tr>
<td>Cost ($7,000 ea.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling-tower pump duty, gal/min</td>
<td>1,300</td>
<td>1,740</td>
<td>2,600</td>
<td>3,600</td>
<td>5,000</td>
</tr>
<tr>
<td>Number of 1000-gal/min units</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Cost ($3,750 ea.)</td>
<td>$15,000</td>
<td>$15,000</td>
<td>$22,500</td>
<td>$30,000</td>
<td>$37,500</td>
</tr>
<tr>
<td>Tank coil pump duty, gal/min</td>
<td>420</td>
<td>600</td>
<td>900</td>
<td>1,200</td>
<td>1,700</td>
</tr>
<tr>
<td>Number of 1000-gal/min units</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Cost ($12,500 ea.)</td>
<td>$7,500</td>
<td>$7,500</td>
<td>$7,500</td>
<td>$15,000</td>
<td>$15,000</td>
</tr>
<tr>
<td>Electric pump motors, 40-HP</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>(1 spare ea.)</td>
<td>$7,500</td>
<td>$7,500</td>
<td>$10,000</td>
<td>$15,000</td>
<td>$17,500</td>
</tr>
<tr>
<td>Pump and heat-exchanger cell and secondary containment</td>
<td>$51,000</td>
<td>$51,000</td>
<td>$76,000</td>
<td>$76,000</td>
<td>$99,000</td>
</tr>
</tbody>
</table>
Yearly labour costs for operation of the tank farm were assumed to be the same for any combination of waste types stored and for any storage time. Total yearly costs were estimated to be $100,000 based on 8 man-years at $12,500 per man-year, including overhead. The manpower breakdown is: (1) operation and continuous surveillance will require four shift operators plus a supervisor who fills in as a relief operator; (2) maintenance and miscellaneous services will require three man-years (available on as-needed basis from the processing plant).

The wastes that accumulate in one year are the result of continuous operation of 56,000 MW of thermal power generating capacity (1500 t/yr of uranium converter fuel and 270 t/yr of thorium converter fuel, irradiated to 10,000 and 20,000 MWd/t, respectively) with a thermal efficiency of 27%. The electrical capacity is thus 15,000 MW and the total electrical power produced is $1.31 \times 10^{11}$ kWh(e)/yr.

In Fig. 3 the total costs of interim liquid storage are plotted as a function of the storage time. The cost varies from $1.7 \times 10^{-3}$ to $2.2 \times 10^{-3}$ mill/kwh(e) for 0.5 yr storage to $5.1 \times 10^{-3}$ to $9.5 \times 10^{-3}$ mill for 30 yr storage depending on waste combinations chosen. These costs assume that, for a given interim storage period, the optimum dead-storage period is used.

![Fig. 3](image)

Cost of interim liquid storage as a function of storage time for all combinations of acid and alkaline Purex and Thorex wastes

**POT-CALCINATION PROCESS DESCRIPTION**

In the proposed process [8] the waste is fed to an evaporator together with nitric acid or water to maintain the acid concentration in the evaporator
below 6 M to minimize ruthenium volatilization. Evaporation may be either batch or continuous; a catch tank is used between the evaporator and calciner in batch operations. The evaporator concentrates go to an electrically heated pot at essentially their initial concentrations, where they are evaporated to dryness and calcined to 900°C. Chemical additives, such as calcium or magnesium salts and phosphorous acid may be added before calcination to decrease sulphate and fission-product volatility or to produce a melt in the pot after calcination. After being filled with calcined solids, the stainless-steel pot will be sealed and used as both the shipping and permanent storage vessel. About 90% of the nitrogen oxides in the calciner off-gas can be adsorbed during condensation of water vapour in the evaporator condenser, the remainder in the rectifier reflux condenser. About 1 ft³ of non-condensible gas per gallon of feed is anticipated in relatively leak-tight process equipment; only a small final absolute filter and gas clean-up system will be required.

The Purex and Thorex wastes entering the calcination plant may be in acidic or neutralized form, depending on which form was chosen for interim liquid storage. If either or both are neutralized, they must be reacidified to avoid, during calcination, the formation of solid sodium nitrate, which is not sufficiently stable in the presence of high temperatures and radiation for ultimate storage. Chemical compositions of acidic, neutralized, and reacidified (with sulphuric acid) Purex and Thorex wastes are given in Table I. The compositions are not important to this study except as they affect the volume reduction factor in passing from the liquid to the solid phase.

Waste volumes per metric ton of fuel processed are listed for the waste types in Table I. Specific volumes for liquid wastes entering the plant range from 50 gal/t for acid Purex to 770 gal/t for reacidified Thorex, and for wastes after calcination range from 7.1 gal/t for acid Purex to 133 for reacidified Thorex.

The processing cycle consists of three phases: (1) solids deposition, during which liquid waste is pumped into the vessel at a sufficient rate to maintain a constant liquid level near the top of the vessel and the walls are held at 900°C, so that the vessel fills with solids by evaporation; (2) calcination, during which the solid is heated to 900°C to drive off volatile constituents; and (3) change-out, during which feed and off-gas lines are detached from a filled and calcined vessel, a storage fitting is welded on the top, the filled vessel is replaced by an empty one, and feed and off-gas lines are attached. Melting occurs during calcination with reacidified wastes because of the low melting point of Na₂SO₄ (884°C), so that after the calcination only about the lower half of the vessel is occupied. It might be desirable with a reacidified waste to allow the melt to freeze after calcination and repeat the solids deposition and calcination parts of the cycle to improve utilization of space in the vessel.

Engineering studies of processing rates in 6- and 8-in-diam. by 7-ft-high calcination vessels have been carried out with acidic Purex, Darex, and TBP-25 wastes and reacidified Purex waste [9-11]. The TBP-25 waste is similar to Thorex waste, both being composed mostly of aluminium nitrate and nitric acid and both being about 1.5 M in aluminium. Hence the results
of the experimental work with TBP-25 waste may be applied to Thorex waste also. Engineering studies showed that the average processing rate during filling is directly proportional to the length of the calcination vessel and independent of the diameter.

The calcination vessel height was fixed at 10 ft for this study, with the lower 8 ft designated as active heat-transfer surface and the upper 2 ft as a vapour-liquid disengaging space. From processing rate considerations, the vessel should be as long as practicable, but a length exceeding 10 ft was considered impracticable for handling, shielding and transportation during and after calcination. From the engineering studies, an average processing rate of 26.7 l/hr was calculated for acidic and reacidified Purex and Thorex wastes for a vessel with an active height of 8 ft and in which the solids deposition is terminated when the active volume is 90% filled with solids. This processing rate and the specific waste volumes in Table I were used to calculate the number of calcination vessels required per year and the number of calcination units working in parallel (or processing lines) for these four waste types for vessel diameters of 6, 12 and 24 in. Calcination and change-out times of 3 and 8 hr were assumed, both of which are thought to be conservative.

The number of calcination vessels per year and number of processing lines were also calculated for the production of an acidic Thorex glass in 6-in-diam, cylinders, based on United Kingdom pilot-plant information for the volume reduction factor and the processing cycle time [12]. Other vessel diameters were not considered for the glass because the effect of diameter on cycle time was not given by the United Kingdom work. The glass is a silica-borax-alumina type, containing about 30% Al₂O₃ and melting at 1050 - 1100°C. This composition corresponds to a specific volume of 78 gal/t. A cycle time of 65 hr was assumed, based on the United Kingdom estimate of 48 hr for a 5-ft-high vessel filled to 3.75 ft.

The numbers of calcination vessels required per year ranged from 58 for acidic Purex in 24-in-diam. vessels to 6170 for reacidified Thorex in 6-in-diam. vessels (Table IV).

The numbers of processing lines required for these wastes, allowing 15 to 20% downtime, ranged from 2 for acidic Purex in 12- and 24-in-diam. vessels to 16 for acidic Thorex glass in 6-in-diam. vessels (Table IV). An example calculation for reacidified Purex in a 12-in-diam. vessel follows:

**Occupied volume of vessel** = \( \pi (0.5)^2 (4) (7.48) = 23.3 \text{ gal} \)

**Filling rate** = \( (16.7 \text{ liters liquid/hr}) (13.5/80) (1 \text{ gal/3.79 l}) \)

\[ = 1.19 \text{ gal solid/hr} \]

Therefore the processing cycle is

- Filling time 19.7 hr
- Calcination 3
- Change-out 8

\[ = 30.7 \text{ hr} \]

**Waste volume/yr** = \( (1500 \text{ t/yr}) (13.5 \text{ gal/t}) \)

\[ = 20300 \text{ gal solid/yr} \]
<table>
<thead>
<tr>
<th>Waste type</th>
<th>Number of calcination vessels</th>
<th>Number of lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Purex</td>
<td>925</td>
<td>231</td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>3490</td>
<td>872</td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>2320</td>
<td>580</td>
</tr>
<tr>
<td>filled twice</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidic Thorex</td>
<td>1390</td>
<td>348</td>
</tr>
<tr>
<td>Acidic Thorex glass</td>
<td>1800</td>
<td>-</td>
</tr>
<tr>
<td>Reacidified Thorex</td>
<td>6170</td>
<td>1540</td>
</tr>
<tr>
<td>filled twice</td>
<td>4110</td>
<td>1028</td>
</tr>
</tbody>
</table>

TABLE IV
NUMBERS OF CALCINATION VESSELS PER YEAR AND PROCESS LINES REQUIRED FOR WASTES FROM 6-t/d PROCESSING PLANT
Number of vessels/yr = (20 300)(1/23.3) = 872

Number of processing lines = (30.7 hr/vessel)(872 vessels/yr) x

\[ \frac{4 \text{ lines required}}{1 \text{ yr}/8750 \text{ hr}} = 3.06 \]

In calculating the time cycle for filling twice, it was assumed that 2 hr was required for melting and freezing in between the two fillings. Thus the total filling time for reacidified Purex in a 12-in-diam. vessel filled twice would be 41.4 hr and the total cycle time 52.4 hr. The vessel would then have been filled to a 6-ft height.

Estimates of calcination vessel costs used in this study were $500, $855, and $2515 each for 6, 12, and 24-in-diam. vessels, respectively, and were similar in design to those currently proposed for radioactive pilot-plant testing [8].

CAPITAL COSTS FOR POT CALCINATION

The processing-plant cell block was considered to be made up of three areas: (1) calcination area, (2) evaporator and off-gas equipment area, and (3) testing and decontamination area. The required cell-floor area for calcination was assumed to be directly proportional to the number of processing lines and independent of vessel diameter, and was taken to be 100 ft² per process line. An evaporator and off-gas cell area of 200 ft² for a single processing line was assumed. Since the evaporator and off-gas equipment duty peaks sharply during operation of a single processing line, the peaks were assumed to be staggered at equal time intervals, and a plant peak-load factor was obtained from a normalized typical duty profile to which a coincidence factor was added as a conservative measure. The required area for evaporator and off-gas equipment was then assumed proportional to the square root of this plant peak-load factor. The required cell-floor area for decontamination and testing was taken to be 200 ft² plus 9 ft² per vessel for a 3-d production hold-up.

Total cell-floor areas for all 90 combinations of Purex and Thorex waste types in the three vessel diameters were calculated. The range is from 1090 ft² for an acidic Purex-acidic Thorex plant with 24-in-diam. calcination vessels for both waste types to 3490 ft² for a reacidified Purex-acidic Thorex glass plant with 6-in-diam. calcination vessels for both. Fractions of the three sub-areas correlated well with total cell area and were roughly independent of waste type and vessel size, so that three total cell areas spanning the range could be chosen for cost estimation, with costs of intermediate plant sizes to be obtained from a plot. The three plant sizes are 1200, 2300 and 3200 ft².

Operating areas were assumed to be 15 ft wide and to extend the full length and on both sides of the cell block. For plants with various total cell areas the width was assumed constant and only the length of the building was allowed to vary.

Shielding calculations showed that wall thicknesses of 5-7.4 ft of ordinary concrete are required for processing Purex wastes decayed from 30 yr to 120 d. Building costs were obtained by cost-estimating the following items for each of the three plant sizes with 5-, 6-, and 7-ft shielding walls: (1)
cell blocks (figures at $100/\text{yd}^3$ of concrete in place); (2) operating areas, including crane house (operating areas figures at $1.50/\text{ft}^3$, crane house $1/\text{ft}^3$; (3) cell windows (zinc bromide figured at $225/\text{ft}^3$ installed; windows 2 ft square on operating side and 4 ft square on cell side for 5-ft-thick wall and proportionally larger on cell side for thicker walls, windows spaced approximately 8 ft on centres); (4) bridge crane (100 t, to lift 24-\(\times\)10-\(\times\)5-ft roof plug); (5) lead doors (figured at 30 lb installed; (6) stainless-steel cell lining on all cell floors and walls ($10/\text{ft}^2$); (7) sampling stations (three for each waste type, six total); (8) cell ventilation and exhaust (assumed one cell block air change per 10 min); (9) stack for cell ventilation and off-gas (2 ft internal diam. by 200 ft high); (10) site preparation and service facilities. To the totals of the above 10 items were added 40% for construction overhead, 15% for engineering and 20% for contingencies. Total building costs thus ranged from $1.7 \times 10^6$ for a 1200 ft\(^2\) cell block with 5-ft-thick walls to $3.9 \times 10^6$ for a 3200-ft\(^2\) cell block with 7-ft-thick walls. Building costs were amortized over 50 yr at 4% interest, resulting in annual costs ranging from $79 000 to $181 000.

Process equipment items were separated into two groups, those amortized over 20 yr and those over 10 yr. Twenty-year items estimated were: (1) feed and off-gas equipment (includes storage tanks, pumps, evaporators, and condenser and does not vary with the number of processing lines); (2) furnaces (one per processing line at $12 000 each regardless of diameter since average processing rate is independent of calcination vessel diameter); (3) remote welder; (4) remote manipulators (General Mills model 550 plus 3-t hoist at $80 000 each); (5) pipe, valves, fittings, etc. (calculated at 70% of total of the first three items); (6) electrical (10% of total of first four items), (7) insulation (5% of total of first four items); (8) sampling equipment. To the above items were added 40, 15, and 20% for construction overhead, engineering, and contingencies, respectively. Total 20-yr equipment costs ranged from $865 000 for a 1200-ft cell block to $1 715 000 for a 3200-ft\(^2\) cell block. Amortized over 20 yr at 4% interest, the annual costs ranged from $64 000 to $126 000.

Canned rotor pumps and instrumentation were assumed to be 10-yr items. For purposes of cost estimation, instruments were grouped as health physics and process instrumentation and instruments directly associated with control and monitoring of the calcination vessel. Both health physics and process instrumentation were assumed to be independent of plant size. Processing line instrumentation was figured at $10 000 per line. Yearly costs were $26 500, $46 000 and $58 000 for the three hypothetical plants.

Total capital costs per year, figures as the totals of the 50-, 20-, and 10-yr items, and ranged from $169 000 for the 1200-ft\(^2\) cell area plant with 5-ft-thick walls to $365 000 for the 3200-ft\(^2\) plant with 7-ft-thick walls (Fig. 4).

**TOTAL COSTS FOR POT CALCINATION**

Of the conventional operating costs, only labour costs were not negligible when compared with calcination vessel and capital costs. The labour force was broken down into six occupations: (1) manipulator operators;
(2) process-line operators (one operator to monitor and control two process lines); (3) remote-welder operator; (4) instrument mechanic; (5) health physics technician; and (6) supervisor. Labour costs were estimated for three plant sizes spanning the range 1200, 2300 and 3200 ft$^2$ and were plotted against plant size for use in obtaining labour costs of intermediate-sized plants.

The labour force is 41 men for a 1200-ft$^2$ plant with six processing lines and 84 men for a 3200-ft$^2$ plant with 19 processing lines. For each round-the-clock job, 5 man-years/yr were assumed. Thus, for example, 10 men would be required to operate the two manipulators in the 1200-ft$^2$ plant and 15 men would be required to operate the six process lines. Average salaries of $7500/yr were assumed. Yearly maintenance and repair costs for the equipment (in addition to the instrument mechanic's salary) were estimated at 10% of the capital invested in process equipment. An overhead charge of 50% was added, giving operating costs ranging from $650 000/yr for a 1200-ft$^2$ plant to $1 330 000/yr for a 3200 ft$^2$ plant.

Total annual costs of plants handling all 12 combinations of waste types of ages 0.33, 1, 3, 10 and 30 yr in all nine combinations of vessel diameters were calculated. As an example, a plant processing 1-year-decayed acidic Purex and acidic Thorex wastes in 6-in-diam. vessels would require 7-ft-thick cell walls of ordinary concrete and would have the following yearly costs:

![Graph showing total capital cost per year as a function of shield wall thickness and plant-floor area.](image-url)
Calcination vessels $1,157,000
Operating costs 745,000
Capital 208,000
Total $2,110,000

This cost corresponds to $1.61 \times 10^{-2}$ mill/kWh(e).

Some of the possible combinations of waste ages and vessel diameters are not permissible because of the excessive temperatures that would occur in the calcined solid wastes due to internal heat generation. Curves of specific heat-generation rates as a function of time since reactor discharge (Fig. 5) were obtained from plots of total heat-generation rate versus interim liquid storage time (Fig. 1) and the known flow rates of processing wastes.

Fig. 5

Heat-generation rate as a function of age for calcined solid wastes assuming optimum dead-storage times
from the 6-t/d plant. The temperature drop between the axis and wall of a solid cylinder with internal heat generation is given by

\[ T_{\text{axis}} - T_{\text{wall}} = \frac{QR^2}{4k} \]  

(8)

where \( T \) = temperature, °F,

\( Q \) = heat-generation rate, BTU hr\(^{-1}\) ft\(^{-3}\),

\( R \) = radius of cylinder, ft,

\( k \) = thermal conductivity of solid, BTU hr\(^{-1}\) ft\(^{-1}\) °F\(^{-1}\).

Assuming a maximum allowable temperature difference of 1350°F, which would allow the axis of the vessel to reach 1650°F, the maximum calcination temperature, while the surface was held at 300°F, maximum permissible heat-generation rates were calculated for the three vessel diameters, using the following thermal conductivities for the calcined solids:

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Thermal conductivity, BTU hr(^{-1}) ft(^{-1}) °F(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Purex</td>
<td>0.25</td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>0.75</td>
</tr>
<tr>
<td>Acidic Thorax</td>
<td>0.20</td>
</tr>
<tr>
<td>Reacidified Thorax</td>
<td>0.67</td>
</tr>
<tr>
<td>Acidic Thorax glass</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Aging had negligible effect on costs for processing in a given vessel size because vessel and operating costs were much higher than capital costs in all cases. Aging permits larger vessels to be used, however, and costs for processing in 6-in-diam. vessels were 2 to 3 times as high as for processing in 24-in-diam. vessels.

The lowest cost was \( 0.87 \times 10^{-2} \) mill/kWh (e) for processing acidic Purex and Thorax wastes in 24-in-diam. vessels, and the highest was \( 5.0 \times 10^{-2} \) mill/kWh (e) for processing reacidified Purex and Thorax wastes in 6-in-diam. vessels (Table V). About 7 yr of interim liquid storage would be required before acidic Purex waste could be processed in 24-in-diam. vessels.

EFFECT OF AGING ON SHIPPING-CASK SIZE

Heat-transfer calculations were carried out to determine waste ages and permissible carrier sizes in the absence of refrigerating equipment or liquid coolants. Shipping carriers were assumed to be right circular cylinders, with the inner diameter of each carrier and the number of waste cylinders contained by it determined by the necessity of keeping calcined solid temperatures below the maximum calcination temperature of 1650°F. Waste cylinders were assumed held in square arrays as in Fig. 6. A spacing structure would be required to hold the cylinders in the array as shown.

Heat transfer between cylinders in the array and between cylinders and the inner surface of the carrier was calculated as if radiant heat transfer alone was contributing. Cylinders were assumed to have radially symmetric
TABLE V
POT-CALCINATION COSTS AS AFFECTED BY WASTES TYPES AND VESSEL SIZES

<table>
<thead>
<tr>
<th>Waste type</th>
<th>Total processing cost, mill/kWh(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vessels</td>
</tr>
<tr>
<td>Acidic Purex-acidic Thorex</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Acidic Purex-Acidic Thorex glass</td>
<td>2.2</td>
</tr>
<tr>
<td>Acidic Purex-reacidified Thorex</td>
<td>3.8</td>
</tr>
<tr>
<td>Reacidified Purex-acidic Thorex</td>
<td>2.8</td>
</tr>
<tr>
<td>Reacidified Purex-acidic Thorex glass</td>
<td>3.4</td>
</tr>
<tr>
<td>Reacidified Purex-reacidified Thorex</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Fig. 6
Plan view sketch of carriers for cylinders of calcined wastes

Temperature distributions. The conservative procedure of neglecting convective heat transfer and conductive heat transfer through the spacing structure tends to compensate for the less-than-perfect thermal conductivity of the waste, which would tend to impose secondary asymmetric temperature gradients on the cylinders. Temperatures within the carriers were calculated from the methods developed by WATSON in his study of heat transfer in spent reactor fuel-rod assemblies [13]. Temperature differences across the carrier wall are sufficiently small for the different thermal conductivities of lead, iron, and uranium not to affect appreciably the final results. For some cases with lead carriers, the limiting ages were con-
### TABLE VI
MINIMUM PERMISSIBLE SHIPPING AGES FOR CYLINDERS OF CALCINED WASTES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Purex</td>
<td>2.40 yr&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.75 yr&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.35 yr</td>
<td>3.80 yr</td>
<td>3.30 yr</td>
<td>11.30 yr</td>
<td>8.60 yr</td>
<td></td>
</tr>
<tr>
<td>Reacidified Purex</td>
<td>1.00&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.69&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.39</td>
<td>1.40&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.00&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.00</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>Acidic Thorex</td>
<td>0.66&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.47</td>
<td>0.33</td>
<td>1.35</td>
<td>1.15</td>
<td>3.50</td>
<td>3.20</td>
<td></td>
</tr>
<tr>
<td>Reacidified Thorex</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.82</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Acidic Thorex glass</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> 2.80 yr for lead carriers  
<sup>b</sup> 1.90 yr for lead carriers  
<sup>c</sup> 1.70 yr for lead carriers  
<sup>d</sup> 1.10 yr for lead carriers  
<sup>e</sup> 0.82 yr for lead carriers  
<sup>f</sup> 0.63 yr for lead carriers
trolled by the melting point of the lead rather than the maximum waste cylinder temperature.

Carrier inner diameters ranged from 60 in for thirty-six 6-in-diam. cylinders, nine 12-in-diam. cylinders, and four 24-in-diam. cylinders to 16 in for four 6-in-diam. cylinders or one 12-in-diam. cylinder. The exterior surfaces of the carriers were assumed to have fins which halved the heat flux at that surface. Minimum ages ranged from 0.33 yr, the assumed age at the time of discharge from the fuel-processing facility, for many cases to 11.3 yr for shipping acidic Purex waste in a carrier containing four 24-in-diam. cylinders (Table VI). A carrier for more than thirty-six 6-in-diam. cylinders, nine 12-in-diam. cylinders or four 24-in-diam. cylinders would weigh more than 100 t and was assumed to be unmanageably large.

SHIPPING COSTS

Costs were minimum for the 60-in-internal diam. carriers because the ratio of carrier volume per pound of shielding weight increased as the carrier size increased. Shielding thicknesses of lead for the 60-in-internal diam. carriers to give 10 mrem/hr at 3 m at minimum shipping ages ranged from 21 to 25 cm for the various waste types. Iron shielding thicknesses were higher by a factor of 1.7 and uranium thicknesses lower by a factor of 0.56 than lead. Weights and costs for these carriers at minimum ages were about 100 t and $50 000 for iron carriers, 80 t and $120 000 for lead carriers and 65 t and $650 000 for uranium carriers. Carriers loaded with calcined wastes weigh about 15% more than when empty. The total shipping costs calculated for round trip distances of 1000, 2000 and 3000 miles were the sums of carrier, rail freight and handling charges.

Rail freight rates of $24, $44 and $65/t for loaded carriers were assumed for distances of 500, 1000, and 1500 miles with rates 30% less for return of the empty carriers. Handling costs were assumed to be $360 per trip plus $13 000/yr amortization of a 100-t bridge crane. Shipping costs were lowest in all cases for lead carriers, but in some cases the use of lead carriers required higher minimum ages. Costs in lead carriers range from 0.70 X 10^{-3} mill/kWh (e) for acidic Purex in four 24-in-diam. cylinders per carrier at 1000 miles to 32.3 X 10^{-3} mill/kWh (e) for the shipment of reacidified Thorex in smaller cylinders at 3000 miles (Figs. 7 and 8).

CONCLUSIONS

Final conclusions on the optimum conditions for liquid storage, calcination, and shipping cannot be drawn until the effects of age, cylinder size, and waste composition on the costs of a particular disposal method are known; however, based on the results of the three parts of the study completed to date, acidic storage to a sufficient age to permit calcination and shipping in 24-in-diam. cylinders appears to give lowest costs. The total cost for these three operations can be as low as 2 X 10^{-2} mill/kWh (e).
Fig. 7
Shipping costs using carriers containing thirty-six 6-in-diam. cylinders or nine 12-in-diam. cylinders
**Power-Reacto**, Reactor Fu**- Re**-Processing Wastes

![Graph showing shipping costs using carriers containing four 24-in-diam. cylinders](image)

**Fig. 8**

Shipping costs using carriers containing four 24-in-diam. cylinders

**References**


L. THIRIET: Does the interest rate of 4% on investments which you use in your study correspond to the average rate for financing AEC investments or to some other criterion?

J. T. ROBERTS (on behalf of J. J. PERONA et al.): In the United States, as elsewhere, interest rates are a matter of controversy. This rate in question presupposes a Government-owned installation. The current rate of interest on United States Government bonds is about 4% per annum. The cost in all cases would be significantly higher if Union Carbide operated the installations privately instead of as a contractor for the AEC.

J. A. BUCKHAM: In determining the volume of pot-calcined solids, about half of which are fission-product oxides, what data did you use or what assumptions did you make to determine the volume occupied by such oxides? For example, did you use porosity data on calcined solids containing simulated fission products?

J. T. ROBERTS: Small-scale laboratory experiments done at Oak Ridge with simulated high-burnup fission-product wastes gave approximately the same porosities for calcined solids as those obtained in similar experiments with simulated low-burnup wastes. It is hoped that this result will be confirmed on an engineering scale. It should be mentioned that "simulated fission products" can be quite expensive in the amounts required for experiments, on an engineering scale.

J. A. McBRIDE: I have two comments on this paper. First, the Atomic Energy Division of the Phillips Petroleum Company is issuing a report on an economic study of fluid-bed calcination and storage. Using the same assumptions as those reported by Dr. Roberts for the ORNL work, as well as cost factors based on actual construction costs for the Idaho DWCF (modified to correspond to the anticipated costs of a production-type facility) and operating costs based on actual experience with the DWCF thus far, we find the costs of calcination and storage to be over 30% less than the corresponding costs for pot calcination and storage.

Secondly, in view of the fact that the primary reason for converting wastes to solids is not an economic consideration but the desire to obtain greater safety in the containment of fission products, can you comment on the benefits to be expected from a process which (as I read the paper) contemplates 10-20 yr of liquid storage of waste before reduction to solid, rather than immediate reduction to solid and interim storage of solid (in cooled bins, as would be possible with the fluidized-bed process)?

J. T. ROBERTS: As far as your first comment is concerned, I suspect that 30% is less than the probable error of the cost estimates and comparisons. A hazards cost must be added to both estimates to make them truly comparable. It is hoped that the hazards evaluation will lead to an "insurance cost" that will settle some of these points of disagreement. Actually, 5-10 yr of acidic storage would be my estimate of the "optimum", not the 10-20 yr which you mention in your second comment.

R. L. BRADSHAW: I might add that in our study at Oak Ridge, we are now far enough along with the economics of interim solid storage to see that its cost will not be much greater than that of liquid storage. Thus, the interim liquid storage could be eliminated.
J. T. ROBERTS: Of course, complete elimination of interim liquid storage would limit us to smaller-diameter pots and thus increase the costs. We hope that the hazards evaluation will show whether this is economically justified.

W. H. HARDWICK: In view of the differing degrees of hazard incurred in storing dry wastes as calcined solids and as glass (in that, for example, the temperature in the calcine cannot be permitted to rise as high as in glass and therefore stricter cooling conditions are required), the relative costs of storage must be in favour of glass. Can you comment on this?

J. T. ROBERTS: It may well be that conversion to glass would be preferable to plain calcination as far as safety is concerned. We are hoping that the Oak Ridge study will succeed in placing an economic evaluation on the hazards of the various processing and disposal steps, thus making it possible to compare the disposal of liquids, calcined solids and glasses on a more quantitative basis.
IV

SOLIDIFICATION AND FIXATION OF LIQUIDS - VITRIFICATION

(Part 2)
INTRODUCTION TO SESSION IV
BY THE CHAIRMAN, PROFESSOR B. KOLYCHEV

B. KOLYCHEV: It is a particular pleasure to me to have been chosen to take the Chair during our consideration of the question of the solidification of radioactive wastes by vitrification, because I myself have been a strong champion of this type of treatment, which permits the safe burial of wastes. In our country, as everywhere else, advances in the use of atomic energy have raised the question of what to do with the resulting radioactive waste, of finding methods of dealing with waste in such a way that it should not be the cause of incalculable suffering to mankind but also that it should not be an economic barrier to the development of atomic energy.

We have in our country many areas where the population is very sparse and the land very unproductive, for example, the eternally frozen regions or the unpopulated shores of the Arctic. For this reason, there might be a great temptation to disperse radioactive wastes in these regions. But after discussing the matter, we adopted one general principle: no method of treating and storing radioactive waste should permit the possibility of its uncontrolled seepage into the environment. This is our only criterion in evaluating any new method which is proposed.

For this reason, our present practice in dealing with radioactive wastes takes the following form: in order to reduce their volume and concentrate their activity, liquid wastes are subjected either to concentration by evaporation or, where lower activity is involved, to processing involving precipitation of the activity in sesquioxides. The water resulting from the evaporation or coagulation process, after additional purification in an ion exchanger where necessary, is used for industrial purposes within the undertaking and forms a fully closed cycle.

The concentrated activity is channelled into stainless-steel tanks, no special neutralization being required. In the case of rarefied sources of radioactive waste, there are central processing and cleansing stations at which this waste is further concentrated and the concentrated activity is stored in tanks. The water formed in this process after being brought down by purification in ion exchangers and subsequent evaporation to the very low level of activity prescribed in the health regulations, is permitted to flow into the general drainage system.

Of course, we realize that steel tanks cannot be used for the ultimate storage of concentrated activity and although these vessels have thus far proved quite satisfactory, we are nevertheless engaged in extensive preparatory work with a view to enabling this waste to be converted to a more reliable form for permanent burial. To this end, we have considered the use of salt beds. However, over and above the fact that it is most unlikely that salt beds will be available near every undertaking, we are afraid that the salt might prove slightly soluble for liquid waste, i.e. 'be slightly inferior to soils, and give rise to uncontrolled seepage of radioactive waste. As far as the burial of solid waste is concerned, salt beds have no substantial advantages over any other reliable places of storage.

Burial of liquid radioactive wastes in deep geological formations, although very tempting, is a very difficult thing to study and there could never
be any certainty of obtaining entirely reliable results in our tests. For this reason, our attitude towards this method is one of great caution.

We are doing extensive research on the migration of radioisotopes, on their adsorption to various soils and on the occurrence of desorption conditions in relation to such parameters as temperature, dose composition, acidity, etc.

As you know, we are opposed to the discharge of radioactive waste into the sea and into fresh water as well as into soils, because by this method the waste is removed from control and can give rise to disasters whose extent cannot even be estimated by present methods.

We consider that the most promising procedure for the safe burial of radioactive wastes consists in solidification methods and, more particularly, in vitrification, because it is by such techniques that we shall be able in the future to bury radioactive waste permanently, and to do so with feelings of confidence and under reliable control. And that, I repeat, is why I am particularly pleased to have been asked to take the Chair today.
INCORPORATION OF RADIOISOTOPE INTO MELTED SILICATES

J. RÁLKOVÁ AND J. SAIDL
NUCLEAR RESEARCH INSTITUTE, ŘEŽ N. PRAGUE

Abstract — Résumé — Аннотация — Resumen

INCORPORATION OF RADIOISOTOPE INTO MELTED SILICATES. The two aims of this research work are:

(1) The selection of melted rock and of glass-type silicate materials suitable for incorporating biologically dangerous and long-lived radioisotopes; and

(2) the determination of those factors which could influence the rate of release of incorporated isotopes should these could endanger the biosphere.

For raw materials fourteen sorts of basalt-type melted rocks from North and West Bohemia and three sorts of selected glasses were used.

In experimental study due attention was paid to the diffusion of radioisotopes in glass and melted rocks and to the chemical resistance of these materials. For investigation of the diffusion of Sr\(^{90}\) and Cs\(^{134}\) the method of "thin layer", described by Kryukov and Zhuchowickij, was chosen as the most advantageous. In the temperature region of 300 - 600°C the diffusion coefficients of \(10^{-12} - 10^{-5}\) cm\(^2\) /sec were found. The fact that, for caesium, lower activation energy was found than for sodium, verifies the assumption of caesium being the least bound of all glass-forming elements.

By measuring the leaching rate of caesium and strontium from melted rocks the largest portion of leached radioactivity was determined in the initial phase of the leaching process. After 100 hr, the percentage of leached radioisotopes assumed a constant value. The leaching rate after a longer time is probably limited by the corrosion and by the internal diffusion of soluble elements from the inside to the surface of the solid body. The corrosion of glasses and melted rocks was examined in static arrangement at constant temperature (35, 60 and 90°C) and the leaching coefficients of \(10^{-11} - 10^{-8}\) cm\(^2\) /sec were found.

These results show that the materials investigated are suitable substrate for incorporating some high-level radioactive wastes. Should high-active blocks be disposed under controlled conditions in order to exclude any possible contact with water, the safety of this disposal can be guaranteed.
ВВЕДЕНИЕ РАДИОИЗОТОПОВ В РАСПЛАВЛЕННЫЕ СИЛИКАТЫ. Цель данной исследовательской работы является:
1. Выбор каменистых и стекловидных силикатных материалов, пригодных для введения биологически опасных и долгоживущих радиоизотопов.
2. Определение факторов, которые могут оказывать влияние на скорость высвобождения введенных изотопов, чтобы они не представляли опасности для биосферы.

В качестве сырьевых материалов использовались 14 сортов расплавленных пород базальтового типа из северной и западной Богемии и три сорта отдельных видов стекла.

При экспериментальном исследовании было установлено, что диффузия радиоизотопов в стекле и в расплавленных породах, а также химической устойчивости этих материалов. Для исследования диффузии стронция-90 и цезия-134 был выбран метод "тонкого слоя", описанный Крюковым и Жуковицким, как наиболее подходящий. При температурах порядка 300 - 600°C были установлены коэффициенты диффузии 10^{-13} - 10^{-11} см^2/сек. Тот факт, что для цезия была обнаружена более низкая энергия активации, чем для натрия, подтверждает предположение о том, что из всех стеклообразующих элементов цезий имеет наименьшие связи.

При измерении скорости выщелачивания цезия и стронция из расплавленных пород большая часть выщелоченной радиоактивности была обнаружена в начальной фазе процесса выщелачивания. По истечении 100 часов процесс выщелачивания радиоизотопов стал постоянной величиной. Скорость выщелачивания по истечении продолжительного времени, вероятно, определяется общей коррозионной стойкостью, а также внутренней диффузией растворимых элементов из середины твердого тела к поверхности. Коррозионная стойкость стекла и расплавленных пород изучалась в статическом состоянии при постоянной температуре (35, 60 и 90°C), и найденные коэффициенты выщелачивания были в пределах 10^{-11} - 10^{-9} см^3/сек (при 35°C). Эти результаты показывают, что исследованные минералы являются пригодной основой для введения некоторых высокоактивных отходов. Если высокоактивные отходы будут удаляться при контролируемых условиях, исключающих какой-либо контакт с водой, можно гарантировать безопасность этого удаления.

INCORPORACIÓN DE RADIOISÓTOPOS EN SILICATOS FUNDIDOS. La finalidad de este trabajo es doble:
1. Seleccionar tipos de rocas fundidas y de silicatos vitreos que se prestan para la incorporación de radioisótopos de período largo biológicamente peligrosos; y
2. Determinar los factores capaces de influir en la velocidad de liberación de los isótopos incorporados, en caso de que éstos puedan contaminar la biosfera.

Como materia prima, se han utilizado 14 variedades de rocas basálticas fundidas del Norte y el Oeste de Bohemia, así como tres variedades de vidrio.

En el estudio experimental, se ha prestado la debida atención a la difusión de los radioisótopos en el vidrio y en las rocas fundidas, así como a la resistencia química de estos materiales. Para investigar la difusión del 90Sr y del 134Cs, se ha empleado el método de la "capa delgada", descrito por Kryukov y Zhuchowickij, por considerarse que constituye el más indicado. En el intervalo de temperaturas de 300°C a 600°C, se han observado coeficientes de difusión de 10^{-12} a 10^{-11}cm^2/seg. El hecho comprobado de que la energía de activación del cesio sea inferior a del sodio confirma la hipótesis de que el cesio es el más débilmente ligado de todos los elementos vitrificantes.

Por medida de la velocidad de lixiviación del Cs y del Sr contenidos en las rocas fundidas se ha comprobado que la mayor parte de la sustancia radiactiva lixiviada aparece en la fase inicial del proceso. El porcentaje de radioisótopos lixiviados alcanza un valor constante al cabo de 100 horas. Pasado ese tiempo, la velocidad de lixiviación es probablemente reducida por la corrosividad de la estructura y por la difusión interna de elementos solubles del interior del sólido hacia la superficie del mismo. La corrosividad de los vidrios y de las rocas fundidas se ha examinado en condiciones estáticas a temperatura constante (35°C, 60°C y 90°C) obteniéndose coeficientes de lixiviación comprendidos entre 10^{-14} y 10^{-9}cm^2/s (a 35°C).
INTEGRATION OF RADIOISOTOPES INTO MELTED SILICATES

Estos resultados muestran que los materiales investigados constituyen un medio adecuado para la incorporación de algunos desechos de elevada radiactividad. Este método de evacuación puede considerarse completamente seguro, siempre que los bloques activos así formados se depositen en condiciones que excluyan la posibilidad de contacto con el agua.

The deactivation and the disposal of radioactive wastes is one of the most important problems in connection with nuclear research. In some countries, this question is solved in a simple manner: by disposal of radioactive wastes directly into soil or water. Because it is not certain whether or not radioactivity can reach man through biocirculation, the question of radioactive waste disposal arouses interest throughout the world. In Czechoslovakia, which is very densely populated and with no available seacoast, the successful solution of this problem is of paramount importance.

The hazards of radioactivity and of the resultant contamination of the area in the vicinity of the disposal site is the principal factor which has to be taken into consideration when disposing of radioactive wastes.

PRESENT RESULTS

Recently some important laboratories were dealing with the problem of the incorporation into different materials of wastes containing radioisotopes of a high concentration. The incorporation into natural silicate sediments was solved by C.B. AMPHLETT [1] and J.R. GROVER [2] in Great Britain, by R.G. THOMAS and C.W. CHRISTENSON [3] in the USA and by V.J. SPITSYN and V.V. GROMOV [4] in the USSR. Similar research, but by using silicate glasses as "matrix", has been carried out by R.W. DURHAM and L.C. WATSON in Canada [5], R. BONNIAUD, P. COHEN and C. SOMBRET in France [6], and by P.V. ZIMAKOV of the USSR [7]. M.I. GOLDMAN and J.A. SERVIZI et al. worked on glaze-type raw-materials [8].

The greatest part of the research has been made in the laboratory only and has dealt first of all with the chemical resistance of the materials used, and with the investigation of some related phenomena (e.g. the volatility of caesium and ruthenium during thermal treatment). In connection with the problems examined some works included the diffusion of radioisotopes in silicate products but not in great detail. H.C. THOMAS [9] examined some phenomena in the ionic diffusion through a solid body, in relation to the fixation of radioisotopes into glass. He supposes that the leaching of ions from glasses and melted rocks is limited by the diffusion rate in such materials. In his opinion the fixation of radioisotopes would be absolutely safe, when the diffusion coefficients of incorporated isotopes do not exceed the value of $10^{-15}\text{ cm}^2/\text{sec}$. This theory is unique. In general the ionic diffusion in glass has been examined to explain the structure and thermodynamic properties of glass. In the USA, BLAU and JOHNSON [10] and in France, LE CLERC [11] have been dealing with these problems. The work of R.M. BARRER [12] is among the most valuable contributions to the study of diffusion in solids.

The diffusion in metals has been elaborated more exactly than diffusion in glass. All the methods described by ZHUKHOWITZKY in his report [13] are suitable for studying the ionic diffusion in glass.
Czechoslovakia is a country where the glass and ceramic industries, based on rich deposits of excellent raw silicate materials, are widely developed. For our research we have had a wide choice of materials, with both natural deposits (minerals and rocks) and industrial raw and waste materials (slags, melted rocks and glass) at our disposal. The first part of our work included experimental research on selected basalt-type melted rocks and some types of glass.

After careful testing research workers of the National Institute of Glass Research have chosen various materials.

In the melted-rock industry only magmatic rocks, in particular one type - effusive rocks - are used. The chemical composition of magma and the summary of external influences determined the mineral composition of these rocks. The composition changes with the differentiation of the melted magma in such a manner that the lowest layers are richer in heavy elements (Fe) and the upper layers in lighter ones (Si). For the petrological application, the basic volcanic rocks containing less than 52% SiO₂ and having a conveniently low melting point, are the most advantageous. The casts from these volcanic rocks are chemically and mechanically suitable for industrial utilization. It is necessary for industrial products to be homogeneous in composition and surface, to have good mechanical and chemical resistance, durability, and to be constant in form, etc.

The aim of our work is somewhat different. The principal criteria for selecting materials suitable for the incorporation and fixation of radio-isotopes are resistance to water, carbon dioxide and oxygen at normal or moderately higher temperatures. Other requirements are not so vital. It is not necessary for manufactured bricks to preserve their form strictly and they should be sufficiently firm to permit safe transportation. Maximum durability in the chemical sense of the word is required. It is especially desired that the materials be totally "dead" during melting, i.e. that foaming, bubble forming and swelling are at a minimum. For this purpose the silicate materials are very advantageous, but the most convenient technological results were found in those materials which had been previously melted such as waste materials from the glass and melted-rock industries, slags, etc.

The chemical resistance of melted rocks was studied by VOLDÁN and PALEČEK [14]. Their experiments show that the chemical resistance to corrosion depends on temperature, concentration and on the reaction time of the agent given.

For our research work, the temperature influence and the reaction time is extremely significant. The corrosion changes follow this relation:

\[ U = A \exp(-Q/T) \]

U being the weight decrease of the matter examined, A and Q the constants and T the absolute temperature. The exponential dependence was confirmed experimentally. As to the dependence of leachability on the concentration of the agent, the dependence on pH was, in our work, the most remarkable. The
INCORPORATION OF RADIOISOTOPES INTO MELTED SILICATES

3 4 5

minimum leachability was found at pH = 6 - 8. The authors were dealing with the powder samples while other methods indicated nearly zero leachability. The hydrolytical resistance of the rocks mentioned was characterized as excellent, so that it may be considered irrelevant for the melted rock casts.

In selecting methods for diffusion study we have rejected all grinding methods (removal of layers) because they are, for glass containing high-level radioactivity, technically very unpredictable. The "thin-layer" method described by KRYUKOV and ZHUKHOWITZKY was chosen as the most advantageous [15]. This method can be used for isotopes emitting either beta and gamma or for beta radiation only. The method is based on the fact that the substance, the diffusion of which we wish to examine, deposited on one side of a thin plate of the material to be studied, penetrates the plate. The radiation intensity decreases on one side and increases on the other. The plate should be thin enough to be negligible for gamma radiation while it should represent a defined absorption layer for the beta radiation.

The diffusion in solids follows Fick's laws. Assuming the diffusion coefficient to be independent of concentration, the following equation was developed by Barrer for an instantaneous film source of matter, Q, deposited on semi-infinite solid,

\[ C(x,t) = \frac{c_0 h}{\sqrt{\pi D t}} e^{-\frac{x^2}{4Dt}} \]  

(1)

\( C_{(x,t)} \) is the concentration of diffusing substance at any time \( t \), at a distance \( x \) and \( c_0 \) is the initial concentration of the deposited film of the thickness \( h \).

Based on the same dependence, Kryukov and Zhukhowitzky have found the following relationship for the "thin-layer" method:

\[ c = c_0 \frac{h}{L} \left[ 1 - 2 \cos \frac{\pi x}{L} \exp \left( - \frac{1}{2} \frac{\pi^2}{L^2} D t \right) \right], \]  

(2)

valid for the thickness of the deposited film, \( h \), much smaller than that of the plate, \( L \) and having a very long reaction time. When the functions for the absorption and reflection of radiation in this equation are included it follows, in a further solution, that these effects will be eliminated and the final expression has the simple form

\[ \ln \frac{I_1}{I_1 + I_2} = \ln K - mt. \]  

(3)

\( I_1 \) is the intensity of radiation from one side of the plate and \( I_2 \) that from the other side, after a definite time interval, \( t \). In plotting \( \log (I_1 - I_2)/(I_1 + I_2) \) versus \( t \), a straight line results, from whose slope, \( m \), we can calculate the diffusion coefficient

\[ D = 2.3 m \frac{L^2}{\pi^2}. \]

This method was used when studying the diffusion of caesium and strontium in one type of low melting glass.
EXPERIMENTAL PART

According to the data published and by applying experience from research on the resistance of glass and melted rock to corrosion, we started our own experiments. The leachability was examined in melted rocks and glass, which were chosen partly for their high resistance to effects by water and partly for their suitable technological properties. The easy fusibility and treatment of silicates were the technological criteria in this work. From numerous materials the following rocks and glasses were selected:

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Locality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Olivine-basalt</td>
<td>Slapany</td>
</tr>
<tr>
<td>2</td>
<td>Analcite-diabase</td>
<td>Ovčára</td>
</tr>
<tr>
<td>3</td>
<td>Melaphyre</td>
<td>Stará Paka</td>
</tr>
<tr>
<td>4</td>
<td>Nephelinite</td>
<td>Mokrá</td>
</tr>
<tr>
<td>5</td>
<td>Basanite</td>
<td>Mar. Dvůr</td>
</tr>
<tr>
<td>6</td>
<td>Basalt</td>
<td>Církvice</td>
</tr>
<tr>
<td>7</td>
<td>Basalt-olivine</td>
<td>Soutěžka</td>
</tr>
<tr>
<td>8</td>
<td>Nephelinite-basanite</td>
<td>Kondraťovce</td>
</tr>
<tr>
<td>9</td>
<td>Basalt</td>
<td>Hory n. K. Vary</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>Höllberg</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>Těšetice</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>Dolánky</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>Semily</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>Ohafice</td>
</tr>
</tbody>
</table>

Glasses:

<table>
<thead>
<tr>
<th>Type</th>
<th>Mark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Simax P 955</td>
</tr>
<tr>
<td>2</td>
<td>Vycor H 821</td>
</tr>
<tr>
<td>3</td>
<td>S 13 (II) P 1050</td>
</tr>
</tbody>
</table>

Glass sample No. 2 is one of the 5th hydrolytic group; it was deliberately selected for purposes of comparison.

The samples were prepared after mixing model waste solution with the material examined and supplied in a crushed form (grain below 0.2 mm). The prepared samples were then successively dried (at 120°C), calcined (at 900°C) and used (at 1300°C). After fusion they were kept in the furnace at temperatures from 300 to 400°C. Due to many complicated conditions of the recrystallization the thermal history of the material was not changed. Samples prepared in such a manner had a perfect glass surface.

The leaching was carried out with distilled water in static conditions at constant temperature (35, 60 and 90°C). The temperature was held with an accuracy of ± 0.5°C in a Wobser* thermostat. The samples were fused in fire-proof ceramic vessels and were leached in special test-tubes from Sial-glass.

* A thermostatic bath using the Wobser system - Author's note.
Regarding safety, we were obliged to determine the leaching rate of those radioisotopes which have a long half-life and which affect the metabolism of a living organism. We studied the most hazardous from the fission-product mixture, Sr\(^{90}\) and Cs\(^{137}\), the half-lives of which are longer than 20 yr. The results obtained for these radioisotopes are given in Table I.

**TABLE I**

THE LEACHING COEFFICIENTS OF CAESIUM AND STRONTIUM IN SOME BASALT TYPES AT A TEMPERATURE OF 35°C

<table>
<thead>
<tr>
<th>Locality</th>
<th>(L_{\text{Cs}}) cm(^{-2})</th>
<th>(L_{\text{Sr}}) cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollberg</td>
<td>(6.8 \times 10^{-6})</td>
<td>(5 \times 10^{-5})</td>
</tr>
<tr>
<td>Těšetice</td>
<td>(6.0 \times 10^{-6})</td>
<td>(4.8 \times 10^{-5})</td>
</tr>
<tr>
<td>Dolány</td>
<td>(6.25 \times 10^{-6})</td>
<td>(4.25 \times 10^{-5})</td>
</tr>
<tr>
<td>Ohance</td>
<td>(7.0 \times 10^{-6})</td>
<td>(3.5 \times 10^{-4})</td>
</tr>
</tbody>
</table>

The dependence of the leached radioactivity on time is demonstrated in Fig.1. From the plot it is evident that the leaching of strontium and caesium is very high during the first two hours. In a semi-logarithmic scale, linear dependence starts after the initial rinsing and washing of the surface layer. We found for caesium, leaching coefficients were of the order of \(10^{-5}\), and for strontium, \(5 \times 10^{-4}\) cm\(^{-2}\). The leaching coefficients were expressed...
as the ratio between leached activity and original specific activity of the body examined, per unit area exposed to the leaching after a defined time. The values referred to are given for a reacting time of 100 hr.

Simultaneously with the study of the leaching, the diffusion of caesium and strontium in a low melting-point glass was investigated. The "thin-layer" method was used to determine the diffusion characteristics. The diffusion coefficients of strontium and caesium in glass at different temperatures are given in Table II. The logarithm of the diffusion coefficient plotted versus

Table II

THE DIFFUSION COEFFICIENTS OF CAESIUM AND STRONTIUM IN GLASS AT TEMPERATURES FROM 300 TO 600°C

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>DCs cm²/sec</th>
<th>Dsr cm²/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.3 × 10⁻¹³</td>
<td>1.9 × 10⁻¹³</td>
</tr>
<tr>
<td>350</td>
<td>4.0 × 10⁻¹³</td>
<td>5.1 × 10⁻¹³</td>
</tr>
<tr>
<td>400</td>
<td>1.0 × 10⁻¹²</td>
<td>2.0 × 10⁻¹¹</td>
</tr>
<tr>
<td>450</td>
<td>5.9 × 10⁻¹²</td>
<td>1.3 × 10⁻¹¹</td>
</tr>
<tr>
<td>500</td>
<td>1.7 × 10⁻¹¹</td>
<td>1.7 × 10⁻¹¹</td>
</tr>
<tr>
<td>525</td>
<td>2.5 × 10⁻¹¹</td>
<td>1.8 × 10⁻¹¹</td>
</tr>
<tr>
<td>550</td>
<td>2.9 × 10⁻¹¹</td>
<td>2.2 × 10⁻¹¹</td>
</tr>
<tr>
<td>600</td>
<td>2.9 × 10⁻¹¹</td>
<td></td>
</tr>
</tbody>
</table>

the reciprocal value of absolute temperature gives, for caesium and strontium, curves that represent activation-energy changes with temperature. (See Fig. 2.) The equation first conceived by Arrhenius,

\[ D = D_0 \exp(-E/RT) \]

is not valid for glasses in a wide temperature range. On the Arrhenius curves, a discontinuity due to the transformation interval of glass is apparent. The activation energy which, below the transformation interval is very low (ECs = 7600 cal/mol, ESr = 15 000 Cal/mol), increases rapidly at 350°C, reaches a maximum near the softening point (ECs = 30 700 cal/mol, ESr = 49 000 cal/mol) and then decreases again above the softening point.

In this part of work the diffusion coefficients for caesium were found to be lower than those for other alkali ions which have smaller ion radii. (See Table III.) The values for Li, Na and K were taken from the report by LE CLERC [11].

The influence of radiation on the diffusion rate was also examined. The silicate blocks, after having been filled with radioactive wastes, were exposed to high doses of internal radiation which affects the diffusion rate.
For examining the radiation influence informatively, the glass used was exposed to the radiation from a Co$^{60}$ source. The total dose was $10^6$ r. The diffusion curves did not follow the straight lines as was the case with a simple diffusion. At the chosen constant temperature, and with time, the radiation defects were simultaneously disturbed so that the diffusion coefficient was continually changing. From the informative data it becomes evident that the diffusion should be slower for as long as radiation defects exist in the glass, but with their simultaneous disturbance the diffusion rate was found to increase. The precise determination of the radiation influences demands a wide study of radiation chemistry.

DISCUSSION

In accordance with the new hypotheses, the ionic radius, the glass composition and various force-fields influence the diffusion rate primarily. By the term "force-field" we understand electrostatic interaction, that of Van der Waal, and the binding forces of the glass frame-work and of diffusing ions. BLAU[16] confirms this theory by comparing the diffusion coefficients:

(a) Of ions of different radii and of the same valency;
(b) Of ions of the same radius but of different valencies.

The diffusion coefficients of Na and K differ at the same temperature - $D_{Na}$ by one order and $D_{Ca}$ by two orders. From these results Blau deduces that the force-fields are the predominating factor in the diffusion process. However, he carries out this comparison at one temperature only (350°C) which does not present a real picture.

To complete these results we have compared first the diffusion coefficients of univalent (alkali) ions on the dependence of ionic radii and, second, the coefficients of univalent and bivalent ions at various temperatures.
In the first case we have used the values published by LE CLERC [11] in glass of very similar composition to that which was used by us, and we have concurred with the value for caesium found in this work. It may be seen from Table III that there is a difference of three orders between the diffusion coefficients of Li and Na, of two orders between $D_{Na}$ and $D_K$ and of one order between $D_K$ and $D_Cs$ at the temperature of 350°C. (The dependence of the logarithm of the diffusion coefficient on the reciprocal value of ionic radius is a straight line.)

Comparing further the diffusion coefficients of univalent caesium and bivalent strontium (Fig. 2) we see that the diffusion rate of bivalent strontium is slower than that of univalent caesium at lower temperatures, but the values of both coefficients approach higher temperatures. It must be considered, of course, that the caesium radius is much greater than that of strontium ($r_{Cs^+} = 1.7 \text{ Å}; r_{Sr^{++}} = 1.27 \text{ Å}$), so it is possible that, at still higher temperatures, the strontium ion, though bivalent, could migrate more quickly than the univalent caesium. A better picture could be obtained by comparing potassium with strontium ($r_{K^+} = 1.33 \text{ Å}$). For potassium ion, however, only two values of diffusion coefficients have been published, namely for temperatures of 350°C and 450°C. (Table IV.)

Even from these incomplete results it may be seen that the difference of diffusion coefficients of ions of the same size but of different valency, which reaches one order at 350°C, has been lowered by half an order when the temperature increases by 100°C.

**Table III**

THE DIFFUSION COEFFICIENTS OF ALKALI IONS:
DEPENDENCE ON IONIC RADII AT A TEMPERATURE OF 350°C

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D_{cm^2/sec}$</th>
<th>Ionic radius Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>$4.0 \times 10^{-7}$</td>
<td>0.6 - 0.78</td>
</tr>
<tr>
<td>Na</td>
<td>$2.5 \times 10^{-10}$</td>
<td>0.95 - 0.98</td>
</tr>
<tr>
<td>K</td>
<td>$3.0 \times 10^{-12}$</td>
<td>1.33</td>
</tr>
<tr>
<td>Cs</td>
<td>$4.0 \times 10^{-13}$</td>
<td>1.65 - 1.69</td>
</tr>
</tbody>
</table>

**Table IV**

COMPARISON OF K AND Sr DIFFUSION COEFFICIENTS

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$D_K_{cm^2/sec}$</th>
<th>$D_{Sr}_{cm^2/sec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>$3.0 \times 10^{-12}$</td>
<td>$2.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>450</td>
<td>$1.0 \times 10^{-11}$</td>
<td>$2.0 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
We may estimate from these data that Blau's hypothesis about the pre-dominating effect of the force fields can be applied to the solid phase in the right sense. In glass, where bound movements at relatively low temperatures occur, the effect of the diffusing particle size prevails much more than its valency. Above the temperature "liquidus" the diffusion coefficient should be dependent only on the ionic radius and on the viscosity of the medium, following Stokes' law:

$$D = \frac{kT}{6\pi\eta r}.$$

The low values of diffusion coefficients of caesium and strontium show that the fixation of high-level radioactivity into glass would be safe provided that the leaching rate is limited only by the diffusion. The leaching data show, however, that, in the initial stage of leaching, the surface layer was washed and rinsed and eventually partly dissolved at a rate somewhat higher than that of the diffusion rate.

Two opinions exist about the leaching mechanism of the silicate glasses. ABRAMJAN [17] explains the large initial leachings and their simultaneous decrease with time by removing weakly bonded soluble ions from the surface layer. A surface film is formed, consisting of the remaining frame-work -SiO₄-, which is very resistant and practically insoluble. This film protects the body from further washing. A second opinion was expressed by DURHAM and BELL [18]. They suppose that the surface film begins to be disturbed on different sites after a complete leaching so that a fresh surface is denuded and further leached in this manner. This theory is based on experimental data. The leached radioactivity increased periodically after the first rinsing. These peaks become lower with time until equilibrium is reached.

We feel that these hypotheses do not exactly explain the leaching mechanism. In our experiments we did not obtain the whole resistance of the glass matter or periodic fluctuations of the leaching, or a great dispersion in measured values, because of the steady disturbance of the surface film.

The first process, which takes place in leaching, is beyond dispute. This is the surface rinsing which mechanilly eliminates all that which is not chemically bonded, irrespective of solubility.

Further, a basic exchange of most soluble cations occurs (alkali metals, alkaline earths, Fe³⁺ etc.), resulting in a thin microporous membrane, formed by the framework -SiO₄- and eventually modified by the molecules of Al₂O₃. The oxides SiO₂ and Al₂O₃ enter the water medium more or less mechanically while they break away from the surface after the metallic bonds have been disturbed. This process occurs very seldom because the framework mentioned is very resistant and firmly bonded. We can imagine the further mechanism as follows; the silicate body is protected with a surface film formed by a frame-work -SiO₄-, the pores of which are filled with a solvent (water). The water, after having passed through the surface membrane, touches the "internal" surface below the membrane, from which it further removes more soluble constituents which pass back into the body of the solvent after having penetrated through the surface membrane pores. The soluble elements come from inside to this "internal" surface by internal diffusion, which results in the steady renewal of the concentration gradient.
After a definite time, the length of which depends on the pore size of the washed framework and on the diffusion rate, total leaching of all soluble constituents occurs. Of course, some portion of alkali ions that are permanently built into the lattice cannot be transported by diffusion to the surface. The size of this portion depends on the lattice form and on the firmness of the chemical bonds.

The justification of this hypothesis was verified partly by the chemical analysis of the leaching water, which showed relatively more Na, Ca, Fe, etc. by comparison with the composition of the leached glassy matrix, and partly by the values of diffusion rates which approach the leaching rates after a longer leaching time.

REFERENCES

[18] DURHAM, R.W., BELL, D., "The durability of some silicate glasses that could be used in fission product disposal", EACL, CRDC-841 (1958).

DISCUSSION

E. GLUECKAUF: Could you indicate whether, in the case you are describing, there are grounds for thinking that Fick's law governs the diffusion process over longer time intervals? Figure 1 does not seem to support
such an assumption and Figure 2 indicates that more than one activation energy, and hence more than one diffusion mechanism, is operative. When that happens, Fick's law is usually only a very crude approximation.

J. SAIDL: Figure 1 shows the leachability of caesium by water. I agree with you that in this case a complex process is involved and not merely the influence of diffusion in the solid phase. Certainly we do not think that Fick's laws are anything other than an approximation, like all the simple laws formulated several years ago.

W. H. HARDWICK: I would like to refer to the work of Douglas and Raman at Sheffield. They have found that the diffusion, or leaching, of sodium and potassium ions from silicate glasses is at first a \( \sqrt{t} \) dependency (Fick's law) but then changes to a linear time dependency. The ratio of metallic ions to silica in the leach liquor is at first high, but as calcium is added to the glass, this ratio falls nearly to unity, which seems to indicate that the fusion mechanism no longer applies and that the whole glass network is being destroyed. Could Dr. Saidl comment on this?

J. SAIDL: The change from \( \sqrt{t} \) dependency to linear dependency (t) in the solid-phase diffusion region can apparently take place after a very long period of time.

We have not yet made an exact study of the influence of calcium on the rate of diffusion of the metallic ions, but we have unfortunately found an increase in the leachability of the strontium fixed in matter containing a large amount of calcium.

R. BONNIAUD: I would like to make a comment on ion diffusion in glass. As a result of tests on the leachability of active glasses, we found that, when the leaching test was halted for a certain length of time after we had reached the equilibrium leaching rate, upon resuming the test we obtained an activity peak whose magnitude varied directly with the length of the period of stoppage. This might be explained by a diffusion phenomenon.

J. SAIDL: When we began our work, we obtained some results which were very similar to yours. This was one of our reasons for doing research on solid-phase diffusion and for believing that the main reason for the leachability might be that the ions in question were diffused in the solid despite the fact that, in theory, its resistivity to fixation was extremely high.
VITRIFICATION OF CONCENTRATED SOLUTIONS OF FISSION PRODUCTS: STUDY OF GLASSES AND THEIR CHARACTERISTICS. The studies were carried out on two types of high-level radioactive waste: concentrated solutions originating from non-alloyed uranium rods and solutions originating from uranium-molybdenum rods. In each of these cases, various types of glass were developed and studied in tracer, and then in higher-level activity amounts.

Use of a hot-cell installation producing test glasses of standard activity ranging from 0.5 - 1 c/g made it possible to select glasses and adapt them to various technological processes, and to study gas volatility in firing and gas purification.

The glasses are manufactured in the crucible, following gelation of the mass to be vitrified. Loss rate by aqueous leaching attains, under optimum conditions, 1 x 10^{-7} - 2 x 10^{-7} glass g/cm^2/day. Activity lost by volatility in firing remained low (about 0.12% of total activity).

Solutions varying in age were vitrified; the activity lost by volatility is of the same order of magnitude, although slightly higher for the young solution; for the latter, the loss in ruthenium-106 amounts to 1% of total ruthenium, and in caesium-137, to 0.3% of total caesium.

Gas purification is facilitated by a filter having granules of the same composition as the glass which retains at least 93% of the volatilized activity; the filter content may be re-cycled.

In the case of molybdenic solutions, difficulties arose in respect of incorporating high MoO_3 contents in the glasses. Two possibilities are being explored:

(a) Utilization of phosphated compositions, in which incorporation of up to 30% of MoO_3 is possible. However, corrosion by glass in fusion limits their use, and activity losses by aqueous leaching are 10-100 times greater than in silicated glasses;

(b) Utilization of phospho-silico-borated compositions for which the MoO_3 content is lower.

Work is in progress on a cell to produce glass blocks of 10 000 - 15 000 c, which will enable measurement of aqueous leaching to be carried out under true storage conditions.
a) L'utilisation de compositions phosphatées dans lesquelles il est possible d'incorporer jusqu'à 30% de $\text{MoO}_3$. La corrosion par le verre en fusion limite cependant leur emploi et les pertes d'activité par lixiviation à l'eau sont 10 à 100 fois plus fortes que les verres silicatés.

b) L'utilisation de compositions phosphosilicoboratées pour lesquelles la teneur en $\text{MoO}_3$ est plus réduite.

Une cellule produisant des blocs de verre de 10000 à 15000 c'est en voie de réalisation. Elle permettra d'effectuer des mesures de lixiviation à l'eau dans les conditions réelles de stockage.

OSTEKЛОВЫВАНИЕ КОНЦЕНТРИРОВАННЫХ РАСТВОРОВ ПРОДУКТОВ ДЕЛЕНИЯ: ИССЛЕДОВАНИЕ И ХАРАКТЕРИСТИКА СТЕКОЛ. Исследования были проведены на двух типах высокоактивных отходов: концентрированные растворы, получившиеся при растворении чистого урана и ураномолибденовых сплавов. Для каждого из этих случаев были разработаны различные виды стекол, которые сначала исследовались с индикаторными количествами, а затем с большими уровнями радиоактивности.

Установка для получения стандартных образцов в горячей камере с удельной радиоактивностью от 0,5 до 1 кюри/г позволяет выбрать наиболее подходящие стекла и применить их к различным технологическим процессам, изучить летучесть в процессе обжига и очистку газов.

Стекла изготовляются в тигле после расплавления стекольной массы.

Скорость выщелачивания стекла водой достигает в лучшем случае $1 \times 10^{-7}$ - $2 \times 10^{-7}$ г/см²/день.

Потеря радиоактивности в результате улетучивания при обжиге невелика (приблизительно 0,12% общей радиоактивности).

В стекло превращались растворы различной длительности охлаждения. Потеря радиоактивности в результате летучести несколько выше для раствора с малой выдержкой: для рутения-106 она составляет 1% общего количества, для цезия-137 - 0,3%.

Очистка газов обеспечивается зернистым фильтром того же состава, что и стекло, который удерживает, по крайней мере, 98% активности, теряемой за счет летучести. Конструкция фильтра обеспечивает его регенерацию.

В случае молибденовых растворов возникает трудность, связанная с введением в стекло больших количеств $\text{MoO}_3$. Для проведения эксперимента имеются две возможности:

a) использование фосфатных компонентов, в которые возможно ввести до 30% $\text{MoO}_3$. Однако коррозия в процессе стеклообразования ограничивает их применение, кроме того, потеря радиоактивности при выщелачивании водой в этом случае в 10-100 раз больше, чем в случае силикатных стекол;

b) использование фосфорборосиликатных стекол, для которых допустимое содержание $\text{MoO}_3$ несколько меньше.

Камера для изготовления стеклянных блоков активностью 10 000 - 15 000 кюри находится в предпусковой стадии. Это позволяет осуществлять измерения скорости выщелачивания водой в реальных условиях хранения.

VITRIFICACION DE SOLUCIONES CONCENTRADAS DE PRODUCTOS DE FISIÓN: ESTUDIO Y CARACTERÍSTICAS DE LOS VIDRIOS. Los autores han estudiado dos tipos de desechos de elevada radiactividad: por un lado, soluciones concentradas procedentes de las barras de uranio no aleadas y, por otro, soluciones procedentes de las barras de uranio-molibdeno. En ambos casos, han preparado diferentes tipos de vidrio a fin de estudiarlos con vestigios de actividad y luego, con actividades más elevadas.

Mediante una instalación de célula caliente, que produce probetas de actividad variable entre 0,5 e 1 c/g pudieron seleccionar los vidrios y adaptarlos a los distintos procedimientos tecnológicos, así como estudiar la volatilidad durante la cocción y la purificación de los gases.

Los vidrios se obtuvieron en crisol, después de gelificar la masa vitrificable.

El coeficiente de pérdida por lixivión por el agua alcanza, en condiciones óptimas, de $1 \times 10^{-7}$ a $2 \times 10^{-7}$ g/cm²/d.

Las pérdidas de actividad por volatilización durante la cocción permanecen bajas (alrededor del 0,12% de la actividad total).

Al vitificar soluciones de diferentes edades se comprobó que la actividad perdida por volatilización es del mismo orden de magnitud, si bien resulta ligeramente superior en el caso de la solución más joven; en esta última, la pérdida de rutenio-106 representa el 1% del total de rutenio en tanto que la de cesio-137 el 0,3% del total de cesio.

La purificación de los gases se facilita mediante un filtro de gránulos de composición análoga a la del vidrio, que retiene por lo menos el 98% de la actividad volatilizada; el contenido del filtro puede recircularse.
En el caso de las soluciones de molibdeno, se presentaron dificultades para incorporar las elevadas proporciones de MoO₃ a los vidrios. Se están estudiando dos posibilidades a fin de resolver ese problema:

a) El empleo de compuestos fosfatados a los cuales es posible incorporar hasta un 30% de MoO₃. Sin embargo, el efecto de corrosión que ejerce el vidrio fundido limita la posibilidad de recurrir a dichos compuestos y las pérdidas de actividad debidas a la lixiviación por el agua son de 10 a 100 veces mayores que en el caso de los vidrios al silicato;

b) El empleo de compuestos de fósforo, silicio y boro, para los cuales el contenido de MoO₃ es más reducido.

Se está construyendo una instalación capaz de producir bloques de vidrio de 10 000 a 15 000 c. Permitirá efectuar medidas de la lixiviación por el agua, en condiciones de almacenamiento reales.

I. INTRODUCTION

En vue d'effectuer la solidification des solutions concentrées de produits de fission, nous avons recherché des compositions verrées susceptibles de fixer quasi irréversiblement les éléments radioactifs à vie longue.

La vitrification offre l'avantage sur la calcination simple de fournir un produit plus compact, donc de volume moindre, de conductibilité thermique plus grande, de solubilité dans l'eau plus faible, donc offrant une meilleure garantie au stockage.

Le verre doit cependant répondre à certains critères, parmi lesquels sa résistance à l'action de l'eau, sa parfaite tenue au rayonnement, son élaboration aisée et, si possible, conduire à une diminution du volume à stocker compatible avec l'échauffement qui peut se produire et la composition des liquides à vitrifier.

Les études ont porté sur deux types de solutions distinctes provenant soit du traitement de barreaux d'uranium non-allié, soit du traitement des alliages uranium-molybdène.

Dans le premier cas (type Marcoule), les eaux mères de dissolution des barreaux sont concentrées d'un facteur 100, avant stockage liquide.

Dans le second cas, le facteur de concentration envisagé est de 80.

Les verres étudiés pour la vitrification des solutions du type Marcoule n'ont pas pu s'appliquer au cas des solutions molybdéniques, par suite de la difficulté de digestion de l'anhydride molybdique. Pour résoudre ce problème, différentes possibilités sont en expérimentation et leur sélection sera faite ultérieurement.

II. VITRIFICATION DES SOLUTIONS DU TYPE MARCOULE

Les essais de laboratoires, réalisés avec des activités inférieures au millicurie, avaient permis la sélection de différentes compositions de verre [1].

Il s'avérait alors nécessaire, pour poursuivre cette sélection et pour permettre la mesure du taux de «léchabilité» à long terme des verres, de fabriquer des échantillons standard très actifs. L'installation de vitrification montée en cellule chaude a donc permis de réaliser les compositions type, de les modifier éventuellement en liaison avec les impératifs technologiques et de les sélectionner d'après leur facilité d'élaboration, leur taux de perte par lixiviation à l'eau, leur aptitude à la volatilisation des éléments actifs;
- d'étudier la vitrification en creusets, et en particulier l'entraînement des composés volatils et l'épuration des gaz de cuisson.

Les verres ont été fabriqués en creuset de graphite de 150 mm de haut et 65 mm de diamètre, afin de permettre le démoulage des éprouvettes et d'obtenir des formes reproductibles.

1. Techniques de fabrication

Deux voies ont été expérimentées :

1.1 Imprégnation directe par la solution active de panneaux de fibres comprimées

Le verre constitutif présentait au test D.G.G. [2] 2 mg de perte de poids pour 100 g. Les panneaux utilisés ont une charge de 320 kg/m³, une épaisseur de 8 mm environ, et sont imprégnés sur la base de 640 l de solution/m³. Pour leur utilisation, ils sont découpés en rondelles, empilés dans le creuset et arrosés de 75 cm³ de solution active, puis séchés et fondus à 1100°.

Après évaporation, une seconde imprégnation identique est possible. L'avantage de la méthode est de supprimer la phase de mélange et de fournir un grand coefficient de réduction de volume. Par contre, la formule finale du verre est tributaire de la composition des solutions à vitrifier.

Il est à remarquer que ce procédé se rapproche de la nouvelle technique américaine des céramiques poreuses [3].

1.2 Méthode par gélification de la masse

Le verre est fabriqué à partir de 150 cm³ de solutions actives, après addition à la solution et mélange des matières premières complémentaires et d'un adjuvant gélifiant en milieu acide. L'agent de gélification est l'argile SA 938 de la Société Carbonisation et charbons actifs. Le mélange est coulé encore fluide dans le creuset ; sa prise s'effectue rapidement en donnant une masse dure et compacte qui est calcinée et fondue à 1100°.

Les adjuvants complémentaires du verre sont introduits sous forme de fritte préalablement verrée, permettant d'une part de réduire la perte d'activité par volatilité, d'autre part, d'éviter le foisonnement du verre à la cuisson.

Cette technique permet, par réajustement de la fritte verrée, de garder constante la formule du verre final, en compensant les éventuelles variations de composition des solutions actives.

L'installation de vitrification est protégée par 10 cm de plomb. Elle est équipée d'un four de 2,5 kW, que l'on a cherché à isoler de la contamination par un fourreau en Inconel étanche (figure 1). Le creuset est introduit automatiquement à l'intérieur du fourreau. Celui-ci est connecté à un circuit d'épuration des gaz, comprenant un condenseur, un filtre destiné à piéger le 106Ru et de 4 colonnes d'absorption à la soude, garnis d'anneaux de Raschig. La cuisson s'effectue sous dépression. L'extraction des pastilles de verre actif est réalisée par une ventouse commandée par système téléflex.
Figure 1
Schéma de l'installation de vitrification.
2. Composition des verres et des solutions utilisées

Les essais ont été réalisés avec une solution de produits de fission à 2 c/l environ, âgée d'environ 4 ans, contenant, par suite, peu de $^{106}$Ru; puis avec une solution à 140 c/l, plus récente. Les caractéristiques de ces solutions sont données sur le tableau I.

**TABLEAU I**

**CARACTÉRISTIQUES DES SOLUTIONS VITRIFIÉES**

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Activité</th>
<th>Composition chimique</th>
<th>Composition radiochimique</th>
</tr>
</thead>
<tbody>
<tr>
<td>N°1</td>
<td>2 c/l</td>
<td>$\text{NO}_3\text{H}$ 1,2 N</td>
<td>$^{137}\text{Cs}$ 13,0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Na}^+$ 8,5 g/l</td>
<td>$^{144}\text{Ce-Pr}$ 19,5%</td>
</tr>
<tr>
<td>N°1</td>
<td></td>
<td>Produits de corrosion</td>
<td>$^{0}\text{Sr} + ^{89}\text{Y}$ 85,0%</td>
</tr>
<tr>
<td>N°2</td>
<td>140 c/l</td>
<td>$\text{NO}_3\text{H}$ 1,96 N</td>
<td>$^{137}\text{Cs}$-Ba 21%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Na}^+$ 22,2 g/l</td>
<td>$^{87}\text{Sr} + ^{89}\text{Y}$ 13,1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Fe}^{+++}$ 5 g/l</td>
<td>$^{186}\text{Os-Rh}$ 5,9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Ce}^{+++}$ 0,95 g/l</td>
<td>$^{144}\text{Ce-Pr}$ 6,4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Mo}^{6+}$ 0,3 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Al}^{3+}$ 0,3 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NH}_4^+$ 0,3 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Po}^{4-}$ 1,3 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{U}$ 0,2 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{NO}_3\text{H}$ total 275 g/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>densité 1,245</td>
<td></td>
</tr>
</tbody>
</table>

Les compositions de verre fabriquées sont reproduites sur le tableau II. Le poids des échantillons correspond généralement à la limite inférieure possible, compte tenu de la composition des verres et de la teneur en sodium des solutions.

L'activité spécifique des verres obtenus à partir de la solution n°2 a atteint environ 0,4 c/cm$^3$ pour la technique de gélification, 0,7 c/cm$^3$ pour les fibres imprégnées une fois, 1,3 cm$^3$ pour les fibres imprégnées deux fois. Dans ce dernier cas, pour compenser la teneur en Na$_2$O et pour permettre le décollage du verre, une charge d'Al$_2$O$_3$, d'environ 4% du verre a été ajoutée à la fibre.

3. Pertes d'activité au cours de la cuisson - Epuration des gaz

Les pertes d'activité au cours de la cuisson des verres ont été déterminées par mesure de l'activité du condensat, de la soude des colonnes,
<table>
<thead>
<tr>
<th>Verre</th>
<th>Viscosité à 1100°C</th>
<th>Densité</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>ZrO₂</th>
<th>B₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>Divers</th>
<th>Volume de solution</th>
<th>Poids de l'échantillon</th>
<th>Facteur de réduction de volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGS-composition des fibres</td>
<td>2,6</td>
<td>58,7</td>
<td>4</td>
<td>+ K₂O</td>
<td>13,2</td>
<td>12,6</td>
<td>4</td>
<td>4,5</td>
<td>3</td>
<td>75 cc</td>
<td>38 g</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°4</td>
<td>24 770 poises</td>
<td>2,42</td>
<td>62,5</td>
<td>11,5</td>
<td>14,9</td>
<td>0,8</td>
<td>-</td>
<td>-</td>
<td>9,4</td>
<td>0,8</td>
<td>0,1</td>
<td>150 cc</td>
<td>120 g</td>
<td>3</td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td>12 000 poises</td>
<td>2,42</td>
<td>67,1</td>
<td>4,95</td>
<td>15,9</td>
<td>0,9</td>
<td>-</td>
<td>-</td>
<td>10,15</td>
<td>0,9</td>
<td>0,1</td>
<td>150 cc</td>
<td>203 g</td>
<td>1,8</td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td></td>
<td>2,4</td>
<td>66,4</td>
<td>4,9</td>
<td>15,75</td>
<td>0,9</td>
<td>-</td>
<td>1</td>
<td>10</td>
<td>0,9</td>
<td>0,1</td>
<td>150 cc</td>
<td>205 g</td>
<td>1,8</td>
</tr>
<tr>
<td>1% B₂O₃</td>
<td></td>
<td>2,4</td>
<td>66,7</td>
<td>4,85</td>
<td>15,6</td>
<td>0,9</td>
<td>-</td>
<td>2</td>
<td>9,96</td>
<td>0,85</td>
<td>0,1</td>
<td>150 cc</td>
<td>207 g</td>
<td>1,75</td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td></td>
<td>2,4</td>
<td>64</td>
<td>4,7</td>
<td>15,1</td>
<td>0,37</td>
<td>-</td>
<td>4,76</td>
<td>9,7</td>
<td>0,8</td>
<td>0,07</td>
<td>150 cc</td>
<td>213 g</td>
<td>1,7</td>
</tr>
<tr>
<td>5% B₂O₃</td>
<td>780 poises</td>
<td>2,4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td></td>
<td>2,4</td>
<td>64</td>
<td>4,7</td>
<td>15,1</td>
<td>0,37</td>
<td>-</td>
<td>4,76</td>
<td>9,7</td>
<td>0,8</td>
<td>0,07</td>
<td>150 cc</td>
<td>213 g</td>
<td>1,7</td>
</tr>
<tr>
<td>V₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150 cc</td>
<td>210 g</td>
</tr>
</tbody>
</table>
des prélèvements gazeux en fin de circuit avant le filtre de sortie, par décontamination de l'appareillage, notamment du fourreau, et comptage des solutions de décontamination, par extraction de l'activité de la charge céramique du filtre à ruthénium.

La décontamination du fourreau n'étant pas totale (60 à 80%), l'activité comptée a été multipliée par un facteur de correction égal au rapport des taux d'irradiation avant et après décontamination.

Au cours des opérations de cuisson, un courant d'azote est injecté dans le fourreau, pour maintenir une atmosphère inerte. Les incondensables, avant filtration finale, dilués par de l'air pour éviter une éventuelle humidification du filtre de sortie.

Il est à noter que les pertes d'activité ne dépendent pratiquement pas de la composition des verres fabriqués, mais de la technique utilisée.

Au cours de la première campagne de vitrification, le débit d'azote injecté dans le fourreau a été progressivement réduit afin de diminuer l'activité non négligeable des incondensables décelés dès les premières manipulations. Cette réduction n'a été effectuée que pour la phase de fusion, un débit de 150 l/h d'azote a été maintenu pendant la phase d'évaporation, car il s'est avéré que les gaz n'entraînaient alors qu'une activité négligeable. De même, le piège à ruthénium n'a été inséré dans le circuit qu'à partir de la vingtième manipulation, et placé entre le condenseur et les colonnes d'absorption.

Les bilans de perte d'activité sont reproduits sur le tableau III pour les solutions âgées et sur le tableau IV pour les solutions jeunes.

Les résultats permettent les remarques suivantes :

a) L' entraînement d'activité observé est plus grand pour les fibres verries imprégnées, qui, dans les conditions identiques de cuisson ont perdu environ trois fois plus d'activité qu'un verre obtenu après gelification. La perte est également plus grande pour le verre V9. La raison en est certainement la présence de kaolin dans les adjuvants complémentaires, introduit pour éviter le foisonnement du verre, mais diminuant également la consistance du gel. La présence de 90Sr dans le condensât et le fourreau laisse penser à un entraînement de poussières.

b) La réduction du débit d'azote de balayage a une influence favorable non seulement sur l'activité des gaz de queue, mais aussi sur la contamina tion du fourreau. Le facteur de décontamination global mesuré avant le filtre de sortie s'est abaissé de 4 × 10^4 pour un débit de 100 l/h, à 2 × 10^5 pour un débit de 25 l/h. Avec l'introduction du filtre à ruthénium, ce facteur est passé à 10^7.

c) Le piège à 106Ru et 137Cs a permis d'augmenter l'épuration des gaz. Le piège est constitué d'un mélange granulé d'argile SA 938, oxyde de fer, et adjuvants complémentaires du verre, de même composition que le verre ASA 15 n°4. Après saturation, la charge peut être fondue; il est cependant nécessaire de lui ajouter alors 10% en poids d'alumine, pour éviter le foisonnement du verre. La température de fonctionnement du filtre à ruthénium est de 500°.

La charge a été changée trois fois au cours des manipulations. L'efficacité de rétention déterminée a été successivement de 98%, 94,5%, 97,8%. L'évolution du rapport (Activité de la soude des colonnes)/(Activité du con-
## TABLEAU III

**PERTE D'ACTIVITÉ AU COURS DE LA VITRIFICATION DES SOLUTIONS ÂGÉES**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SG3 (essais 5 à 10)</td>
<td>Condensat 0,054% Plège à 106 Ru - 0,127% Incondensables 0,13% Foureau moyenne 1,1% Bilan total moyen 1,43%</td>
<td>2,4</td>
<td>Débit d'azote 150 l/h</td>
</tr>
<tr>
<td></td>
<td>ASA 15 n°4 Essais 11 à 13</td>
<td>0,016% - 0,03% 0,039% 0,056% 0,17% 1,89</td>
<td></td>
<td>Débit d'azote 150 l/h</td>
</tr>
<tr>
<td></td>
<td>ASA 15 n°7 Essais 15 et 16</td>
<td>0,010% - 0,0147% 0,0015% par défaut 0,095% 0,12% 1,44</td>
<td></td>
<td>Azote 100 l/h</td>
</tr>
<tr>
<td></td>
<td>ASA 15 n°7 Essais 17 à 19</td>
<td>0,0080% - 0,0105% 0,0014% 0,068% 0,088% 1,32</td>
<td></td>
<td>Azote moy. 60 l/h</td>
</tr>
<tr>
<td></td>
<td>ASA 15 n°7 Essais 20 à 22</td>
<td>0,0051% 0,0034% 1,25 · 10^{-4} 4,8 · 10^{-4} 0,088% 0,077% 0,024</td>
<td></td>
<td>Azote 25 l/h Filtré à Ru inséré</td>
</tr>
<tr>
<td></td>
<td>V9 Essais 24 à 27</td>
<td>0,0025% 0,0054% 0,3 · 10^{-4} incomptable 0,26% 0,27% 0,013</td>
<td></td>
<td>id.</td>
</tr>
<tr>
<td>Verre</td>
<td>Condensat</td>
<td>Piège à Ru</td>
<td>Colonnes d'absorption</td>
<td>Incondensables</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
<td>------------</td>
<td>----------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>ASA 15 n° 4</td>
<td>0.0068%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.0046%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.0037%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% B₂O₃</td>
<td>0.0047%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.0047%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% B₂O₃</td>
<td>0.0093%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.0034%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% B₂O₃</td>
<td>0.0034%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Par gélification</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.0062%</td>
<td>1.62 10⁻³%</td>
<td>0.55 10⁻⁴%</td>
<td>0.49 10⁻⁵%</td>
</tr>
<tr>
<td>1% B₂O₃</td>
<td>1.02 10⁻⁴%</td>
<td>0.13 10⁻⁴%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>1.2 10⁻⁴%</td>
<td>0.06 10⁻⁴%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% B₂O₃</td>
<td>4.71 10⁻³%</td>
<td>0.96 10⁻⁴%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>0.38 10⁻⁴%</td>
<td>0.13 10⁻⁴%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% B₂O₃</td>
<td>0.96 10⁻⁴%</td>
<td>0.98 10⁻⁴%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Par imprégnation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG3</td>
<td>0.028%</td>
<td>1.8 10⁻³%</td>
<td>0.89 10⁻⁴%</td>
<td>0.039 10⁻⁴%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLEAU IV
PERTES D'ACTIVITÉ AU COURS DE LA VITRIFICATION DES SOLUTIONS JEUNES
ÉTUDES ET CARACTÉRISTIQUES DES VERRES

densat) permet de se rendre compte de l'efficacité du filtre. Préalablement égal à 1,89, il s'est trouvé réduit progressivement à 1,32 par réduction d'azote et à atteint 0,024 avec le filtre à ruthénium. Un rapport de 0,005 a même été obtenu au cours de la deuxième campagne de vitrification.

Les essais de fusion des granulés actifs, après addition d'alumine, ont donné une perte globale d'activité de 0,74% par rapport à l'activité contenue.

d) Les pertes totales d'activité obtenues sont assez faibles. Au point de vue répartition, on note qu'une partie importante se fixe sur le fourreau de cuisson.

Les principaux éléments volatilisés sont le $^{106}$Ru et $^{137}$Cs (tableau V). Il est à remarquer que, pour les essais effectués avec une solution âgée, la perte en $^{137}$Cs des verres ASA a été proportionnellement plus importante que celle du $^{106}$Ru. Par contre, avec les solutions récentes $^{106}$Ru a été davantage entraîné. La nature chimique du ruthénium dans les deux cas est peut-être en cause.

TABLEAU V
PERTES EN $^{106}$Ru ET $^{137}$Cs AU COURS DES OPÉRATIONS DE VITRIFICATION

<table>
<thead>
<tr>
<th>Solution et verre</th>
<th>$^{106}$Ru</th>
<th>$^{137}$Cs</th>
<th>$^{90}$Sr + $^{90}$Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASA 15 n° 4</td>
<td>Fourreau</td>
<td>0,35%</td>
<td>0,40%</td>
</tr>
<tr>
<td></td>
<td>Absorption</td>
<td>0,039%</td>
<td>0,17%</td>
</tr>
<tr>
<td></td>
<td>Perte totale</td>
<td># 0,39%</td>
<td>0,63%</td>
</tr>
<tr>
<td></td>
<td>Répartition de l'élément dans</td>
<td>90%</td>
<td>74%</td>
</tr>
<tr>
<td></td>
<td>Fourreau</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Absorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n° 7</td>
<td>Fourreau</td>
<td>0,25%</td>
<td>0,35%</td>
</tr>
<tr>
<td>Solution âgée (débit azote réduit)</td>
<td>Absorption</td>
<td>0,025%</td>
<td>0,125%</td>
</tr>
<tr>
<td></td>
<td>Perte totale</td>
<td># 0,28%</td>
<td># 0,48%</td>
</tr>
<tr>
<td></td>
<td>Répartition de l'élément dans</td>
<td>90,8%</td>
<td>73,7%</td>
</tr>
<tr>
<td></td>
<td>Fourreau</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Absorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V9</td>
<td>Perte totale (-filtre Ru)</td>
<td>1,4%</td>
<td>0,77%</td>
</tr>
<tr>
<td></td>
<td># 1,45%</td>
<td># 0,14%</td>
<td></td>
</tr>
<tr>
<td>Solution jeune</td>
<td>ASA 15 n° 4</td>
<td>Fourreau</td>
<td>1,35%</td>
</tr>
<tr>
<td></td>
<td>Filtre Ru</td>
<td>0,011%</td>
<td>0,007%</td>
</tr>
<tr>
<td></td>
<td>Absorption</td>
<td>0,089%</td>
<td>0,007%</td>
</tr>
<tr>
<td></td>
<td>Perte totale</td>
<td># 1,46%</td>
<td>0,14%</td>
</tr>
<tr>
<td></td>
<td># 0,77%</td>
<td># 0,14%</td>
<td></td>
</tr>
<tr>
<td>SG3</td>
<td>Absorption</td>
<td>0,224%</td>
<td>0,018%</td>
</tr>
</tbody>
</table>


4. Perte d'activité des verres par lixiviation à l'eau

Les échantillons de verre fabriqués ont été testés dans une installation annexe. Les pastilles sont arrosées avec 500 cc d'eau selon un cycle déterminé; l'eau est renouvelée tous les jours.

Le taux de lixiviation est exprimé en poids de verre correspondant dissous par 2 cm$^2$ et par jour.

Les tests ont été effectués à l'eau de mer synthétique et à l'eau de ville de caractéristiques moyennes Ca$^{++}$ 140 mg/l - Na$^+$ 5 mg/l - K$^+$ 20 mg/l - Sr$^{++}$ 0,15 mg/l.

Les remarques suivantes peuvent être faites :

a) Après élimination d'une activité de surface plus importante, un équilibre est assez rapidement atteint (figures 2, 3, 4 et 5). Les valeurs obtenues en sont données sur le tableau VI.

![Figure 2](image)

Evolution de la perte d'activité par lixiviation à l'eau de mer du verre SG3.

L'activité de surface est facilement extraite. Au cours du premier jour de test, on a noté que 60% de l'activité totale perdue en 24 heures, est passée dans l'eau en 1 h 15 et 80% en 4 h. Un prélavage systématique serait utile avant stockage définitif.

b) Du point de vue composition des verres, on peut observer que l'excès de Na$_2$O apporté par les solutions à 22 g Na$^+/l$ s'est traduit par une augmen-
ÉTUDES ET CARACTÉRISTIQUES DES VERRES

Figure 3
Evolution de la perte d'activité par lixiviation à l'eau de mer du verre ASA n°4.

...tation du taux de léchage du verre SG3 pour lequel un réajustement de formule ne fut pas possible.

Par contre, l'influence de B₂O₃ est moins nette; les faibles teneurs ajoutées au verre ASA 15 n° 7 n'ont pas affecté la solubilité des verres à l'eau de ville. Nous avions pourtant trouvé préalablement, pour une teneur voisine de 5% de B₂O₃ une perte sept fois plus grande à l'eau de mer.

Du point de vue nature de l'eau de lixiviation, il apparaît que l'eau de mer est légèrement plus corrosive. D'ailleurs, nous avons observé au cours du test à l'eau de mer des verres ASA une certaine hydrolyse ferrique, provoquant un très léger précipité, qui a peut-être faussé quelque peu les valeurs trouvées.
Evolution de la perte d'activité par lixiviation à l'eau de mer du verre V9.

Evolution de la perte d'activité par lixiviation à l'eau des verres ASA 15 n°7.
### Tableau VI

**Taux de «léchabilité» moyen des verres en fin de test de lixiviation**

(Exprimé en grammage de verre dissous/cm².j)

<table>
<thead>
<tr>
<th>Verre</th>
<th>Eau de mer synthétique</th>
<th>Eau de ville</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG3 imprégné de solution à 8,5 g Na⁺/l.</td>
<td>1·10⁻⁷</td>
<td>1 à 2·10⁻⁷</td>
</tr>
<tr>
<td>Imprégné de solution à 22 g Na⁺/l.</td>
<td>5·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>Double imprégnation de solution à 22 g Na⁺/l mais chargée en Al₂O₃</td>
<td>5·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°4</td>
<td>2·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td>1·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td>1 à 2·10⁻⁷</td>
<td>1·10⁻⁷</td>
</tr>
<tr>
<td>1% B₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td>1·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>2% B₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASA 15 n°7</td>
<td>7,5·10⁻⁷</td>
<td></td>
</tr>
<tr>
<td>5% B₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V9</td>
<td>3·10⁻⁷</td>
<td></td>
</tr>
</tbody>
</table>

C) Il faut remarquer également que le taux de lixiviation présente parfois des fluctuations en fonction du temps. Plusieurs phénomènes peuvent en effet augmenter la perte d'activité. Citons, par exemple :

- la température (facteur 30 environ entre la température ambiante et 100°C);
- les éventuels arrêts de lixiviation. Une pastille de verre, laissée au contact d'eau sans renouvellement pendant plusieurs jours, présente, au renouvellement suivant, une perte d'activité plus forte que si l'eau avait été changée. De même, une pastille à l'équilibre, laissée au repos sans eau, perd une activité à la reprise du test, d'autant plus forte que l'arrêt a été prolongé. Ainsi, une éprouvette de verre laissée 43 jours au repos après 80 jours de lixiviation continue, et présentant un taux de lixiviation de 1·10⁻⁷ g de verre/cm².j a donné à la reprise une perte correspondant à 17·10⁻⁷ g de verre/cm².j et n'a atteint de nouveau son équilibre qu'après 10 jours de test.

Ces faits laissent penser à un phénomène de diffusion. Cependant, si l'eau n'est pas renouvelée, un échantillon de verre à l'équilibre continue à perdre son activité, sans qu'aucune saturation ne soit observée; on note même une perte assez linéaire tout au moins pour les durées où le test a été prolongé (40 jours). Toutefois, la perte moyenne journalière ainsi mesurée est inférieure à la perte obtenue en renouvelant l'eau.
d) Du point de vue influence du volume d'eau de lixiviation, il apparaît qu'il n'y a pas proportionnalité, et que l'activité perdue croît plus lentement que le volume.

e) Les analyses radiochimiques ont décelé dans l'activité perdue du $^{137}$Cs, mais également une teneur parfois importante de $^{90}$Sr.

III. VITRIFICATION DES SOLUTIONS MOLYBDIQUES

Les solutions provenant du traitement des barreaux en alliage U-Mo, peuvent contenir après concentration des quantités importantes de molybdène.

Il a été tenté tout d'abord d'incorporer de l'oxyde de molybdène aux verres silicatés précédemment étudiés, mais il n'y a digestion d'anhydride molybdique que pour des teneurs très faibles (de l'ordre de 1% en MoO$_3$). Pour des teneurs plus élevées, on constate au sein du flux vitreux une décantation de l'anhydride molybdique qui se rassemble sous forme de concrétion solide à la partie inférieure des échantillons.

1. Verres phosphatés molybdéniques

Il convenait alors de choisir un autre formateur de réseau B$_2$O$_3$ et P$_2$O$_5$, les plus courants après la silice, ont été employés. Si l'emploi de B$_2$O$_3$ seul ne permet de digérer qu'une très faible partie de molybdène, par contre, un mélange MoO$_3$-borax admet jusqu'à 23% de MoO$_3$ sans séparation de ce dernier. Mais ce produit présente une solubilité très importante et l'addition de certains éléments (Al$_2$O$_3$ par exemple) en vue de diminuer cette solubilité, diminue également la teneur maximum admissible en MoO$_3$.

L'emploi de P$_2$O$_5$ permet de vitrifier des quantités plus importantes de molybdène. Si les produits obtenus sont également assez solubles, l'introduction d'éléments destinés à diminuer la solubilité permet cependant d'obtenir un verre intéressant car la teneur maximum admissible du molybdène, tout en ayant baissé, se trouve à un taux encore acceptable.

Les études faites sur la résistance chimique des verres phosphatés sont très rares. Parmi les précédentes bibliographies, on signale cependant l'influence favorable de ZnO et Al$_2$O$_3$.

Des différentes compositions réalisées ayant comme constituants de base P$_2$O$_5$, Al$_2$O$_3$, ZnO, MoO$_3$ et Fe$_2$O$_3$ (l'ion fer pouvant être présent dans les solutions au cas possible où il serait utilisé pour permettre une meilleure concentration des solutions), le verre suivant a été sélectionné pour être testé en actif :

<table>
<thead>
<tr>
<th>Composé</th>
<th>Teneur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_5$</td>
<td>53,4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>26,6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5</td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>10</td>
</tr>
</tbody>
</table>

100

Ce produit est préparé à partir de calcinat molybdique et d'oxydes purs de fer, aluminium, zinc.
1.1 Propriétés physiques

Densité 2,8, couleur brun-noir, température de fusion 1050°C (la viscosité est suffisante pour permettre la coulée du verre), conductibilité thermique 0,0043 CGS.

Pour obtenir un verre parfait, un palier de cuisson de 4 heures minimum à 1050° est nécessaire, sinon il peut rester au sein de la masse vitreuse des quantités de matières premières non digérées.

La corrosion par les solutions aqueuses a été étudiée par traceurs radioactifs. Cependant, le fait que les échantillons soient vitreux ou dévitrifiés, pouvant influer sur ce test, il a été décidé de voir dans quelles conditions il était possible d'obtenir une dévitrification. Après l'utilisation de différentes vitesses de refroidissement, il apparaît que celle-ci doit être inférieure à 50°C/h pour obtenir une cristallisation. A cette vitesse en effet, bien que l'analyse aux rayons X ne permette pas de déceler une dévitrification quelconque, l'examen au microscope montre la formation de germes cristallins (figure 6).

Figure 6
Dévitrification d'un verre phosphaté.

1.2 Evolution au cours de la cuisson

Au cours de l'élaboration du verre, le molybdène qui est volatil se dégage en partie. Des analyses effectuées sur les verres obtenus ont montré que la quantité de molybdène volatilisé pouvait se chiffrer jusqu'à 30% de la quantité initiale. Il est probable également que, d'une part, P₃O₅ subisse le même phénomène et que, d'autre part, lors de l'élaboration à partir d'un calcinat réel, c'est-à-dire contenant des produits de fission, il se produise des pertes en radioéléments, soit par volatilisation réelle (Ru, Cs), soit par entraînement mécanique. Cependant, cette perte est variable car elle
dépend des conditions opératoires (débit d'aspiration des gaz, surface de l'échantillon, nature de l'atmosphère).

1.3 Tests de lixiviation

Les échantillons obtenus après cuisson en creuset de graphite sont démoulés et arrosés par 600 cm$^3$ d'eau de mer recyclés chaque minute. L'eau est renouvelée tous les jours. Le test a été effectué sur des échantillons d'activité inférieure au millicurie.

On obtient à l'équilibre pour des éprouvettes marquées par $^{137}$Cs une perte voisine de $10^{-6}$ g de verre/cm$^2$·j et pour des éprouvettes marquées par un ensemble de produits de fission, de l'ordre de $5 \cdot 10^{-5}$ g/cm$^2$·j (figure 7). Ce dernier chiffre est très approximatif car la marge d'erreur sur les mesures est grande, l'évaluation ayant été faite par comptage direct de la solution. Par contre, le chiffre relatif au césium est plus précis car on a opéré par dosage.

Il a été remarqué qu'un échantillon testé pendant un certain temps présentait, si on le soumettait à un nouveau léchage, une perte dans les premiers jours très supérieure à la valeur de l'équilibre.

Un échantillon a été testé de cette façon avec des arrêts de 70, 40 et 20 jours, mais il n'a pas été possible d'établir une loi reliant la durée de l'arrêt à la durée nécessaire à la reprise de l'équilibre après l'arrêt (figure 8).

![Figure 7](image_url)

Perte par léchage à l'eau de mer d'un verre phosphaté.
Un échantillon dévitrifié marqué au $^{137}$Cs a été testé. Les résultats indiquent que la perte est environ dix fois supérieure à celle d'un échantillon normal. Le même phénomène est observé à la reprise de léchage après une période d'arrêt.

1.4 Perspectives d'emploi

Les procédés technologiques permettant l'élaboration d'un tel verre sont limités en raison, d'une part, de l'impossibilité d'utiliser une technique de gélification, le verre ne contenant pas de silice, et d'autre part, des problèmes posés par son action corrosive.

En effet, des tests de corrosion effectués avec différents matériaux ont montré que, à chaud, il n'existait aucun métal ni alliage métallique capable de résister à la corrosion de ce verre en fusion pendant un temps acceptable. Quelques matériaux céramiques pourraient offrir une meilleure résistance, mais leur utilisation est limitée par d'autres inconvénients (faible résistance aux chocs thermiques, difficultés d'obtention de la forme désirée, etc.).

C'est pourquoi deux autres études ont été mises en œuvre afin de trouver des compositions moins riches en phosphore. La première a porté sur l'introduction de silice dans un verre phosphaté dans le but de diminuer la teinture en $P_2O_5$ et éventuellement de pouvoir gélifier, la seconde a porté sur l'introduction d'un minimum d'anhydride phosphorique dans un verre silicate de façon à obtenir une digestion correcte du molybdène.
2. Verres phosphatés contenant de la silice

En dehors de l'oxyde de molybdène, les constituants de ces verres sont initialement :
- de l'anhydride phosphorique nécessaire à la digestion de MoO₃
- SiO₂, Al₂O₃, Na₂O, constituants de l'argile gélifiante utilisée comme matière première.

L'étude a porté sur la mise au point d'une composition ayant à l'origine les caractéristiques suivantes :

a) Teneur en P₂O₅ comprise entre 20 et 50% et teneur en SiO₂ comprise entre 50 et 20%.

b) Point de fusion ne dépassant pas 1100°, le but immédiat à atteindre étant la possibilité d'une quantité non négligeable de molybdène et la non-formation d'une zone de démixion au sein des produits obtenus. En effet, il était à craindre que l'on obtienne deux phases bien distinctes, l'une riche en P₂O₅ et pauvre en SiO₂ et la seconde inversée, le molybdène étant en majeure partie dans la phase la plus riche en phosphore.

Le diagramme SiO₂ - P₂O₅ - Al₂O₃ + Na₂O a été exploité avec un rapport pondéral Al₂O₃/Na₂O = 1. Une seule composition a été retenue :

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅</td>
<td>40</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20</td>
</tr>
<tr>
<td>Na₂O</td>
<td>20</td>
</tr>
</tbody>
</table>

On obtient à 1100° un verre homogène transparent, incolore. Les autres compositions du diagramme sont à la même température plus ou moins incuites.

À ce verre ont été ajoutées des quantités croissantes de MoO₃. Plus la teneur est importante, plus le produit passe de l'aspect vitreux à l'aspect grésé. À 20% de MoO₃, le produit est grésé et manque de cuisson. Comme cette teneur est intéressante, il convenait donc d'abaisser le point de fusion. Pour cela, on a remplacé une partie de P₂O₅ par B₂O₃ fondant énergique, ce qui offre également l'avantage de diminuer le pouvoir corrosif du verre. On obtient à 1100° un produit vitrifié non translucide mais très homogène, de formule suivante :

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅</td>
<td>18,4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>16</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>Na₂O</td>
<td>16</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>13,6</td>
</tr>
<tr>
<td>MoO₃</td>
<td>20</td>
</tr>
</tbody>
</table>

Ce produit est liquide à partir de 900°, mais à cette température le molybdène n'est pas entièrement digéré.

L'influence de chaque constituant sur la digestion du molybdène a été examinée afin de diminuer encore si possible la teneur en P₂O₅ tout en conservant un point de fusion acceptable.
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2.1 Influence de la soude

La diminution de la teneur en soude ne nuit pas à la digestion du molybdène, mais si l'on réduit parallèlement la teneur en $P_2O_5$, il faut diminuer également la teneur en molybdène. Les limites trouvées sont pondéralement $P_2O_5/MoO_3 > 1$ avec $P_2O_5 > 11\%$.

2.2 Influence de l'alumine

L'augmentation de la teneur en alumine est sans influence sur la digestion du molybdène tout au moins jusqu'à une certaine teneur en $Al_2O_3$ au delà de laquelle la réfractarité devient telle que l'examen des produits obtenus ne peut donner aucune indication. Une diminution corrélative de la teneur en $P_2O_5$, même accompagnée d'une réduction de la teneur en $MoO_3$ ne semble pas favorable.

2.3 Influence de la silice

La diminution de $SiO_2$ semble, dans des limites restreintes, favorable à la digestion du molybdène.

2.4 Influence de l'anhydride borique

Il est difficile de se rendre compte de l'effet de la variation de la teneur en $B_2O_3$ en raison de la non-continuité des résultats obtenus:

- dans tous les essais on a observé:
  - soit des verres,
  - soit deux phases, l'une vitreuse, l'autre grésée,
  - soit deux phases grésées,
  - soit une seule phase grésée.

Jamais deux phases vitreuses n'ont été observées, tout au moins par examen visuel, dans un même produit.

Lorsque deux phases sont en présence, la phase inférieure est toujours en quantité plus faible et plus dense que la phase supérieure. Des analyses ont montré également que la teneur en $MoO_3$ y était beaucoup plus importante.

De tout ceci, plusieurs compositions ont été retenues afin de pousser leur étude plus loin (tableau VII). Ces produits sont tous vitrifiés et ont une teneur en $P_2O_5$ inférieure à celle du verre initial. La composition pratique diffère de la composition théorique par l'emploi comme matière première de l'argile gélifiante qui contient des impuretés. De plus, la composition réelle, c'est-à-dire la formule du verre après cuisson doit différer également de la composition pratique en raison des phénomènes de volatilisation pouvant intervenir lors de la cuisson ($P_2O_5 - MoO_3$).

Les compositions retenues devront être présélectionnées en actif.

3. Verres silicatés contenant de l'anhydride phosphorique

On a cherché à obtenir une composition en majorité silicreuse, en gardant comme composition de base les verres ASA 15 précédemment définis.
TABLEAU VII

VERRES SILICO-PHOSPHATÉS MOLYBDÉNIQUES À FAIBLE TENEUR EN SiO₂

<table>
<thead>
<tr>
<th></th>
<th>Composition théorique</th>
<th>Composition pratique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1° M</td>
<td>1° P</td>
</tr>
<tr>
<td>B₂O₅</td>
<td>16,50</td>
<td>16</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14,35</td>
<td>17,35</td>
</tr>
<tr>
<td>Al₃O₃</td>
<td>28,80</td>
<td>30,25</td>
</tr>
<tr>
<td>Na₂O</td>
<td>14,35</td>
<td>17,35</td>
</tr>
<tr>
<td>B₃O₃</td>
<td>12,20</td>
<td>14,70</td>
</tr>
<tr>
<td>MoO₃</td>
<td>13,80</td>
<td>5,35</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLEAU VIII

VERRES SILICO-PHOSPHATÉS A FORTE TENEUR EN SiO₂

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>Na₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>MoO₃</th>
<th>B₂O₃</th>
<th>UO₂</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Verres à 5% MoO₃</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33,5</td>
<td>10</td>
<td>12,95</td>
<td>0,5</td>
<td>9,5</td>
<td>4,1</td>
<td>0,4</td>
<td>5</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>35,2</td>
<td>7,5</td>
<td>12,95</td>
<td>0,5</td>
<td>9,8</td>
<td>4,4</td>
<td>0,4</td>
<td>5</td>
<td>20</td>
<td>4</td>
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<tr>
<td>42,4</td>
<td>7,5</td>
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<td>11</td>
<td>5,4</td>
<td>0,5</td>
<td>5</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>37,6</td>
<td>5</td>
<td>12,95</td>
<td>0,5</td>
<td>9,75</td>
<td>4,8</td>
<td>0,5</td>
<td>5</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Verres à 7,5% MoO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31,7</td>
<td>10</td>
<td>12,85</td>
<td>0,5</td>
<td>9,12</td>
<td>3,85</td>
<td>0,4</td>
<td>7,5</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>33,4</td>
<td>7,5</td>
<td>12,85</td>
<td>0,5</td>
<td>9,5</td>
<td>4,1</td>
<td>0,3</td>
<td>7,5</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>37</td>
<td>7,5</td>
<td>13</td>
<td>0,55</td>
<td>10,1</td>
<td>4,85</td>
<td>0,35</td>
<td>7,5</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Verres à 10% MoO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37,6</td>
<td>5</td>
<td>12,95</td>
<td>0,55</td>
<td>9,7</td>
<td>4,8</td>
<td>0,45</td>
<td>10</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>33,96</td>
<td>5</td>
<td>12,7</td>
<td>0,5</td>
<td>9,1</td>
<td>4,3</td>
<td>0,4</td>
<td>10</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>31,6</td>
<td>7,5</td>
<td>12,7</td>
<td>0,5</td>
<td>9,2</td>
<td>3,8</td>
<td>0,4</td>
<td>10</td>
<td>20</td>
<td>4</td>
</tr>
</tbody>
</table>
Des quantités croissantes de $P_2O_5$ ont été introduites dans ces verres; il s'avère qu'il est possible d'assimiler une teneur de 10% de $P_2O_5$ sous forme de phosphate de soude, ou mieux, pyro-phosphate de soude.

Par contre, la digestion d'anhydride molybdique s'est avérée difficile. Elle n'est pas favorisée par un excès de $Na_2O$; par contre, l'addition de $B_2O_3$, à partir de 5%, améliore l'homogénéité et donne des masses vitrifiées légèrement opaques. L'aspect du verre s'améliore quand $B_2O_3$ augmente.

A la suite des essais préliminaires, des compositions contenant en particulier $SiO_2 - Al_2O_3 - Na_2O - Fe_2O_3 - MoO_3 - B_2O_3 - UO_2 - P_2O_5$, ont été étudiées, pour les teneurs de $MoO_3$ de 10% maximum, de $B_2O_3$ de 10 à 20%, de $P_2O_5$ de 10% maximum.

Les produits obtenus sont tous vitrifiés. Par contre, nous avons noté:
- l'opacité augmente avec la teneur en $B_2O_3$ et diminue avec l'augmentation de $P_2O_5$,
- l'accroissement de $P_2O_5$ entraîne l'apparition de mousses en surface, dues certainement à la volatilité du $P_2O_5$; ces mousses diminuent lorsque $B_2O_3$ augmente,
- des décantations apparaissent quand $P_2O_5$ diminue et pour les fortes teneurs de $MoO_3$. La phase inférieure noire très bien verrée présente des analogies de couleur et d'éclat avec les verres très phosphatés molybdéniques.

Un certain nombre de compositions ne présentant pas ou peu ces phénomènes a été sélectionné pour étude plus complète et mesure de la solubilité (tableau VIII).

IV. CONCLUSION

La vitrification des solutions du type Marcoule est pratiquement résolue par la production de verres silicatés. La composition de ces verres est telle qu'il est possible d'admettre une certaine variation dans les compositions des solutions, notamment la teneur en sodium. Il reste uniquement un ultime choix à faire entre les différentes formules envisagées et il est probable que ce choix portera sur un verre réalisable par gélification en raison de la faible perte d'activité enregistrée lors de l'élaboration.

L'étude du traitement des solutions molybdiques qui est à un stade moins avancé, permet, en dépit des difficultés rencontrées, de voir quelles sont les voies possibles à la réalisation du solide répondant parfaitement aux conditions requises.

RÉFÉRENCES

N. BREZHNEVA: What is the effect of temperature on the process of devitrification of the glass obtained, and how does the appearance of the crystalline phase affect the leaching of radiocaesium from the glass?

C. SOMBRET: Devitrification of the glass can be brought about by irradiation or by a slow cooling rate during preparation. In the latter case, we found that we had to use a cooling rate of less than 50°C/hr to obtain devitrification, although at that rate the samples observed may be regarded as completely vitreous under X-ray examination and only microphotography permits the appearance of crystalline nuclei to be observed. If we used rates of a few degrees Centigrade per hour, we would probably observe true crystals.

Leaching tests with Cs$^{137}$ as a tracer indicated that a sample cooled in this way showed a loss ten times higher than that of a normal sample. This phenomenon had also been observed by our Canadian colleagues. Normal glass, even though not tempered and cooled at a rate much higher than 50°C/hr, is therefore perfectly trustworthy in this regard.
FIXATION OF RADIOACTIVE WASTE IN GLASS.
PART II. THE EXPERIMENTAL EVALUATION
OF PHOSPHATE AND BOROSILICATE GLASSES

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ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL

Abstract — Résumé — Аннотация — Resumen

FIXATION OF RADIOACTIVE WASTE IN GLASS. PART II. THE EXPERIMENTAL EVALUATION OF PHOSPHATE AND BOROSILICATE GLASSES. A glass suitable for long-term storage of fission-product wastes must be chosen firstly with regard to the method of storage, and secondly with regard to reliability of manufacture in a highly radioactive plant. The factors that are relevant to storage include leach resistance, thermal and radiation stability and the percentage of waste that can be incorporated, while the physical and chemical nature of glass-forming additives together with the melting point and viscosity of the glass relate to the manufacturing process. The relative importance of these factors is discussed. Experimental studies of the borosilicate glasses that have been chosen for pilot-plant work are described, including the effect of radiation doses of up to $10^{12}$ rad on their physical and chemical properties. Glasses of other kinds have also been examined and their potential value as storage media is compared with the borosilicate glasses.

FIXATION DES DÉCHETS RADIOACTIFS DANS LE VERRE, DEUXIÈME PARTIE: ÉVALUATION EXPÉRIMENTALE DES VERRES AU PHOSPHATE ET AU BOROSILICATE. Un verre convenant au stockage de longue durée des déchets de fission doit être choisi; premièrement, en fonction de la méthode de stockage et deuxièmement, eu égard à la sécurité des opérations de traitement dans une unité de haute activité. En ce qui concerne le stockage, les facteurs importants sont la résistance à la corrosion, la stabilité thermique, la stabilité vis-à-vis des rayonnements et le pourcentage de déchets pouvant être incorporés. Au point de vue de la sécurité des manutentions, il faut tenir compte de la nature physique et chimique des éléments intervenant dans la composition du verre, du point de fusion et de la viscosité du verre. Les auteurs examinent l'importance relative de ces facteurs. Ils décrivent les études expérimentales faites sur les verres au borosilicate choisis pour l'usine pilote, de même que l'influence des rayonnements sur leurs propriétés chimiques et physiques pour des doses allant jusqu'à $10^{12}$ rad. Ils ont étudié d'autres espèces de verre et examiné la possibilité de les employer comme milieu de stockage, en les comparant aux verres au borosilicate.

ФИКСАЦИЯ РАДИОАКТИВНЫХ ОТХОДОВ В СТЕКЛЕ. ЧАСТЬ II. ЭКСПЕРИМЕНТАЛЬНАЯ ОЦЕНКА КАЧЕСТВ ФОСФАТНЫХ И БОРОСИЛИКАТНЫХ СТЕКОЛ. Стекло для длительного хранения отходов, содержащих продукты деления, должно выбираться, во-первых, с учетом предполагаемого метода хранения и, во-вторых, с учетом возможности его получения на высокорадиоактивных установках. Важными факторами с точки зрения хранения являются: стойкость против выщелачивания, теплостойкость и радиационная стойкость, а также предельная доля вводимых отходов; что же касается физического характера и химических свойств элементов, добавляемых для стеклообразования, а также точки плавления и вязкости стекла, то эти факторы харизмеряются процессом изготовления. Обсуждается относительная важность этих факторов. Приводятся данные исследования боросиликатных стекол на экспериментальной установке; среди входят также исследования влияния дозы облучения (до $10^{12}$ рад) на их физические и химические свойства. Были исследованы также и стекла других сортов. Потенциальные возможности использования этих стекол в качестве среды для хранения радиоактивных отходов сопоставляются с возможностями в отношении боросиликатных стекол.

FIJACIÓN DE DESECHOS RADIOACTIVOS EN VIDRIO, PARTE II: EVALUACIÓN EXPERIMENTAL DE LOS VIDRIOS AL FOSFATO Y AL BOROSILICATO. El principal factor que es preciso tener en cuenta al proceder a la elección de un vidrio adecuado para almacenar por largos periodos desechos de productos de fusión es el método de almacenamiento que se va a aplicar; el segundo factor es el grado de seguridad que ofrece la ela-
If it is desired to achieve the maximum safety during the storage of waste fission products, then they must be rendered both immobile and insoluble. There is little doubt that this is most nearly achieved when the fission elements are incorporated as cations in the matrix of a high melting-point vitreous or ceramic substance. But the rate at which fission products are produced in civil power reactors is such that for some 3000 MWe, $10^8$ c/d have to be placed in storage and if a process of fixation in glass is to be employed, it must be a process that is industrially feasible, by remote operation and certainly of extreme reliability. The operation of the fixation process thus dictates certain properties of the storage medium and the choice of glass must lie within the practical limitations of its manufacture. This paper first attempts to define the properties of glasses that are both suitable for incorporation of the high-activity wastes from British fuel reprocessing plants and that could also be produced by the Harwell fixation process. The experimental evaluation of these properties for a number of glass systems is then described. We use the term "glass" throughout in referring to ceramic bodies, although many of the systems of interest are not single-phase supercooled liquids, but form massive polycrystalline blocks of material of low surface area.

2. PROPERTIES OF GLASS FOR THE HARWELL PROCESS

2.1. Melting point and viscosity

It is generally observed that the durability of a glass in a given system increases with its melting point and glasses are known with melting points as high as 1800°C. The furnace we have chosen has Kanthal elements which limit its maximum temperature to 1300°C but it is considered that the elements should last indefinitely at 1150°C and we may set this as the maximum operating temperature. Taking an arbitrary definition of melting point as the temperature at which all bubbles disappear from a glass when it is formed by heating sintered oxides, it is evident that the process is suitable for the production of glasses with melting points below 1150°C and so investigations have been largely concerned with glasses melting between 900 and 1100°C.
Another important process consideration is that the temperature at which the sinter begins to melt and fall under its own weight should be well below the melting point (Part I, Section 2.2).

2.2. Leach resistance

It is quite obvious that the more insoluble is the storage medium, the smaller is the risk of accidental contamination of ground water either as a result of access of water to a storage area, or uncontrolled dispersal of the stored waste. It is not proposed to attempt to assess the magnitude of these risks when for example a mass of dry waste material will by its own fission-product decay heat almost certainly ensure the dryness of its environment for many years. It is a condition of maximum safety that the glass be as durable as process limitations will allow, notwithstanding that the glass is to be produced and stored in vessels of a highly corrosion-resistant steel in a dry environment.

2.3. Thermal stability and devitrification

The fission-product decay heating will raise the temperature of glass during storage. The limitation that should be placed on this temperature will depend on the ability of the glass to maintain its massive form and insolubility. The maximum temperature that the glass may be allowed to attain during storage is that temperature below which there should be no change of physical or chemical form causing reduced durability. The effect of temperature is likely to be modified by that of radiation.

2.4. Radiation stability

During storage, between $10^{11}$ and $10^{12}$ rad of energy will be deposited by $\beta$ and $\gamma$ radiation in glass made from high burn-up wastes and it is important to estimate the effect of this radiation on the long-term stability of the glass.

2.5. Waste-oxide content

The more waste oxide the glass contains the smaller will be the volume of glass in storage. However, increasing the waste-oxide content will affect the leach resistance and also increase the specific activity, and thus the heat rating of the cylinders, and a compromise must be sought.

2.6. Nature of glass-forming constituents

In the Harwell process both the waste solution and glass-formers have to be metered to the process vessel. For the borosilicate system the borax and silica are added as a slurry but this operation, in addition to its technical difficulty, adds an undesirable load to the evaporation process. This
could be avoided by adding sodium borosilicate glass as a dry solid, providing of course, that the technique could be established. A highly concentrated liquid feed, as is possible for the production of glasses based on the phosphate system, is much the simplest, but again some surplus water is added, and factors such as compatibility and volatility have to be considered.

2.7. Compatibility

It is essential that there should be no reaction between the glass constituents and the process vessel at any stage during production or storage that might destroy the integrity of the process vessel.

3. EXPERIMENTAL EVALUATION OF BOROSILICATE GLASSES

Pilot-plant studies to date have employed almost exclusively glasses from the system formed by fusion of the oxides with borax and silica, and the waste oxides have been those representative of the reprocessing of natural uranium fuels of low burn-up (300-600 MWd/t(metric)). The oxides are principally those of uranium, iron and aluminium with a few percent of fission and corrosion products (Table I). Much information on the preparation and properties of these glasses has already been published [1].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Major constituents of waste solution (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural uranium low burn-up (300-600 MWd/t)</td>
<td>U 45%, Fe 32%, Al 14% Fission products 7% Corrosion products 2%</td>
</tr>
<tr>
<td>Natural uranium high burn-up (3000 MWd/t)</td>
<td>U 8%, Fe 13%, Al 17% Fission products 60% Corrosion products 2%</td>
</tr>
</tbody>
</table>

3.1. Melting point and viscosity

Melting-point data have been obtained for compositions richer in boron and these together with previous results are given in Fig. 1. Between 950°C and 1100°C the melting point, as defined above, is largely determined by the boron content of the glass. The other important property, that of the temperature interval between the onset of melting and the release of air bubbles from the melt, called the flux range, is shown in Fig. 2. The accuracy of this measurement is low as the interval is not well defined, but
the action of the relatively low melting-point borax is to flux the oxide particles at temperatures well below the melting point. The relevance of this to the process has been fully discussed in Part I.

3.2. Leach resistance

Information concerning the effect of composition on leach factor has been published [1]. This has been extended to compositions to include the glass that is currently being produced in the pilot plant, which contains 32% borax. Incidentally, the leach factor, $F$, as defined by GROVER and CHIDLEY [1] has the units (cm/week)$^{-1}$ and represents the reciprocal of the mean depth or thickness of the surface layer from which a constituent is dissolved away in a week. Values of $F_U$, the leach factor for uranium, have been determined for samples taken from two large blocks of glass produced during two pilot-plant runs. One of these incorporated a spent filter containing ferric oxide for ruthenium adsorption. (See Part III*). The $F_U$ values obtained at the positions of sampling are shown in Fig. 3 and they are

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* ELLIOT, M. N. et al., "The fixation of radioactive waste in glass, Part III. The removal of ruthenium and dust from nitric acid and vapours," These proceedings.
the means of six weeks leaching. They show very good agreement with $F_U$ obtained from the test preparation ($3 \times 10^6$) and the incorporation of the filter has had no significant effect. Preliminary values for iron, $F_{Fe}$, show the same order of solubility as uranium. The glass had become devitrified during manufacture but nevertheless it shows the same degree of insolubility as borosilicate apparatus glass [2] and this is considered to be very satisfactory.

However, the $F$ values obtained with such glasses are only relevant providing radiation does not have a significant effect on durability. The effects of irradiation on the durability of some borosilicate glasses have recently been studied for very high radiation doses and this investigation is next discussed.

3.3. Radiation stability

Previous work by GROVER and CHIDLEY [1] has shown no deterioration in leach resistance after irradiation of glasses to $10^8$ rad, and WATSON [3] had irradiated a glass based on the nepheline syenite-waste oxide system to $4 \times 10^{10}$ rad using Co$^{60}$ $\gamma$ rays without deterioration of strength or leach resistance.
However, the energy deposition in a glass containing waste from high-burn-up natural-uranium fuel containing 30% waste oxides is shown in Fig. 4 and it is seen that in general, cumulative doses of between $10^{11}$ and $10^{12}$ rad are anticipated. Most of this is deposited in the first few years of storage. It was therefore decided to irradiate glass to doses in excess of $10^{11}$ rad. Since the rate of deposition would necessarily have to be faster than in actual storage, effects due to the rate as well as the magnitude of the dose should be sought. The method of preparation was another variable to be considered. The effect of radiation on the glass would be studied as an observed change of leach factor, providing of course that the massive form of the specimen were retained. X-ray examination would also be employed, to see if crystallization occurred.

3.3.1. Method of irradiation

The most practicable method of achieving doses greater than $10^{11}$ rad in a reasonable time was considered to be neutron irradiation of a borosilicate glass. Reasons for this are discussed in detail elsewhere [4] but in brief, methods such as the use of particle accelerators are only suitable for small water-cooled targets, while irradiation by spent fuel-element
or Co$^{60}$ sources require excessive times. The incorporation in the glass of a radioactive isotope such as Ce$^{144}$ poses difficult radioactivity handling problems and would require 11 wt. %CeO$_2$. While this composition is not representative of actual glass systems, the radiation would be typical and furthermore effects of transmutation, such as valency and ionic size changes, would be observable. The advantage of the reactor irradiation method is that the glass system to be used was the one that had already been demonstrated to be suitable for process manufacture and to be unaffected by moderate doses of radiation. It was admittedly a composition chosen for the incorporation of low burn-up waste but it is very probable that glasses for high burn-up waste will be derived from the borosilicate system. Also a number of samples can be irradiated simultaneously and the induced activities due to (n, $\gamma$) and U$^{235}$ fission reactions are low compared with the Ce$^{144}$ inclusion method, making handling easy. The energy deposition is principally due to the Bi$^{115}$(n, $\alpha$) Li$^7$ reaction which is likely to be more damaging than that resulting from fission-product decay and be a more severe test of the ability of a glass to withstand irradiation. One objection to the neutron irradiation method is that because of the high neutron cross-section of boron the dose received decreases with distance below the surface. ELLIOT [4] has calculated the variation of dose with depth for the irradiation conditions used and concluded that the depth of neutron penetration was several orders larger than the depth of the glass dissolved in leaching. This was confirmed by the observation that small pieces of glass irradiated together with the large samples showed induced radioactivity that was independent of sample weight up to at least 150 mg.
3.3.2 Irradiation and leaching

Four batches of glass were prepared by Grover and Chidley's method [1], and heat-treated according to the conditions shown in Table II. This was intended to discover if radiation damage was affected by the time the glass spent at temperatures above its melting point and the rate of cooling after preparation. The composition of the glass is given in Table III. Pieces weighing about 3 g together with smaller pieces, were taken from each batch and irradiated according to the conditions summarized in Table IV with the doses and dose rates as calculated by ELLIOT [4]. Irradiations 2 and 3 were intended to be the same dose but to differ in dose rate by a factor ten. Owing to the uncertainty in predicting the neutron flux in the reactor, these irradiations in fact differed both in dose as well as dose rate, and the difference in the rate factor was less than three.

After removal from the reactor the 3 g samples were leached with distilled water. All samples were leached for ten weeks and the leach solutions changed and analysed at the end of each week. Leaching of the short irradiation and unirradiated samples was continued for about six months but without analysis of the solutions. The solutions arising from a further ten weeks leaching were analysed producing a second series of results, which together with the first series of leach results were analysed statistically.

3.3.3 X-Ray examination

The smaller pieces of glass which had been irradiated were examined by X-ray diffraction. The results are presented in Table V.
TABLE III

GLASS COMPOSITION (MIX 279)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt. % Oxide</th>
<th>wt. % Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{U}_3\text{O}_8$</td>
<td>12.0</td>
<td>10.2</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>11.3</td>
<td>7.9</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>6.7</td>
<td>3.6</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>7.1</td>
<td>5.3</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>15.9</td>
<td>4.2</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>47.0</td>
<td>22.0</td>
</tr>
<tr>
<td>balance oxygen</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE IV

IRRADIATION CONDITIONS

<table>
<thead>
<tr>
<th>Irradiation number</th>
<th>Mean surface dose (rad)</th>
<th>Irradiation time (d)</th>
<th>Dose rate (rad/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$6.6 \times 10^9$</td>
<td>1.5</td>
<td>$4.5 \times 10^9$</td>
</tr>
<tr>
<td>2</td>
<td>$4.5 \times 10^9$</td>
<td>12.4</td>
<td>$3.6 \times 10^9$</td>
</tr>
<tr>
<td>3</td>
<td>$2.0 \times 10^{11}$</td>
<td>126</td>
<td>$1.6 \times 10^9$</td>
</tr>
<tr>
<td>4</td>
<td>$5.7 \times 10^{11}$</td>
<td>130</td>
<td>$4.4 \times 10^9$</td>
</tr>
</tbody>
</table>

3.3.4. Analysis of leach data

It must be stressed that the physical appearance of all the glass samples was unaltered by the radiation they received.

The leach solutions were analysed for uranium by the fluorometric method which has the necessary sensitivity but relatively poor precision. Caesium values were also obtained by counting induced Ca$^{134}$ activity and by radioactivation analysis. These results will be discussed separately.

(a) Uranium. Results were obtained from two series of leaching experiments, the first analyses being obtained immediately after irradiation and the second after an interval of six months. They showed a considerable variation, the variation in the second series of leach values being greater than in the first. The results are summarized in Table VI, and while interpretation of the observations is very difficult, there appears to be a dose effect although it is improbable that $F_U$ has been reduced by more than an order
TABLE V

<table>
<thead>
<tr>
<th>Radiation dose</th>
<th>Batch type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>20°C above, 6 hr</td>
</tr>
<tr>
<td></td>
<td>12 hr cooling</td>
</tr>
<tr>
<td>Unirradiated</td>
<td>Δ ( \alpha Fe_2O_3 )</td>
</tr>
<tr>
<td></td>
<td>( Na_x UO_3 )</td>
</tr>
<tr>
<td>6.6 \times 10^8 rad</td>
<td>( \alpha Fe_2O_3 )</td>
</tr>
<tr>
<td>4.5 \times 10^{10} rad</td>
<td>( \alpha Fe_2O_3 )</td>
</tr>
<tr>
<td>2 \times 10^{11} rad</td>
<td>( \alpha Fe_2O_3 )</td>
</tr>
<tr>
<td>5.7 \times 10^{11} rad</td>
<td>( \alpha Fe_2O_3 )</td>
</tr>
</tbody>
</table>

\( \Delta = \) unidentified phase.

...
MEAN LEACH FACTORS FOR URANIUM, \( F_u \)

First series

<table>
<thead>
<tr>
<th>Glass Preparation</th>
<th>Batch A</th>
<th>Batch B</th>
<th>Batch C</th>
<th>Batch D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>( 3.6 \times 10^6 )</td>
<td>( 9.7 \times 10^5 )</td>
<td>( 2.1 \times 10^6 )</td>
<td>( 2.1 \times 10^7 )</td>
</tr>
<tr>
<td>( 6.6 \times 10^9 ) rad</td>
<td>( 2.9 \times 10^5 )</td>
<td>( 1.9 \times 10^5 )</td>
<td>( 1.1 \times 10^6 )</td>
<td>( 2.5 \times 10^6 )</td>
</tr>
<tr>
<td>( 4.5 \times 10^{10} ) rad</td>
<td>( 2.7 \times 10^5 )</td>
<td>( 1.2 \times 10^5 )</td>
<td>( 7.5 \times 10^5 )</td>
<td>( 1.2 \times 10^6 )</td>
</tr>
<tr>
<td>( 2 \times 10^{11} ) rad</td>
<td>( 1.7 \times 10^5 )</td>
<td>( 2.4 \times 10^5 )</td>
<td>( 5.3 \times 10^5 )</td>
<td>( 6.2 \times 10^5 )</td>
</tr>
<tr>
<td>( 5.7 \times 10^{11} ) rad</td>
<td>( 3.2 \times 10^5 )</td>
<td>( 2.6 \times 10^5 )</td>
<td>( 3.2 \times 10^5 )</td>
<td>( 4.9 \times 10^5 )</td>
</tr>
</tbody>
</table>

Second series

<table>
<thead>
<tr>
<th>Glass Preparation</th>
<th>Batch A</th>
<th>Batch B</th>
<th>Batch C</th>
<th>Batch D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>( 1.0 \times 10^6 )</td>
<td>( 1.3 \times 10^6 )</td>
<td>( 4.8 \times 10^6 )</td>
<td>( 4.9 \times 10^7 )</td>
</tr>
<tr>
<td>( 6.6 \times 10^9 ) rad</td>
<td>( 1.9 \times 10^5 )</td>
<td>( 2.4 \times 10^5 )</td>
<td>( 2.5 \times 10^6 )</td>
<td>( 1.7 \times 10^6 )</td>
</tr>
<tr>
<td>( 4.5 \times 10^{10} ) rad</td>
<td>( 4.8 \times 10^5 )</td>
<td>( 2.7 \times 10^5 )</td>
<td>( 7.2 \times 10^5 )</td>
<td>( 3.5 \times 10^6 )</td>
</tr>
</tbody>
</table>

There were variations in durability due to preparation method, dose, rate, time of leach etc. The actual leach factors could be calculated from the specific activity of the caesium in the glass.

The values for \( F_{Cs} \) were of the order of \( 10^6 \) and varied between \( 2 \times 10^5 \) and \( 5 \times 10^6 \), but no correlation could be found between the variations in \( F_{Cs} \) and the factors such as preparation, dose and dose rate. Any effects that resulted must have been very small and it must be concluded that radiation is unlikely to increase the leachability of caesium from borosilicate glass during storage. The similarity in behaviour of uranium and caesium show that the structure of the glass must have remained essentially intact.

4. GLASS SYSTEMS FOR HIGH BURN-UP WASTES

As higher burn-up of nuclear fuel is achieved so the waste solution will contain a progressively higher percentage of fission products and less uranium, iron and aluminium. In Table I is given the latest estimate of the composition of waste from processing near-natural uranium fuel irradiated to 3000 MWd/t and it is seen that fission products account for about 60%
of the total weight. Inspection of Fig. 1 shows that for this system the melting point will rise with addition of waste oxides, if the substitution of 60% fission products for iron and uranium has little effect. A glass containing 40% waste oxides is likely to have a melting point in excess of 1200°C. Other systems have been examined to see if good, low melting point, leach-resistant glasses could be prepared to contain 40% waste oxides of the high burn-up composition. Some of these were chosen because they offered the possibility of a liquid as opposed to slurry addition of glass-formers and also by eliminating boron to reduce the nuisance of volatile solids in the process. The more promising compositions, as revealed by the preliminary tests reported below, are being further evaluated.

4.1. Nepheline syenite - calcium oxide - boric oxide - waste oxides

This system was examined for three waste oxide contents 22, 30 and 40%. The glass forming region has been determined in each case up to 1100°C. Leach factors for calcium, sodium and potassium ($F_{Ca}$, $F_{Na}$, $F_{K}$) have been determined for distilled water and values greater than $10^4$ obtained for 40% waste oxides. There was in general a small increase in durability with decreasing waste content, $F_{K}$ for 22% being rarely greater than $10^5$.

4.2. Sodium phosphate - calcium oxide - silica - waste oxides

The better glasses were obtained in the absence of calcium oxide. Leach factors were higher than $10^5$ and $10^6$ for potassium and sodium respectively for two compositions.

4.3. Lead borosilicate - waste oxides

Glasses were obtained containing 20% waste oxides melting at 1100°C but it was not possible to prepare glasses at 950°C.

4.4. Sodium phosphate - lead oxide - boric oxide - waste oxides

This system was investigated for glasses melting below 950°C. Values for $F_{Na}$ and $F_{K}$ greater than $10^5$ were observed for two compositions and it is possible that higher values could be obtained for higher melting points.

4.5. Sodium phosphate - lead oxide - silica - waste oxides

These glasses containing 40% waste oxides and melting below 950°C had $F_{Na}$ and $F_{K}$ values of about $10^8$. The presence of lead did not increase leach factors but slightly increased the mobility of the melts.

4.6. Sodium phosphate - silica - waste oxides

The most durable glasses based on sodium phosphate were obtained with addition of silica. Glasses were prepared at 950°C and 1100°C. $F_{Na} > 10$ and $F_{K} > 10^5$ were observed and these were not affected by the temperature
of preparation. The resistance to N/100 nitric acid was moderate, values of \( F_{Na} \) and \( F_{K} \) being about \( 10^3 \) and \( 10^4 \) respectively.

One of these glasses containing 54% \( \text{Na}_2\text{O}:\text{P}_2\text{O}_5 \) and 6% \( \text{SiO}_2 \) was made in a 4-in diam. stainless-steel vessel by the Harwell process. The interior of the vessel was badly scaled and pitted after 3 hr operation and further work would be necessary before phosphate systems could be seriously considered.

4.7. Sodium phosphate - sodium silicate - waste oxides

The attraction of this system is that a completely soluble glass-forming addition is possible and boron is eliminated. However the glasses prepared with 40% waste oxides at 950°C were not as durable as when silica is used instead of sodium silicate, \( F_{Na} \) being an order lower.

4.8. Boron phosphate - sodium oxide - silica - waste oxides

The glass-forming region has been examined at 950°C with 40% waste oxide content. Although increasing silica causes increased leach factors they are generally poorer than \( 10^5 \).

5. THERMAL STABILITY AND DEVITRIFICATION

Several glasses containing 40% waste oxides from the systems in sections 4.2, 4.4, 4.5 and 4.6 were thermally devitrified. Temperatures of between 510 and 590°C for periods between 24 and 72 hr were required. A glass from the sodium phosphate - silica system (4.6) showed a decrease in \( F_{Na} \) and \( F_{K} \) by about 5, and this was typical. X-ray diffraction analysis showed that glass-forming and waste constituents are crystallized from the glass. Irradiation studies are in progress.

The practical implication of devitrification is hard to assess. With one exception the glasses so far produced by the Harwell process have been found to be devitrified when the steel vessel has been cut open. The leach resistance of the devitrified glass has not been found to be significantly different from the small non-crystalline test preparations, at least as measured by uranium solubility. It is likely to be difficult to avoid devitrification during preparation and storage since temperature differences will always be present in the glass blocks due to the method of manufacture and especially owing to fission-product heating. However the devitrified glass in the steel vessel has been found to be massive and stable, whereas the one non-crystalline product was brittle and very easily shattered. Thus while devitrification is likely to occur it should not necessarily be deleterious.

6. COMPATIBILITY

Visual, metallographic and dimensional evidence, show that the borosilicate glasses that have been made in the Harwell pilot plant do not react with the stainless-steel process vessel. On the other hand the phosphate
containing glasses are very corrosive to steels that are at present used for process vessels. For example steel specimens immersed for 60 hr at 950°C in molten-lead borophosphate glass containing 40% waste oxides were completely disintegrated. Calorising* the steel, a process which gives the steel a coating of $\alpha$-$\text{Al}_2\text{O}_3$, did not improve the resistance to phosphate melt corrosion, excepting when the calorised steel was preheated to 1150°C for 16 hr when there was a 30% loss in weight after 53 hr at 950°C in the lead borophosphate melt.

7. CONCLUSIONS

It has been demonstrated that a borosilicate glass containing 25% waste oxides can be manufactured in the Harwell process. As far as it has been possible to carry out tests relevant to a 500-yr period, this glass would be a very satisfactory medium for storage of fission-product wastes, being almost insoluble in water and this insolubility is not significantly affected by devitrification or even by very high radiation doses. It does not react with the stainless-steel process vessel even at the high temperatures of its manufacture.

The borosilicate system may not be suitable for incorporation of waste oxides to a greater extent than 30% if the present melting-point limitations persist. Nevertheless, up to 40% waste oxides may be included in many other glass compositions and several of these show high durability. In particular the phospho-silicate system gives very good glasses and while such glasses offer advantages in metering and handling the glass-forming additives, this is offset by the corrosive nature of phosphate melts. There is little doubt that a range of glass compositions is available each of which would satisfy the needs of a storage medium equally well. The choice will thus rest largely on the ease by which the glass can be produced in a process subject to the most exacting requirements of handling very high activities at high temperatures.

ACKNOWLEDGEMENTS

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REFERENCES


* Calorisation Company of Great Britain.
J.A. BUCKHAM: Could you make a comparison between the activity levels of leachate which has contacted your glass and the permissible contamination limits on drinking water that have been established in the United Kingdom?

W.H. HARDWICK (on behalf of M.N. ELLIOT et al.): We do not intend that the glass containing full activities should ever come into contact with drinking water. The leach resistance is very much a last line of defence because, in the first place, we would provide a dry environment (and this is ensured by fission decay heat for many years) and, in the second place, the stainless-steel containers on which the glass is prepared are highly corrosion-resistant. I think the Canadians showed early on that putting glasses directly into ground was quite impractical. The fixation in glass gives you immobility and control.

J.M. HOLMES: Was any attempt made during your irradiation tests on glass to simulate the effect of fission-product heating on the changes in glass properties? In other words, did you heat the glass at all during the irradiation?

W.H. HARDWICK: We did not do this directly, but the samples were of course at reactor temperatures during irradiation, which would be comparable with the surface temperatures of the process vessels during storage in air-cooled environments (about 50°C).
ON THE BEHAVIOUR OF RADIOISOTOPES INCORPORATED IN GLASS BLOCKS. As several isotopes have a long half-life, it is necessary to ensure that they remain securely fixed over a lengthy period. This necessitates study of their behaviour in vitreous blocks after prolonged storage, during which spontaneous heating and radiation occur and they are submitted to influence of the environment.

The efforts made to reduce the volume of the blocks for burial and to lessen the volatility of the isotopes during preparation (temperature not exceeding 1200°C) result in the blocks acquiring a heterogeneous structure, so that they are no longer true glasses but vitreous compounds. The characteristics of such blocks and their ability to immobilize fission isotopes depends to a great extent on their chemical composition (quantity and nature of flux), manner of preparation and subsequent storage.

Temperature rises brought about by the release of heat from the high-activity blocks in the burial ground lead to chemical and physical processes within them and greatly influence the retention of wastes, especially at the block surfaces. The leachability of isotopes from vitreous blocks normally increases once the temperature exceeds 400°C. It is therefore inadvisable to allow excessively high temperatures to build up in the burial grounds.

The high level of radiation from high-activity blocks also has a marked influence on changes in the structure of the blocks and consequently in the durability of the bond between them and the fission isotopes. The changes also proceed in the first instance from surfaces in contact with the surrounding media (air, water). The leachability of isotopes from radioactive blocks normally increases.

An increased release of radioisotopes from the surface into gaseous phase was established experimentally in the case of radioactive blocks.

In view of all the influences to which the vitreous blocks are subject over a considerable time, their chemical composition and manner of preparation (flux) must be carefully selected so as to ensure that the radioisotopes remain securely fixed in the buried blocks. In this connection, titanium compounds are especially interesting as fluxes.

LE COMPORTEMENT DES RADIOISOTOPES VITRIFIÉS. Etant donné la longue période de certains radioisotopes, il est nécessaire de les contenir pendant un temps prolongé, en évitant toute fuite; il faut donc étudier leur comportement dans des blocs de verre lors d'une conservation de longue durée: auto-échauffement, irradiation réciproque, influence du milieu ambiant.

Si l'on cherche à limiter la dimension des blocs aux fins d'enfouissement, et à réduire la volatilité des radioisotopes en cours de préparation (température maximum: 1200°C), on obtient des blocs de structure peu homogène. Ceux-ci se composent d'ailleurs non pas de verre véritable, mais de mélanges «vitreux». Les propriétés de ces blocs, notamment leur aptitude à fixer d'une façon durable les produits de fission radioactifs, dépendent dans une large mesure de leur composition chimique (quantité et nature des fondants), ainsi que des conditions de leur préparation et de leur conservation ultérieure.

La chaleur dégagée par les blocs fortement radioactifs, dans l'entrepôt souterrain, donne lieu à des modifications chimiques et physiques de leur structure et influe fortement sur la durée de la fixation des produits de fission, notamment près de la surface des blocs. Le risque de lixiviation s'accroît, en règle générale, lorsque la température dépasse 400°C. Il est donc souhaitable d'éviter la formation de températures trop élevées dans les entrepôts.

D'autre part, la forte densité des rayonnements émis par les blocs influe sensiblement sur la transformation de la structure des blocs et, de ce fait, sur la durée de la fixation des produits de fission qui s'y trouvent. D'ailleurs, ces transformations se produisent avant tout à partir de la surface, au contact du milieu extérieur (air, eau). D'une manière générale, le risque de lixiviation va croissant.

Les expériences ont montré que les radioisotopes des couches superficielles ont fortement tendance à passer à l'état gazeux.
Etant donné les nombreux facteurs qui agissent sur les blocs pendant un entreposage prolongé, il convient de veiller spécialement à la composition chimique de ces blocs (tondants) et aux conditions de leur préparation, si l'on veut éviter toute fuite de radioisotopes dans les blocs enfouis. A cet égard, l'emploi de composés du titane comme fondant présente un intérêt particulier.

О поведении радиоактивных изотопов, локализованных в стекловидных блоках. В связи с тем, что некоторые изотопы имеют большие периоды полураспада, необходимо обеспечить их надежную локализацию на длительное время, а это требует изучения поведения таких изотопов в стекловидных блоках под влиянием условий, которые создаются при длительном хранении: саморазогрев, самооблучение, влияние окружающей среды.

Стремление ограничить объем блоков для захоронения и летучесть изотопов при их приготовлении (температура — не выше 1200°С) приводит к неоднородной структуре таких блоков. Они не являются истинными стеклом, а "стекловидными" соединениями. Свойства таких блоков и прочность локализации в них осколочных изотопов сильно зависят от их химического состава (количество и природа флюса), условий приготовления и последующего хранения.

Повышенная температура, развивающаяся в результате тепловыделения высокорадиоактивных блоков в могильнике, вызывает химические и физические процессы в их структурах и сильно влияет на прочность локализации в них осколков, особенно с поверхности блоков. Выщелачиваемость изотопов из стекловидных блоков, как правило, возрастает после их прогрева свыше 400°С. Отсюда нежелательно допускать образования слишком высоких температур в могильниках.

Высокая плотность радиации высокорадиоактивных блоков также сильно влияет на изменение структуры блоков, а следовательно и прочности локализации в них осколочных изотопов. Изменения также идут в первую очередь с поверхности при контакте с внешней средой (воздух, вода). Выщелачиваемость изотопов из облучаемых блоков, как правило, увеличивается.

Компаративно установлен повышенный выход радиоактивных изотопов с поверхности в газовую фазу для радиоактивных блоков.

Учитывая совокупность факторов, действующих на стекловидные блоки в течение длительного времени, нужно путем специального подбора их химического состава (флюса) и условий приготовления, обеспечить надежную локализацию радиоактивных изотопов в захороненных блоках. Особый интерес в этом отношении представляет применение для флюсования соединений титана.
Безопасность захоронения радиоактивных отходов атомных производств может быть обеспечена лишь в том случае, если будет исключено попадание радиоизотопов в окружающую среду. Наличие в отходах долгоживущих изотопов (табл. 1) заставляет задуматься о прочной их локализации на долгие годы. Отсюда стремление к переводу осколочных изотопов в плавленые препараты типа стекла, которые из всех исследованных материалов, содержащих радиоизотопы, обладают максимальной химической устойчивостью [2,3,4].

Для перевода осколочных изотопов в стекловидные плавленые препараты жидкие радиоактивные отходы подвергаются обезвоживанию, кальцинированию и, после смешения с флюсовыми добавками, переводу в расплав при температуре выше 1000°С. В качестве компонентов флюсовых добавок используются некоторые глины, B₂O₃, SiO₂ и т.п. [5-8]. Стремление получить осколочный концентрат небольшого объема приводит к внесению флюсовых добавок в минимально возможном количестве, а стремление ограничить переход радиоизотопов в парогазовую fazу в процессе переработки отходов заставляет ограничить температуру при плавлении 1100 - 1200°С.

Получающийся в этих условиях препарат, строго говоря, не является стеклом, - это стекловидный материал с кристаллическими включениями. При этом стекловидную fazу составляют плавленые силикаты, растворенные в них окислы, а кристаллическую - окислы, непрореагировавшие с силикатами. Так, рентгеновский анализ показал наличие в охлажденных на воздухе плавленых препаратах кристаллических окислов железа Fe₂O₃ и Fe₃O₄, твердых растворов системы Fe₂O₃ - Cr₂O₃, а при повышенном содержании окиси магния - магnezитоферрита MgFe₂O₄. Есть основание полагать, что часть радиоизотопов также не входит в силикатные структуры (например Sr⁹⁰).
Ранее было показано, что при взаимодействии таких стекловидных блоков с водой наблюдается избирательное выщелачивание отдельных компонентов [4]. В табл. 2 приведены данные, подтверждающие избирательное выщелачивание отдельных изотопов из препарата.

Таблица 2

ВЫЩЕЛАЧИВАНИЕ ОТДЕЛЬНЫХ РАДИОИЗОТОПОВ ИЗ РАЗЛИЧНЫХ ВЫСОКОАКТИВНЫХ ПЛАВЛЕНЫХ ПРЕПАРАТОВ, % ОТ КОЛИЧЕСТВА РАДИОИЗОТОПА В ОБРАЗЦЕ

<table>
<thead>
<tr>
<th>№ образца</th>
<th>Zr$^{95}$ + Nb$^{95}$</th>
<th>Sr$^{80}$</th>
<th>Y$^{80}$</th>
<th>Ce$^{144}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.10$^{-5}$</td>
<td>6.10$^{-3}$</td>
<td>2.10$^{-3}$</td>
<td>5.10$^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>4.10$^{-5}$</td>
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<td>3.10$^{-5}$</td>
<td>8.10$^{-6}$</td>
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<tr>
<td>3</td>
<td>4.10$^{-5}$</td>
<td>3.10$^{-3}$</td>
<td>6.10$^{-5}$</td>
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</tr>
<tr>
<td>4</td>
<td>-</td>
<td>2.10$^{-4}$</td>
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</tr>
</tbody>
</table>

Избирательностью при выщелачивании объясняется, в частности, и тот факт, что выщелачиваемость Cs$^{137}$ из плавленых препаратов в значительной мере зависит от содержания в них натрия, эта выщелачиваемость обычно на порядок выше выщелачиваемости других осколочных изотопов (рис. 1). При исследовании под микроскопом
препарата после контакта с водой подтверждается наличие неоднородных участков на поверхности плава (рис.2). Очевидно сравнительно низкое содержание SiO₂ в препаратах (обычно 30–50%) не позволяет образоваться силикатной пленке, которая играет защитную роль при выщелачивании обычных стекол [9]. Это приводит к тому, что в первую очередь наблюдается выщелачивание наименее связанных с силикатным каркасом структур.

В процессе радиоактивного распада выделяется большое количество тепла, что приводит к разогреву высокоактивных плавленых препаратов [4,10]. При организации могильников тепло снимается лишь частично, и образцы длительное время будут находиться при повышенной температуре. Благодаря этому можно ожидать изменения некоторых свойств препаратов в процессе хранения. Было замечено, что обжиг (при 500°С в течение 270 часов) образца, в котором в качестве плавня использовался B₂O₃, уменьшает механическую прочность незначительно (с 21 до 19 кг/мм²); в том случае, когда в качестве плавня использовались фтористые соединения, прочность увеличивается более чем в 2 раза (с 23,5 до 53,0 кг/мм²). Длительная выдержка образцов выше 400°C приводит к увеличению выщелачиваемости материала водой (рис.3 и 4).

Изменение свойств препарата в результате термической обработки прежде всего связано с изменением его структуры. При 400°C на поверхности блока начинают появляться кристаллические образования, в то время как при 500° поверхность кристаллизуется почти полностью (рис.5). При кристаллизации истинная поверхность блока увеличивается, что и приводит к увеличению перехода в раствор вещества с единицы кажущейся поверхности. До 500°C расстекловывание наблюдается лишь в слое, прилегающем к поверхности (рис.6),
Влияние термической обработки на химическую устойчивость плавленых препаратов:
- препарат без добавок фторидов;
- фторсодержащий препарат;
- препарат типа базальта.

Влияние тепловой обработки на выщелачивание Sr⁸⁰ из плавленого препарата.

И только при более высокой температуре кристаллические образования растут в объеме образца (рис. 7а, б); при этом доля стекловидной фазы остается достаточно большой, а кристаллические вкрапления могут несколько уменьшить прочность материала. Структура термически обработанных блоков существенно изменяется в случае добавки некоторых минерализаторов, например фторидов. Такие образцы имеют более мелкие кристаллические зерна и значительно меньший процент остаточного стекла (рис. 7 в), что существенно повышает их механическую прочность.
РАДИОАКТИВНЫЕ ИЗОТОПЫ В СТЕКЛОВИДНЫХ БЛОКАХ

Изменение структуры поверхности препарата при тепловой обработке (увел. 250 раз):
а — препарат после обработки в течение 504 часов при 400°С;
б — препарат после обработки при 500°С в течение 504 час.

Внутренний слой препарата, примыкающий к естественной поверхности (увел. 250 раз):
а — препарат без нагрева;
б — препарат после обработки при 500°С в течение 504 час.
Характер стекло-кристаллической структуры плавленых препаратов (внутренний слой, увел. 250 раз):

а - препарат без нагрева;
б - препарат после термической обработки при 700°С в течение 400 час.;
в - фторсодержащий препарат после термической обработки при 700°С в течение 400 час.;
г - препарат типа базальта, без нагрева.

На рис. 8 показано, что при повышении температуры изменяется вязкость плавленых препаратов, и при переходе от 500°С к более высоким температурам значительно увеличивается пластичность образцов. Известно, что с уменьшением вязкости увеличивается вероятность протекания химических реакций в твердой фазе, что может привести к изменению состава соединений препарата и послужить одной из причин изменения химической устойчивости.

Исследовалась возможность создания из высокоактивных отходов материалов типа некоторых природных камней, обладающих хорошими антикоррозионными свойствами и высокой прочностью. В условиях...
Влияние температуры на величину деформации и релаксационные свойства плавленого препарата.

Восстановительной атмосферы при добавке двуокиси титана и других окислов удалось получить препараты, сходные по составу и свойствам с природными базальтами. Такие блоки закристаллизовывались по всей массе с образованием равномерной мелкокристаллической структуры (рис. 7 г) и обладают повышенной химической устойчивостью (рис. 3).

Помимо температурных воздействий концентраты осколочных изотопов при захоронении подвергаются также воздействию собственного β- и γ-излучения. Наблюдения за реальными образцами показали, что поверхность блока быстро теряет блеск, а в случае большого содержания борного ангидрида (свыше 20%) появляется белый налет.

Исследование растворимости модельных плавленых препаратов, облученных на источнике Co⁶⁰, показало, что с увеличением дозы поглощенной энергии увеличивается выщелачиваемость материала препарата (рис. 9). Как видно из данных табл. 4, облучение вызывает особенно сильное изменение выщелачиваемости лишь в первые минуты взаимодействия блока с водой. С повышением температуры при растворении разница между облученным и необлученным образцом становится менее отчетливой.

При дозах порядка $10^6 - 10^8$ рентген у всех исследованных препаратов в большей или меньшей степени наблюдается изменение
Таблица 3

СКОРОСТЬ РАСТВОРЕННОЙ ПРИ РАЗНЫХ ТЕМПЕРАТУРАХ ОБЛУЧЕННЫХ И НЕОБЛУЧЕННЫХ ПРЕПАРАТОВ В РАЗЛИЧНЫЕ МОМЕНТЫ ВРЕМЕНИ, Å/мин

<table>
<thead>
<tr>
<th>Интервал времени с начала растворения, минуты</th>
<th>Необлученный блок</th>
<th>Облученный блок D = 8,6·10⁸ р.</th>
<th>Облученный блок D = 2,1·10⁸ р.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Температура растворения</td>
<td>30°C</td>
<td>60°C</td>
</tr>
<tr>
<td></td>
<td>0 - 1</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1 - 2</td>
<td>2,5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2 - 5</td>
<td>1,2</td>
<td>5,7</td>
</tr>
<tr>
<td></td>
<td>5 - 10</td>
<td>0,9</td>
<td>4,4</td>
</tr>
<tr>
<td></td>
<td>10 - 20</td>
<td>0,6</td>
<td>2,7</td>
</tr>
<tr>
<td></td>
<td>20 - 30</td>
<td>0,5</td>
<td>2,5</td>
</tr>
<tr>
<td></td>
<td>30 - 40</td>
<td>0,6</td>
<td>2,3</td>
</tr>
<tr>
<td></td>
<td>40 - 50</td>
<td>0,5</td>
<td>2,5</td>
</tr>
<tr>
<td></td>
<td>50 - 60</td>
<td>0,5</td>
<td>2,5</td>
</tr>
</tbody>
</table>

Рис. 9

Влияние облучения на химическую устойчивость плавленого препарата.

структуры поверхности (рис.10). При этом образование различного рода неоднородностей является только поверхностным эффектом (рис.10 а, б). Препарат, содержащий около 20% B₂O₃, покрывается кристаллической коркой (рис.10 в). Рентгеноструктурным анализом установлено, что кристаллическую fazu в этом случае составляют борные кислоты.
Рис.10
Структура плавленых препаратов, облученных на источнике Co^{60}(увел. 500 раз):
а - поверхность облученного препарата, D = 1,6·10^9р
б - внутренний слой того же препарата;
в - поверхность того же препарата, облученного в вакууме, D = 2,0·10^8р;
г - поверхность облученного препарата с большим содержанием B_2O_3, D = 1,6·10^8р.

Можно предположить, что ионизирующее излучение инициирует на поверхности препарата химические реакции с компонентами воздуха. Полученные соединения слабо связаны со структурным каркасом стекла и, не подвергаясь его защитному действию, легче переходят в раствор. Возможно, при этом имеют место и другие процессы. При облучении препарата в вакууме (1·10^{-5} мм рт. ст.) с предварительным удалением адсорбированной влаги также наблюдается появление неоднородностей, равномерно расположенных на поверхности (рис.10 г). Можно предположить, что при облучении происходит увеличение сорбционной способности силикатных материалов, что
приводит к быстрой реакции с влагой воздуха после вскрытия ампулы. Этот вопрос требует дополнительного изучения.

Внутреннее γ- и особенно β-облучение вещества может сказаться не только на растворимости препарата [12,13], но также на диффузии радиоизотопов в твердых телах и упругости пара материи [11,14]. Предварительные опыты показали, что при хранении плавленого высокоактивного (10 000 кюри/л) препарата на воздухе без оболочки в замкнутом пространстве в течение двух месяцев при комнатной температуре и атмосферном давлении активность газовой фазы составила 10^{-6} милликюри с 1 см² поверхности образца. Очевидно, что попадание радиоактивности в окружающую среду через газовую фазу будет в значительной мере затруднено и, возможно, полностью предотвращено благодаря тому, что блоки поступают на захоронение в металлической оболочке. В табл.4 приведены данные

Таблица 4

<table>
<thead>
<tr>
<th>Материал фольги</th>
<th>Радиоактивность изотопов, прошедших через фольгу, импульс/мин</th>
</tr>
</thead>
<tbody>
<tr>
<td>Алюминий</td>
<td>5000</td>
</tr>
<tr>
<td>Слюда</td>
<td>300</td>
</tr>
<tr>
<td>Медь</td>
<td>120</td>
</tr>
<tr>
<td>Стали-э</td>
<td>-</td>
</tr>
<tr>
<td>Тантал</td>
<td>-</td>
</tr>
<tr>
<td>Цирконий</td>
<td>-</td>
</tr>
<tr>
<td>Нержавеющая сталь</td>
<td>-</td>
</tr>
</tbody>
</table>

по диффузии радиоизотопов через тонкую металлическую фольгу, расположенную на расстоянии 2 мм от препарата с поверхностью 2 см² и удельной активностью 40 000 кюри/л.

Дальнейшее изучение высокоактивных твердых осколочных концентратов должно быть направлено на выяснение условий делокализации радиоизотопов с целью ее предотвращения и обеспечения полной безопасности при вечном захоронении радиоактивных отходов.

ЛИТЕРАТУРА

DISCUSSION

C. SOMBRET: Professor Zimakov has spoken about the way in which the mechanical resistance of these glasses is affected by certain forms of thermal treatment and by their composition, especially the presence or absence of boric anhydride. I would like to ask what importance Professor Zimakov attaches to the devitrification and lower mechanical resistance which he has described and whether, in particular, he thinks these matters have any possible implications for subsequent storage of the glass.

P. V. ZIMAKOV: In our opinion, high mechanical resistance in vitreous concentrates goes hand in hand with their chemical stability. In the interest of safe burial, we therefore attempt to ensure that our highly radioactive vitreous preparations are both chemically and mechanically resistant. The (considerable) $\text{B}_2\text{O}_3$ content of the glasses lowers their melting point and thereby facilitates their preparation. However, such glasses are chemically and mechanically unstable (especially as a result of thermal treatment) and are not safe for burial. Obviously, if we are faced with the prospect of complete devitrification, there is little purpose in preparing glass blocks at all. On the other hand, we should make certain reservations when we speak of devitrification as an undesirable factor. There are certain glasses which, precisely because of their very small crystalline structure, show enormous mechanical resistance. For instance, sample bearings prepared from such
glasses have been tested for a fairly long time and have shown excellent mechanical properties. Let me state, however, that we do not yet know how to prepare vitreous radioactive concentrates of such stability.

I should also mention that the addition of compounds of fluorine, and especially of titanium, imparts great resistance to glass.

E. GLUECKAUF: The results shown by Professor Zimakov are interesting but they are probably typical for poor glasses only, i.e. glasses which would not be used in actual practice. Could he say in what respect he would expect the situation to improve if better glasses, say those with a higher silica content, were tested?

P. V. ZIMAKOV: I do not refer in my paper either to "poor" glasses or to "good" glasses. What I tried to do is set out our views on the influence exerted by various factors on the properties of glasses in connection with the problem of their safe burial.

As regards $\text{SiO}_2$ content, it is true that an increase in silica does exert a favourable effect on the fixation of radioisotopes, but at the same time the melting point and the viscosity of the glasses would be too high in this case. We believe that in actual practice, vitreous concentrates of isotopes should not be prepared with a silica content of much more than 50%. The quality of the glasses should be improved by including other suitable elements (e.g. titanium) in their composition and by preparing them under the most favourable conditions.

W. H. HARDWICK: Have you studied the effects of the transmutation of elements occurring during the storage of fission products?

P. V. ZIMAKOV: The effect of nuclear transformations (transmutation) in highly radioactive vitreous concentrates is one of our principal concerns in our research on glass behaviour. We believe that, at high specific values of radioactivity, thermonuclear transformations, along with the great release of energy accompanying them, have a powerful effect both on the materials of the glasses and on the environment. This is of very great importance for the behaviour of concentrates in long-term storage. The research that is being carried out on this subject in certain countries will form the basis of a new branch of radiochemistry, namely "radiation radiochemistry".

W. G. BELTER: You have presented some interesting results of laboratory studies on the fixation of radioisotopes in glass. Could you tell us whether these studies have progressed to the point where the results are being utilized in the design and construction of some unit on an engineering scale? Are engineering-scale studies now underway?

P. V. ZIMAKOV: The experiments described in the paper are the result of both laboratory research and work with experimental models. Many of them were carried out on small amounts of highly active industrial waste. The results of the tests reported in the paper, as well as of many other tests, are being used in preparing for the industrial processing of highly radioactive waste into glass blocks for the purpose of safe burial in large industrial burial-sites. I believe that at the close of our discussions on vitrification Dr. Kolychev intends to present certain data which will, inter alia, illustrate how our results have been used for studying the optimum design or structure for such burial-sites.
FIXATION OF SIMULATED HIGHLY RADIOACTIVE WASTES IN GLASSY SOLIDS

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Abstract — Résumé — Аннотация — Resumen

FIXATION OF SIMULATED HIGHLY RADIOACTIVE WASTES IN GLASSY SOLIDS. Current laboratory development work at ORNL aims at incorporating high-activity-level wastes in high-density insoluble glasses, containing all radioactive constituents in the solid. Experiments with simulated TBP-25 (aluminium, HNO₃), Purex and Darex (stainless steel, HNO₃) wastes have indicated the technical feasibility of such a process. Dense, microcrystalline solids may be as acceptable as true glasses; their greater thermal conductivity compensates somewhat for the increase in surface area over that of true glasses.

Phosphate and borophosphate glasses were prepared from all three types of waste in the laboratory. Caesium volatility was limited to the ~ 0.1% due to physical entrainment, and ruthenium volatility was lowered to <0.5% by addition of phosphite or hypophosphite. Other additives included PbO, Ca(OH)₂, NaOH, and MgO. Bulk densities varied from 2.36 to 2.90 g/cm³ for TBP-25 and from 2.63 to 2.80 g/cm³ for Purex waste. Corresponding volume reductions from the concentrated waste solutions were 7.2 - 9.3 and 5.7 - 8.3; initial softening points varied from 875 to 1000°C and from 830 to 975°C respectively. Darex tests are still preliminary.

Semi-continuous operation on a semi-engineering scale produced a true glass from TBP-25 waste and a microcrystalline solid from Purex. The thermal conductivity of the glass varied from 1.05 BTU/hr-ft-F° at 320°F to 1.6 at 1050°F, about 10 times higher than that of the calcine without additives. Ruthenium volatility was held to <10% by phosphite addition.

Stainless steel is a satisfactory material for construction of the calcination-fixation container. Essentially all the internal corrosion takes place during the relatively short (2-6 h) period in which the last of the acid and water are expelled at the maximum temperature. Melt production increased the corrosion of 304L stainless steel from 5 to 42 mil/month for a 24-hr evaporation-fixation cycle on TBP-25 waste and from 8 to 140 mil/month on Purex waste. Operation above 900°C with Purex waste plus fluxing agents may result in catastrophic local corrosion.

FIXATION DE DÉCHETS SIMULÉS DE HAUTE ACTIVITÉ DANS DES SOLIDES VITREUX. Le Laboratoire national d’Oak Ridge s’efforce actuellement de mettre au point un méthode d’incorporation des déchets de haute activité dans des verres insolubles de densité élevée, tous les éléments radioactifs se trouvant contenus dans la partie solide. Des expériences avec des déchets simulés résultant des procédés TBP-25 (aluminium, HNO₃), Purex et Darex (acier inoxydable, HNO₃) montrent qu’une telle méthode est techniquement réalisable. Des solides denses, de structure microcristalline, peuvent convenir aussi bien que de véritables verres; leur meilleure conductibilité thermique compensée dans une certaine mesure le fait que la surface doit être plus grande que dans le cas des verres.

Avec les types de déchets susmentionnés, on a préparé des verres au phosphate et au borophosphate. La volatilité du caesium était limitée à 0,1% environ du fait de l’entraînement mécanique et la volatilité du ruthénium a été abaissée à moins de 0,5% par addition de phosphite ou d’hypophosphite. Parmi les autres additifs figuraient PbO, Ca(OH)₂, NaOH et MgO. Les densités brutes variaient entre 2,36 et 2,90 g/cm³ pour les déchets du procédé TBP-25 et entre 2,63 et 2,80 g/cm³ pour les déchets du procédé Purex. Les réductions de volume correspondantes, à partir des solutions concentrées de déchets, étaient comprises entre 7,2 et 9,3 et entre 5,7 et 8,3; le passage initial à l’état pâteux se produisait entre 875 et 1000°C et entre 830 et 975°C, respectivement. Les essais avec les déchets Darex en sont encore au stade préliminaire.

En opérant de manière semi-continue à l’échelle semi-industrielle, on a obtenu un verre véritable à partir de déchets TBP-25 et un solide microcristallin à partir de déchets Purex. La conductibilité thermique du verre variait entre 5,07 W/cm°C à 100°C et 7,73 W/cm°C à 585°C, c’est-à-dire qu’elle est 10 fois supérieure à celle de la masse calcinée sans additifs. La volatilité du ruthénium a été maintenue à moins de 10% par addition de phosphite.

Le récipient de calcination-fixation peut être construit en acier inoxydable. Pratiquement toute la corrosion interne se produisit au cours de la période relativement brève (2 à 6 h) au cours de laquelle les derniers
W. E. CLARK and H. W. GODBEE

rédus d'acier et d'eau sont chauffés à la température maximum. La formation de verre fondu a augmenté la corrosion de l'acier inoxydable 304L de 0,12 à 1,05 mm par mois, pour un cycle d'évaporation-fixation de 24 heures, dans le cas des déchets du procédé TBP-25 et de 0,20 à 3,5 mm par mois dans celui des déchets Purex. Si l'on travaille à plus de 900°C sur des déchets Purex en présence de fondants, une corrosion localisée extrêmement grave risque de se produire.

FIJACIÓN DE DESECHOS SIMULADOS DE ELEVADA RADIACTIVIDAD EN SÓLIDOS VÍTREOS. En el Oak Ridge National Laboratory se procura perfeccionar métodos para incorporar desechos de elevada radiactividad a vidrios insolubles de gran densidad, que contengan todos los componentes radiactivos en la fracción sólida. Los experimentos con desechos simulados de los procesos TBP-25 (aluminio, HNO₃), Purex y Dárez (acero inoxidable, HNO₃) demuestran que tales métodos son técnicamente factibles. Los sólidos densos, de estructura microcrystalina pueden ser tan aceptables como los vidrios verdaderos; su mayor conductividad térmica compensa el incremento de superficie con respecto a la de los vidrios verdaderos.

En el resultado del seminuevo proceso de la producción de vidrio se obtuvo un verdadero partiendo de los mencionados tipos de desechos. Con los mencionados tipos de desechos se preparó en el laboratorio vidrio al fosfato y al borofosfato. Los resultados experimentales correspondientes a las soluciones concentradas de desechos están comprendidas entre 7,2 y 9,3; entre 5,7 y 8,3; y entre 0,1 y 1,0 por ciento, aproximadamente, debido al arrastre mecánico y la volatilidad del cesio se limitó al 0,1 por ciento, aproximadamente, debido al arrastre mecánico y la volatilidad del rutenio se rebajó a menos de 0,5 por ciento, aproximadamente, debido al arrastre mecánico.
HIGHLY RADIOACTIVE WASTES IN GLASSY SOLIDS

1. INTRODUCTION

Conversion to solids and storage in a permanently dry environment appears to be an acceptable solution to the problem of disposal of highly radioactive wastes. The pot-calcination process is being developed at Oak Ridge National Laboratory as a solidification method either by direct evaporation-calcination [1] or by fixation of the fission products in glasses. In the latter case, glass-forming materials are added to the waste after preliminary evaporation and the mixture is evaporated to dryness and raised to the solids melting point (~900°C) in a cylindrical stainless-steel pot 8-24 in diam. by 8-10 ft high. The pot would be welded shut and shipped to the ultimate disposal site [2, 3]. A pilot plant under construction at Hanford Atomic Products Operation, Richland, Washington will be used to test calcination initially and fixation in glasses in a second phase of the programme.

Fixation of waste in glasses produces a final product with desirable properties, i.e. the glassy solid residues are non-volatile up to their formation temperatures, have mechanical strength so that their containment is not completely dependent upon the integrity of an outer container during shipment and storage, have good thermal conductivities so that heat-transfer problems during formation and storage are minimized and have low solubilities in environmental erosion media. The product need not be a true glass if it has these properties. The addition of glass-making additives does not necessarily increase the volume of waste to be stored since the volume of the final glassy products is generally essentially the same as that obtained by calcination because of the higher density of the glasses.

A number of different approaches are being made toward the problem of glass formation. Nepheline syenite, a naturally occurring mineral, has been used as a glass former by WATSON et al. at Chalk River [4]. ELLIOT et al. at Harwell [5] have considered various silicate-glass compositions for waste disposal. In the United States a number of different approaches have been made with various combinations of silicate, phosphate, borate and sulphate glasses [6-11].

Objectives of the development programme at Oak Ridge National Laboratory are retention of radioactivity and thermally stable salts, including sulphate and fluoride, in the glass to minimize recycle; decrease in waste volume; production of solid products that will be insoluble, homogeneous, mechanically strong, heat-conductive and stable over long storage times; and economical operation. Softening points below 1000°C are desirable to permit the use of a stainless-steel fixation container (pot). Studies have been confined to laboratory scale and semi-engineering scale in a 24-in-high by 4-in-diam. pot with synthetic waste solutions and radioactive tracers. Studies on an engineering scale with synthetic solutions are in progress.
2. LABORATORY PREPARATION OF GLASSY SOLIDS

Phosphate and borophosphate glasses and ceramic solids with desirable characteristics were prepared from synthetic Purex, TBP-25 (aluminium), and Darex or electrolytic (stainless steel) wastes (Table I). Further improve-

TABLE I

<table>
<thead>
<tr>
<th>Component</th>
<th>Purex</th>
<th>TBP-25 (aluminium)</th>
<th>Darex (stainless steel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>0.1 M</td>
<td>1.72 M</td>
<td>--</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.5 M</td>
<td>0.16 mg/ml</td>
<td>1.25 M</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.01 M</td>
<td>--</td>
<td>0.38 M</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.01 M</td>
<td>--</td>
<td>0.18 M</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>--</td>
<td>--</td>
<td>0.04 M</td>
</tr>
<tr>
<td>H$^+$</td>
<td>5.6 M</td>
<td>1.26 M</td>
<td>0.75 M</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>--</td>
<td>4.02 mg/ml</td>
<td>--</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>--</td>
<td>0.05 M</td>
<td>--</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.6 M</td>
<td>2.4 mg/ml</td>
<td>--</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>6.1 M</td>
<td>6.6 M</td>
<td>6.0 M</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.0 M</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>165 ppm</td>
<td>160 ppm</td>
<td>260 ppm</td>
</tr>
<tr>
<td>Ru</td>
<td>0.2 mg/ml</td>
<td>0.2 mg/ml</td>
<td>0.2 mg/ml</td>
</tr>
<tr>
<td>Density, g/ml</td>
<td>1.30</td>
<td>1.32</td>
<td>1.33</td>
</tr>
</tbody>
</table>

ment is desirable, particularly with the high-sulphate Purex waste. Phosphate and borate were assumed to be present as the meta ions, PO$_3^{3-}$ and BO$_2^{2-}$, and sulphate as SO$_4^{2-}$. In calculating equivalents of anions and cations, only sodium, calcium and magnesium were considered; it was assumed that aluminium and the ferrous metals would be converted to oxides at the temperatures required for glass formation. Prior work without glass-making additives had indicated that sodium (and presumably caesium) volatilization can be prevented by the presence of non-volatile anions (e.g. SO$_4^{2-}$) in excess of the amount equivalent to the combined caesium and sodium and that sulphate can be simultaneously retained if the ratio of total equivalents of sodium, caesium, calcium and magnesium to total equivalents of sulphate is greater than unity [12]. The effect of the presence of extra anion equivalents (e.g. borate, phosphate, silicate) necessary to form the glass network is difficult to predict and further work is required to obtain the data necessary to define precisely the regions of glass formation. Most of the Purex glasses lost sulphate slowly at temperatures approaching 900°C.
The development of phosphate rather than silicate glasses was emphasized since it was desired to use phosphite or hypophosphite as reducing agents to decrease ruthenium volatility. Also, phosphates are more soluble than silicates and hence are easier to transfer by pumping. In some cases borate was added to the solutions to lower the softening points of the products and/or to improve their glassy character. A disadvantage of borate systems is the occurrence of a foamy stage during evolution of gases.

2.1 Purex waste [13]

Conversion of Purex waste to a suitable glass is difficult because of its high sulphate content. Also, sulphate increases the solubility of the glass (Section 2.5). The presence of the anion network formers, phosphate and borate, causes loss of sulphate at the high temperatures required for glass formation. For a fixed amount of magnesium or calcium, the softening point of the mixture decreased as the sodium-to-phosphorus ratio decreased. As the sodium-to-phosphorus mole ratio approached 1, the mixtures softened at 850°C (Table II), but when the sodium-to-phosphorus ratio approached 3 the mixtures did not soften below 1000°C. For a given sodium-to-phosphorus ratio, the softening point increased with increasing magnesium or calcium. With calcium equivalent to or greater than the original sulphate (1 M), the mixtures tended to be heterogeneous and to have softening points higher than 1000°C. The highest magnesium addition (1.2 M) gave a mixture which softened at 975°C (Table II, Melt 9b). The rate and temperature at which sulphate volatilizes varies with the composition of the fixation melt. In some cases SO₃ is visible at temperatures well below the softening point, while in others it can be detected only by collection and analysis of the off-gases or by the thermogravimetric analysis. In general, the presence of alkaline and alkaline earth metals decreases sulphate volatilization and in the presence of alkaline metals aluminium assists in retaining sulphate in the melt.

Glassy borophosphate and phosphate solids were prepared from Purex waste (Table II) with volume reductions of 6.5 to 9.2 (volume of waste solution/volume of solids produced). Though a number of these melts appeared to be glassy, it is likely that they would become devitrified if allowed to cool slowly. One melt (Section 3.1), prepared on a semi-engineering scale, formed a hard, crystalline mass which lost 10% of the sulphate, though a similar loss was not observed in small-scale experiments. Generally, the addition of magnesium produced a more glasslike (Fig. 1) product than did calcium, but based on the thermal stability of their sulphates, calcium would be expected to retain sulphate at higher temperatures.

2.2 TBP-25 waste (Aluminium)[14, 15]

Aluminium-bearing waste is readily incorporated into phosphate and borophosphate glasses and satisfactory examples of each were prepared (Table III). Volume reductions varied from 7.2 to 9.3 and all the products listed had the appearance of true glasses. The phosphate-lead glass (Table III, Melt 7) that was studied in detail showed an X-ray pattern and a thermal conductivity behaviour typical of a true amorphous substance (Fig. 2). When
**TABLE II**

BOROPHOSPHATE AND PHOSPHATE CERAMICS INCORPORATING PUREX WASTE OXIDES

Purex waste composition (M): 6.1 NO₃⁻, 5.6 H⁺, 1.0 SO₄²⁻, 0.6 Na⁺, 0.5 Fe³⁺, 0.1 Al³⁺, 0.01 Cr²⁺, 0.01 Ni²⁺, 0.002 Ru with 165 ppm Cl⁻

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<tr>
<td>Appearance</td>
<td>Gray-glassy</td>
<td>Green, micro-crystal-line</td>
<td>Light gray, micro-crystal-line, slightly segregated</td>
<td>Light gray, micro-crystal-line, slightly segregated</td>
<td>Purplish-black, very glassy</td>
<td>Dark-green, very glassy</td>
<td>Green, very glassy</td>
<td>Gray-green, micro-crystal-line</td>
<td>Green, very glassy</td>
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HIGHLY RADIOACTIVE WASTES IN GLASSY SOLIDS
Borophosphate ceramic incorporating Purex waste oxides. Waste made 1.5 M in $\text{H}_3\text{PO}_4$, 0.8 M in MgO, 0.17 M in Na$_2$B$_4$O$_7$, and 1.7 M in NaOH, evaporated to dryness and heated to 850°C. Density 2.7 g/cm$^3$; product contained 39 wt.% waste oxides; volume reduction factor, 5.5.

Phosphate-lead glass incorporating 26 wt.% TBP-25 waste oxides. Volume reduction, 8.1; density, 2.8 g/cm$^3$; softening point, 900°C.

produced on a semi-engineering scale, the properties of the glass produced closely paralleled those of the laboratory material. The engineering-scale produce maintained its glassy nature after being heated to 900°C for 30 d in a stainless-steel container. Part of the lead was reduced to the metal and
TABLE III

PHOSPHATE AND BOROPHOSPHATE GLASSES INCORPORATING TBP-25 WASTE OXIDES

TBP-25 Waste (M): 6.60 NO$_3^-$, 1.72 Al$^{3+}$, 1.26 H$^+$, 0.10 Na$^+$, 0.05 NH$_4^+$, 0.003 Fe$^{3+}$, 0.002 Hg$^{2+}$, 0.002 Ru with 160 ppm Cl$^-$

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Composition of melt, wt. % oxides

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<tr>
<td>Appearance</td>
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<td>Pale greenish-white glass</td>
<td>Grayish-green glass</td>
<td>Grayish-green glass</td>
<td>Green glass, mottled with white</td>
<td>Green glass</td>
<td>Greenish-white glass</td>
<td>Light-green glass</td>
<td>Greenish-white glass</td>
<td>Light-green glass, mottled with white</td>
<td>Light-yellow glass</td>
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</table>
collected in globules in the glass. Retention of mercury in the solid product does not appear possible at the temperatures required for calcination or glass formation.

2.3 Darex or electrolytic waste (stainless steel) [16, 17]

Production of glass from stainless-steel-bearing waste is more difficult than from aluminium waste since the oxides of the ferrous metals are not glass formers. In order to obtain true glasses (e.g., materials that do not become devitrified on slow cooling), it was necessary to add glass formers such as aluminium. Hence volume reductions were only 3.2 or less (Table IV(a), Fig. 3(a)). Attempts to achieve greater volume reductions by increasing the waste oxide content of the solids to 25 wt. % resulted in materials which underwent devitrification readily although some appeared to be glasses when initially formed (Table IV(b), Fig. 3(b)).

2.4 Ruthenium volatility

Phosphite and hypophosphite ions appear uniquely advantageous for fixing ruthenium in stable solid media. Both are powerful reducing agents and are oxidized in situ to phosphate, which is a glass former. The effect of phosphite on ruthenium volatilization from simulated Purex, TBP-25 and Darex waste solutions was studied during batch evaporation of the solutions and calcination to 500°C and in the batch evaporation of TBP-25 waste and calcination to 1000°C. All waste solutions studied contained 0.2 mg/ml stable ruthenium and 0.1 μg/ml Ru106 tracer added as the chloride.

In the experiments to 500°C with Purex, TBP-25, and Darex waste solutions in a Pyrex container, ruthenium in the condensate varied from 30 to 0.03% or less of that originally present in the waste when the phosphorous acid concentration was increased from 0 to 1.5 M (Fig. 4(a)). In the series of calcination experiments to 1000°C with TBP-25 waste in a quartz container, ruthenium in the condensate varied from 60 to 0.05% of the original when the phosphorous acid concentration was increased from 0 to 2.25 M; with a stainless-steel container the percentages in the condensate were factors of 1.5 to 6.5 less (Fig. 4(b)). The difference undoubtedly represents ruthenium that adhered to stainless steel but not to quartz.

2.5 Leaching tests

Leaching tests were made on selected solid products prepared from Purex (Table II(a), Melt 4) TBP-25 (Table III, Melt 7), and Darex (Table IV(a), Melt 5 and Table IV(b), Melt 3) wastes. In each case the mixture contained either mixed fission products or Cs137 tracer. The rate of removal of the Cs137 in a flowing stream of distilled water was determined and the erosion rate of the glass was calculated (Fig. 5). The water was replaced each week. Rates varied from 10⁻³ g·cm⁻² d⁻¹ for the Purex to 10⁻⁷ g·cm⁻² d⁻¹ for the TBP-25 glasses (Fig. 6). The Darex glass and the Darex ceramic approached values of 4 × 10⁻⁶ and 4 × 10⁻³ g·cm⁻² day⁻¹, respectively. These results with TBP-25 waste compare favourably with those obtained at Harwell [5].
**TABLE IV**

**PHOSPHATE AND BOROPHOSPHATE GLASSES INCORPORATING DAREX WASTE OXIDES**

Darex waste composition (M): 1.25 Fe$^{3+}$, 0.38 Cr$^{3+}$, 0.18 Ni$^{2+}$, 0.04 Mn$^{2+}$, 0.75 H$^+$, 6.0 NO$_3^-$, 0.002 Ru with 260 ppm Cl$^-$

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<td>Additives, mole/l</td>
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<td><strong>Softening point, °C</strong></td>
<td><strong>Bulk density, g/cm³</strong></td>
<td><strong>Waste oxide in melt, wt.%</strong></td>
<td><strong>Volume reduction, vol. Dares/vol. melt</strong></td>
<td><strong>Appearance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>850</td>
<td>850</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>750</td>
<td>800</td>
<td>2.74</td>
<td>-</td>
<td>2.71</td>
<td>2.69</td>
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<td></td>
<td>20.3</td>
<td>19.5</td>
<td>17.4</td>
<td>16.5</td>
<td>15.3</td>
<td>15.1</td>
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<td>3.8</td>
<td>-</td>
<td>3.2</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Black glass, some segregated</td>
<td>Somewhat glassy, segregated</td>
<td>Brown glass</td>
<td>Black glass</td>
<td>Excel- lent black-brown glass</td>
<td>Brown- black glass</td>
<td>Deep brown glass</td>
<td></td>
<td></td>
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</table>

HIGHLY RADIOACTIVE WASTES IN GLASSY SOLIDS
<table>
<thead>
<tr>
<th>Melt</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additives, mole/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaH&lt;sub&gt;2&lt;/sub&gt;P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt; • H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.4</td>
<td>1.34</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>1.8</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;P&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;9&lt;/sub&gt;</td>
<td>0.4</td>
<td>1.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; • 9H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.72</td>
<td>1.44</td>
<td>2.2</td>
<td>1.5</td>
<td>3.0</td>
<td>3.0</td>
<td>1.2</td>
<td>1.2</td>
<td>1.86</td>
<td>1.36</td>
<td>0.4</td>
<td></td>
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<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.0</td>
<td>1.7</td>
<td>0.6</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>1.0</td>
<td>2.8</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition of melt, wt. % oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
<td>6.3</td>
<td>12.3</td>
<td>18.3</td>
<td>13.2</td>
<td>23.4</td>
<td>-</td>
<td>10.1</td>
<td>10.1</td>
<td>16.2</td>
<td>12.0</td>
<td>3.5</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>24.3</td>
<td>18.0</td>
<td>12.0</td>
<td>6.0</td>
<td>13.2</td>
<td>7.1</td>
<td>19.8</td>
<td>-</td>
<td>4.5</td>
<td>23.4</td>
<td>18.0</td>
<td>24.9</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>15.4</td>
<td>15.4</td>
<td>15.4</td>
<td>15.4</td>
<td>13.2</td>
<td>7.1</td>
<td>19.8</td>
<td>23.5</td>
<td>25.0</td>
<td>-</td>
<td>9.6</td>
<td>11.2</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
<td>35.3</td>
</tr>
<tr>
<td>Waste</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Softening point °C</td>
<td>850</td>
<td>850</td>
<td>900</td>
<td>1000</td>
<td>850</td>
<td>-</td>
<td>850</td>
<td>1100</td>
<td>850</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk density, g/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>-</td>
<td>2.56</td>
<td>2.86</td>
<td>-</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Volume reduction, vol. Dearing/vol. melt</td>
<td>-</td>
<td>4.4</td>
<td>4.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Appearance</td>
<td>Green, micro-crystaline</td>
<td>Good black</td>
<td>Good black</td>
<td>Gray-black, metallic</td>
<td>Rock-like, very hard</td>
<td>Sintered, did not melt below 1050°C</td>
<td>Green-crystaline, partly glassy</td>
<td>Gray, metallic</td>
<td>Brown-black micro-crystaline</td>
<td>Brown, crumbly</td>
<td>Did not melt below 1050°C</td>
<td>Green black rock-like segregation</td>
</tr>
</tbody>
</table>

* Did not melt at or below 1050°C
Aluminium borophosphate glass incorporating (a) 15.3 wt.% stainless-steel waste oxides; volume reduction, 2.5; density 2.6 g/cm³; initial softening point, 800°C;
(b) 25 wt.% stainless-steel waste oxides; volume reduction, 4.9; density 2.9 g/cm³; initial softening point, 900°C.
Fig. 4a

Effect of phosphorous acid on ruthenium volatility from Purex, Darex and TBP-25 waste solutions on batch calcination to 500°C.

with silicate-borate glasses containing approximately the same percentage of oxides from waste but are about one order of magnitude higher than the results at Chalk River [18] with nepheline seyenite-lime glasses containing about one-third this amount of waste oxides.

3. SEMI-ENGINEERING SCALE EXPERIMENTS

3.1 Products

Solids incorporating Purex and TBP-25 waste oxides were prepared by evaporation and fixation in a stainless-steel cylinder (pot). The equipment and general procedure were essentially the same as described previously
Fig. 4b

Effect of phosphorous acid on ruthenium volatility from TBP-25 waste on batch calcination to 1000°C

[12]. The equipment consisted of a 24-in-high by 4-in-diam. pot in a 9-kW furnace, a de-entraîner, downdraft condenser, packed absorber column, polyethylene expansion bag and gas-recirculation jet (Fig. 7). Phosphite or hypophosphate and fluxing agents were added to synthetic waste and the solution was allowed to stand, with cooling, at 25°C for 16 h to allow the initial reaction between phosphite or hypophosphite and nitrate. The feed was then pumped continuously at 45-50 ml/min into the heated pot in which evaporation, calcination and finally fusion at 850-1000°C took place. The levels
Fig. 5
Schematic diagram of apparatus for leaching of radioactive samples

Fig. 6
Leach rate of glasses made with Purex, TBP-2b and Darex waste solutions
of the solution, calcine and melt at a given time were determined by the temperature of thermocouples in the pot.

Purex waste with additives of phosphorous acid, calcium hydroxide, sodium hydroxide and sodium borate formed a hard, rock-like material rather than a glass (Table V, Melt 1). Analysis of the condensate and off-gas scrubber streams indicated that 10% of the total $SO_3$ present and less than 2% of the ruthenium (analytical limit for stable ruthenium) had been volatilized. In this experiment a constant liquid level was maintained about 6 in from the top of the pot. Subsequent experiments were operated with a slowly rising liquid level to minimize the possibility of flashing due to sudden meltdowns. Overall feed rates obtained were comparable to those obtained by operating at a constant liquid level in the calcination process [1] because of the factor of 10 higher thermal conductivity of the glass compared to that of the porous calcine (Section 3.2). Feed was pumped to the pot with the liquid level in the pot gradually rising from about 6 in above the bottom to about 4 in from the top during the feeding period.

A series of melts was made with TBP-25 waste solution with additions of sodium hypophosphite and lead oxide (Table V, Fig. 8(a)). In two experiments, $\text{Pm}^{147}$ was added as a non-volatile tracer to differentiate between volatilized and physically entrained ruthenium. Based on the $\text{Pm}^{147}$ in the de-entrainer, condensate and off-gas scrubber streams, the total entrain-
TABLE V
COMPOSITION OF SOLID PRODUCTS PREPARED FROM SIMULATED WASTE SOLUTIONS IN SEMI-ENGINEERING SCALE EQUIPMENT

<table>
<thead>
<tr>
<th>Melt</th>
<th>Purex No. 1</th>
<th>TBP-25 No. 2</th>
<th>TBP-25 No. 3a</th>
<th>TBP-25 No. 3b</th>
<th>TBP-25 No. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additives, mole/waste</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>1.52</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Na₂H₂PO₄·H₂O</td>
<td>--</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.25</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>0.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MgO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Na₂B₄O₇·10H₂O</td>
<td>0.34</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.34</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PbO</td>
<td>--</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Ru¹⁴⁹(μg/ml)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Pm¹⁴⁷(μg/ml)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Composition of melt wt. % oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.8</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>NiO</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.2</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>22.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>19.9</td>
<td>18.6</td>
<td>18.6</td>
<td>18.6</td>
<td>16.8</td>
</tr>
<tr>
<td>SO₃</td>
<td>19.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>26.4</td>
<td>40.5</td>
<td>40.5</td>
<td>40.5</td>
<td>46.2</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>11.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CaO</td>
<td>11.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>MgO</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<tr>
<td>PbO</td>
<td>--</td>
<td>15.9</td>
<td>15.9</td>
<td>15.9</td>
<td>14.4</td>
</tr>
<tr>
<td>RuO₂</td>
<td>0.1</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

ment of solids was less than 0.1% (Table V, Melt 3b). Ruthenium volatilization was approximately 12 to 16% of the total present based on neutron activation analyses (Tables V, Melt 3a) and Ru¹⁴⁹ counting (Table VI) versus less than 2% by chemical analysis of the inactive ruthenium (Table V, Melts 2 and 3a). The ruthenium concentration in the condensate increased in spurts when a large inventory of calcine melted, probably as a result of contact of the ruthenium with the hot wall in the presence of undecomposed nitrate.
salts. Increasing the hypophosphite from 2 M to 2.25 M did not decrease the amount of ruthenium volatilized (Table VI). Ruthenium that has been reduced to a non-volatile form is undoubtedly oxidized to a volatile form by the oxygen liberated when the nitrate salts at ~125°C contact the pot walls at ~900°C.
3.2 Thermal conductivity and product stability

The thermal conductivity of the aluminium glass (Table V, Melt No. 3a) increased from about 1 to 1.6 BTU hr⁻¹ ft⁻¹ °F⁻¹ in going from 400 to 1060°F. Corresponding values for a calcined aluminium waste were 0.1 and 0.4 (Fig. 9). Above the softening point (~ 1100°F), the thermal conductivity decreased from 1.51 to 1.40 BTU hr⁻¹ ft⁻¹ °F⁻¹ in going from 1140 to 1150°F. The shape of the thermal-conductivity-versus-temperature curve corresponds to that expected for an amorphous substance. The X-ray pattern indicated an amorphous substance, i.e. a true glass.

Thermal conductivity was determined by a steady-state method using radial heat-flow in a hollow cylinder [11]. The cylinder had an internal diam. of 1 in and outer diam. of 4 in and was 24 in long. The glass was formed with a 1-in stainless-steel tube down the centre and thermocouples spaced radially throughout it. The glass was formed in this way so that, after a heater was inserted down the 1-in tube, thermal conductivity could be measured without disturbing the glass.

After determination of the thermal conductivity of the solid, the pot was heated to 900°C and held at that temperature for 30 d. About 0.5 g of water
Thermal conductivity of phosphate-lead glass incorporating TBP-25 waste oxides and TBP-25 calcine was given off during the first day (Fig. 10). The pressure in the pot dropped to about 12 in H$_2$O below atmospheric in 8 hr and then decreased more slowly to about 30 in of H$_2$O vacuum. This is probably due to the slow reaction of water with the stainless-steel container to form metal oxides and hydrogen, the latter escaping by diffusion through the walls of the container. It does not appear, therefore, that there is likely to be a pressure build-up during storage of this melt. The solid product retained its glassy properties after
### Table VII

**CONDENSER CORROSION TESTS FOR PUREX® WASTE PROCESSING**

*(All solutions refluxing; all specimens welded)*

<table>
<thead>
<tr>
<th>Material</th>
<th>Specimen position</th>
<th>Initial evaporator solution(^b)</th>
<th>Maximum(^a) corrosion rate, mil/month</th>
<th>Final evaporator solution(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>6 M HNO(_3)</td>
<td>15 M HNO(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290-312 hr 840 hr</td>
<td>0.05 M H(_2)SO(_4)</td>
<td>1 M H(_2)SO(_4)</td>
</tr>
<tr>
<td>Type-347 stainless steel</td>
<td>V</td>
<td>0.80</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.58(^f)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>3.58(^f)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>290 hr</td>
<td>520 hr</td>
</tr>
<tr>
<td>Ti-45A</td>
<td>V</td>
<td>0.04</td>
<td>0.03</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.04</td>
<td>0.03</td>
<td>1.9(^{th})</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>0.04</td>
<td>0.04</td>
<td>3.1(^{th})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500 hr</td>
<td>672 hr</td>
</tr>
<tr>
<td>Hastelloy F(^d)</td>
<td>V</td>
<td>0.31</td>
<td>2.85(^f)</td>
<td>11.2(^f)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.87</td>
<td>0.39</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>1.41</td>
<td>0.41</td>
<td>5.96(^f)</td>
</tr>
<tr>
<td>Ni-o-nel(^e)</td>
<td>V</td>
<td>0.11</td>
<td>2.72(^f)</td>
<td>9.88(^f)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.37</td>
<td>0.18</td>
<td>0.91(^f)</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>1.41</td>
<td>0.82(^f)</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\(^a\)Duplicate specimens exposed
\(^b\)Solution composition: 5.6 M H\(^+\), 6.1 M NO\(_3\)^-, 1.0 M SO\(_4\)^2-, 0.6 M Na\(^+\), 0.1 M Al\(^3+\), 0.5 M Fe\(^{2+}\), 0.01 M Cr\(^{3+}\), 0.01 M Na\(^+\)
\(^c\)Estimated average composition of condensate from evaporation-calcination process
\(^d\)Estimated composition of final condensate from evaporation-calcination process
\(^e\)Solution composition: 0.3 M H\(^+\), 1.3-1.8 M NO\(_3\)^-, 2.0-3.0 M SO\(_4\)^2-, 1.2-1.8 M Na\(^+\), 0.2-0.3 M Al\(^3+\), 1.0-1.5 M Fe\(^{2+}\), 0.02-0.03 M Cr\(^{3+}\), 0.02-0.03 M H\(^{2+}\)

\(^f\)Grain boundary and/or other localized attack observed
\(^g\)Slight weight gain

\(^h\)Some local attack in heat-affected zone near weldments

\(^i\)0.002 M H\(_2\)O\(_2\) had little if any effect on the corrosion of Hastelloy F
the long exposure at 900°C (Fig. 8b) though its colour had changed from green to brown. There was no sign of aggressive corrosion on the container.

4. MATERIALS OF CONSTRUCTION

Type-304L stainless steel has been tentatively selected as the material of construction for the fixation pot. Corrosion of the stainless-steel fixation pot is significant only during the period at the peak temperature when the last of the volatile constituents are expelled provided a chemically stable glass melt is obtained. Corrosion of the condenser and off-gas systems may be a problem particularly if sulphate is evolved; stainless steel, Hastelloy F, and Ni-o-nel underwent localized attack during long-term exposure in these environments. Titanium was much more resistant than any of these materials (Table VII). Since the temperature of the pot wall during storage should never be more than about 300°C [17], the glass next to the wall would be solid and there would be little additional internal or external corrosion during storage.

| Table VIII |
|-----------------|-----------------|-----------------|-----------------|
| CORROSION OF FIXATION CONTAINER |
| (Stainless-steel pot) | | | |

<table>
<thead>
<tr>
<th>Material</th>
<th>Environment (Waste type)</th>
<th>Approx. maximum temperature, °C</th>
<th>Exposure time, hr</th>
<th>Corrosion rate, mil/month</th>
<th>Approx. total penetration, (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>Air</td>
<td>900</td>
<td>24</td>
<td>1.4</td>
<td>0.05</td>
</tr>
<tr>
<td>304L</td>
<td>Purex and additives a</td>
<td>900</td>
<td>24</td>
<td>120-145 b, c</td>
<td>4.0-4.8</td>
</tr>
<tr>
<td>304L</td>
<td>Purex and additives a</td>
<td>110</td>
<td>1</td>
<td>~0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Exposure interrupted</td>
<td></td>
<td>850</td>
<td>~0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>and corrosion measured</td>
<td></td>
<td>950</td>
<td>1330 c</td>
<td>~4</td>
</tr>
<tr>
<td>304L</td>
<td>Overall</td>
<td>-6767</td>
<td>80</td>
<td>57</td>
<td>~6</td>
</tr>
<tr>
<td>304L</td>
<td>Purex and additives a</td>
<td>900</td>
<td>78</td>
<td>80 c</td>
<td>8.7</td>
</tr>
<tr>
<td>304L</td>
<td>TBP-25 and additives a</td>
<td>920</td>
<td>19</td>
<td>42.2</td>
<td>1.1</td>
</tr>
<tr>
<td>304L</td>
<td>TBP-25 and additives a</td>
<td>910</td>
<td>345</td>
<td>5.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

a Additives: Purex: 49.4 g/l Na₂B₄O₇·10H₂O, 105 g/l NaH₂PO₄·H₂O, 167 g/l of 30% H₃PO₄, 8.72 g/l NaOH, 80.1 g/l Ca(OH)₂
Aluminium: 112.1 g/l NaH₂PO₄·H₂O, 11.6 g/l PbO

b Duplicate specimens exposed

c Intergranular corrosion noted
Corrosion rates of type-304L stainless steel in glass-fixation cycles were determined by exposing the sample to the glass media while bringing the temperature up to the maximum over a 3-hr period and then holding at the maximum temperature for the remainder of the time. The penetration was 4.0 to 8.7 mil for the Purex melt over ~80 hr and 1.1-2.6 mil for TBP-25 for 19 and 345 hr. These rates are considered acceptable since the pot will only be used once and the wall thickness will probably be about 250 mil. The worst corrosion case was that of a Purex glass which lost sulphate at the exposure temperature of 950°C (Table VIII). This should be subject to considerable improvement when a glass is perfected which will retain all sulphate.

The time at which failure of the pot is most likely to occur probably coincides with the final heating to drive off the last traces of moisture and acid just before removal of the pot from the furnace. At this point the entire weight of the pot filled with melt is suspended by the upper part of the pot walls, which are at the same time subject to the most corrosive part of the cycle. Experiments are in progress to test these conditions.

REFERENCES

DISCUSSION

J. R. GROVER: In the paper it is stated that ruthenium volatility has been studied using the chloride, whereas in a waste solution the ruthenium will be present as complex nitrates. I should like to ask whether the authors have compared the volatilities from the different chemical species. I might add that in our Harwell process we have done most of our work using nitrates, but we have also carried out some experiments with chlorides. We get a factor-of-ten difference between the volatility from nitrates and that from chlorides, even though we leave the ruthenium chloride in the nitric acid solution for some hours beforehand. Figure 3 of our paper ("Fixation of Radioactive Waste in Glass. Part III. The Removal of Ruthenium and Dust from Nitric Acid Vapours") shows a ruthenium decontamination factor of about 4 at a flow-rate of 15 ml/min. When this run was repeated using ruthenium chloride, we obtained a decontamination factor of about 30.

J. M. HOLMES (on behalf of W. E. CLARK and M. W. GODBEE): As far as I know only the chloride was used.

J. T. ROBERTS: Yes, I understand the stable ruthenium was added in the form of the commercial-grade chloride, because this was the most easily available source of stable ruthenium. The solutions were incubated for some period of time before the calcination in the hope that equilibrium between ruthenium species would be obtained. Pilot-plant demonstration with actual wastes will be required to confirm ruthenium volatility figures. The chloride ion itself is not expected to be significant as regards ruthenium volatility. If it were, chloride might be added. The latter is present to a greater or lesser degree in wastes - especially Darex wastes.

As pointed out in the paper, the dramatic effects of reducing agents on ruthenium volatility were obtained with laboratory equipment. The effect in equipment on a semi-engineering scale was significant but much smaller. It is hoped to learn how to take advantage of this effect on full-scale equipment.

* These proceedings.
SOLIDIFICATION OF RADIOACTIVE WASTE SOLUTIONS. This paper sets out the results of experimental development of a method for the solidification of radioactive waste solutions, based on the drying and vitrification of precipitates of iron-hydroxide obtained by settling from radioactive solutions.

The solidification system is based on the principle of maximum reduction of the waste off-gases after removal of the aerosols and volatile radioactive components.

The authors established optimum conditions to obtain a chemically stable glass and succeeded in lowering the temperature for the melting of the glass by modifying the fluxes added.

An appreciable drop in the chemical stability of the glass was noted when it was stored for a long time at temperatures above 300° – 350°C. The authors studied the leachability of radiocaesium from the glass. They also investigated the volatility of radiocaesium and radioruthenium in the course of drying and melting and showed that in an atmosphere of carbonic acid gas the volatility of ruthenium completely disappears. The volatility of radiocaesium in appreciable quantities becomes noticeable at temperatures above 700°C and increases as the temperature rises.

It is shown that radiocaesium condenses in the drainage tubes at temperatures below 400°C and is easily washed off by weak solutions of nitric acid and water.

Calculations of the heat release from radioactive glass show that the radius of globular glass castings from high-activity materials (10 c/g) must not exceed 25 cm.

The paper includes the flowsheet for a process for the drying and vitrification of radioactive sludge by means of a gas- and heat-remover, together with details of the apparatus required.

SOLIDIFICATION DES EFFLUENTS RADIOACTIFS. Les auteurs exposent les résultats des recherches qu’ils ont faites, dans leur laboratoire, pour mettre au point une méthode de solidification des effluents radioactifs, fondée sur la dessiccation et la vitrification de l’hydroxyde de fer, obtenu par précipitation des solutions radioactives initiales.

Le procédé de solidification a été élaboré de manière à réduire au minimum les gaz d’échappement nécessitant une épuration en raison de la présence d’aérosols et d’éléments radioactifs volatils.

Au cours de leurs travaux, les auteurs ont déterminé les conditions optima permettant d’obtenir du verre chimiquement stable et démontré qu’il est possible de réduire la température de fusion du verre en faisant varier les fondants ajoutés.

Ils ont constaté une diminution notable de la stabilité chimique du verre lorsque celui-ci a été conservé pendant un temps prolongé à une température supérieure à 300° - 350°C. Ils ont examiné dans quelle mesure le radiocaesium risque d’être dégradé du verre par lixiviation. Ils ont également étudié la volatilité du radiocaesium et du radioruthénium au cours de la dessiccation et de la fusion et montré que la volatilité du ruthénium disparaît entièrement dans une atmosphère de gaz carbonique. Quant à la volatilité du radiocaesium, elle se manifeste de façon sensible à partir de 700°C et s’intensifie avec l’augmentation de la température.

Les auteurs montrent que le radiocaesium se condense sur les parois des tuyaux d’écoulement à une température inférieure à 400°C et qu’il peut être facilement étudié au moyen d’une faible solution d’acide nitrique et d’eau.

Il ressort du calcul de la chaleur dégagée par du verre radioactif que le rayon d’une boule de verre contenant une substance fortement radioactive (10 c/g) ne doit pas dépasser 25 cm.

Le mémoire expose les diverses phases du procédé de dessiccation et de vitrification des pâtes radioactives, qui est fondé sur l’utilisation du gaz comme conducteur thermique. Il indique en outre l’appareillage nécessaire à cet effet.
ВВЕДЕНИЕ

Проблема безопасного хранения радиоактивных сбросных растворов, являющихся отходами как радиохимических производств, так и широкого применения радиоизотопов в различных отраслях науки и техники, представляет собою сложную научно-техническую задачу.

Решение этой задачи зависит от состава растворов, их объёмов, уровня радиоактивности и т.д. Радиоактивные сбросы можно условно разделить на три группы:

а) сбросы высокой удельной активности (выше нескольких кюри/л);
б) сбросы средней активности (выше 0,1 кюри/л);
в) сбросы низкой удельной активности (ниже 0,1 кюри/л).

Длительный опыт работы с радиоактивными растворами, накопленный в ряде стран, позволил в настоящее время определить первоначально низкую температуру ртутных уплотнений подается в атмосферу угарного газа. Ртуть в заметных количествах не поднимается в атмосферу. В процессе работы установлены оптимальные условия получения химически стойкого стекла, а также показана возможность снижения температуры плавки стекла варированием добавок флюсов.

Установлено заметное снижение температуры плавки стекла, подвергшегося длительному хранению при температуре выше 300-350°С. Изучена вязкость радиоиспещения из стекла. Исследована летучесть радиоизотопа в процессе сушки и плавки и показано, что в атмосфере углекислого газа летучесть ртутных частиц полностью подавляется. Летучесть радиоизотопа в заметных количествах не поднимается в атмосферу.

Показано, что радиоизотопный компонент может быть отведен на отводящих трубках при температуре ниже 400°С и легко снимается слабым раствором азотной кислоты и воды.

Проведённый расчет тепловыделения радиоактивных стекла показал, что радиоактивный компонент стекла из высоконуклеотированного материала (10 кюри/г) не должен превышать 25 см.

Дается схема и аппаратурное оформление процесса сушки и огнеупорности стекла, основанных на использовании газа теплоносителя в системе.

SOLIDIFICACION DE EFLUENTES RADIACTIVOS. Los autores exponen los resultados de la aplicación de un método de laboratorio para la solidificación de efluentes radiactivos, basado en el secado y la vitrificación del hidróxido de hierro obtenido por precipitación de las soluciones radiactivas iniciales.

El procedimiento de solidificación se elaboró con miras a reducir al mínimo el volumen de los gases de escape que requieren una depuración por razón de la presencia de aerosoles y de componentes radiactivos volátiles.

En el curso del trabajo los autores determinaron las condiciones óptimas de preparación de un vidrio químicamente estable y demostraron la posibilidad de disminuir la temperatura de fusión del vidrio modificando la proporción de fundentes agregados.

Comprobaron que la estabilidad química del vidrio disminuye apreciablemente si se lo almacena durante largo tiempo a una temperatura superior a 300-350°С. Estudiaron la medida en que el radionúclido corre el riesgo de ser extruido del vidrio por lixiviación e investigaron la volatilidad del radiocesio y del radiorutenio en el proceso de desecación y fusión demostrando que la volatilidad del rutenio desaparece totalmente en atmósfera de anhídrido carbónico. La volatilidad del radiocesio adquiere valores apreciables a temperaturas superiores a los 700°C y se intensifica al ascender la temperatura.

Se observó que el radionúclido se condensa en la paredes de las tuberías de evacuación por debajo de los 400°C, pudiendo eluirse fácilmente con una solución diluida de ácido nítrico en agua.

Un cálculo del calor desprendido en los vidrios radiactivos indica que el radio de una esfera de vidrio que contenga un material de elevada radiactividad (10 с/g) no debe exceder de los 25 cm.

Los autores presentan un esquema de las distintas fases del procedimiento de desecación y vitrificación de sustancias radiactivas basado en la utilización de refrigerantes gaseosos. Describen además los aparatos necesarios para llevar a cabo la operación de moldeo.

ВВЕДЕНИЕ

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Длительный опыт работы с радиоактивными растворами, накопленный в ряде стран, позволил в настоящее время определить первоначально низкую температуру ртутных уплотнений подается в атмосферу угарного газа. Ртуть в заметных количествах не поднимается в атмосферу.
специфичность применения того или иного способа переработки каж-дого из перечисленных выше классов.

Для радиоактивных отходов высокой активности наиболее при-емлемым методом переработки представляется превращение их в хи-мически стойкие стекла. Стекло имеет незначительную раствори-мость и соответственно повышенную устойчивость к воздействию подпочвенных вод, что предотвращает распространение радиоизо-топов в окружающей среде. Кроме того процесс остекловывания позво-ляет получить минимальный объем сбросов, подлежащих хранению.

С точки зрения радиационной и термической стойкости, стекло является вполне приемлемым материалом.

Разработкой методов остекловывания радиоактивных отходов высокой активности занимается ряд исследователей в различных странах. Наиболее известны работы канадских ученых, предложив-ших метод остекловывания азотно-кислых сбросов экстракционной схемы переработки ядерного горючего путем замешивания их с нефе-лин-сиенитом и последующим сплавлением до стекломассы [1,2].

В США работы по отверждению проводятся при Комиссии по атомной энергии применительно к экстракционным сбросам растворов, содержащих нитрат аммония [3]. Обращает на себя внимание, что в опубликованных схемах отверждения радиоактивных отходов большое внимание уделяется очистке выходящих газов от радиоактив-ных аэрозолей и летучих радиоактивных компонент. В результате этого основная часть аппаратурных схем отверждения состоит из очистных аппаратов, колонн и фильтров.

В СССР вопросу остекловывания радиоактивных отходов также уделяется достаточно внимания [4].

В настоящей работе излагаются результаты исследований по разработке метода остекловывания радиоактивных отходов, в осно-нову которого были положены следующие соображения:

1. Технические операции должны быть максимально простыми и надежными.
2. Технологический процесс и аппаратура должны быть рассчитаны на дистанционное автоматическое управление.
3. Технологическая аппаратура должна обеспечивать макси-мально длительную эксплуатацию без ремонта.
4. Технологический процесс должен строиться с учетом умень-шения до минимума сбросных сдувочных газов, подлежащих очистке от аэрозолей и летучих радиоактивных компонент.

Исходя из указанных требований, был разработан метод сушки и остекловывания суспензий осадков, образующихся при обработке радиоактивных сбросных растворов.

Очистка от основной массы радиоактивных отходов производит-ся осаждением железа коррозионного происхождения в виде гидроокиси с последующим осаждением из осветленного раствора ферроцианида железа для очистки от радиоцезия. Смесь обоих пуль, со-держащая все продукты деления, подвергается процессу отвержение путем сушки и остекловывания. Поскольку эти процессы про-
текают при высоких температурах, изучалась летучесть радиоактивных цезия и рутения.

Так как из всех продуктов деления наибольшей вымываемостью из стекла обладает радиоцезий, было проведено исследование его вымываемости во времени.

Все опыты поостекловыванию проводились с пульпой гидроокиси железа, так как осадок ферроцианида железа при высокой температуре переходит в окись железа (так же, как основной осадок гидроокиси) и не вносит в процесс остекловывания никаких существенных изменений.

ПОДБОР ОПТИМАЛЬНЫХ ПРИСАДОК ДЛЯ ОСТЕКЛОВЫВАНИЯ ПУЛЬПЫ ГИДРООКИСИ ЖЕЛЕЗА

Для получения химически прочного стекла смесь окислов с флюсом различного состава подвергалась плавлению при различных температурах и временах в тиглях из нержавеющей стали.

Куски полученного плава извлекались из тигля, дробились и после ситового фракционирования испытывались на химическую стойкость по методике, описанной в литературе [5]. Растворимость стекла выражалась в процентах убыли веса к исходному весу.

В качестве сред были выбраны 0,1 N HCl, 0,1 N NaOH и вода; температура испытаний 90°С; время испытаний - 2 часа.

Во всех случаях стойкость полученного стекла сравнивалась со стойкостью стекла, применяемого для изготовления химической посуды марки "Дружная горка", определенной в тех же условиях.

Химический состав стекла

Химическая стойкость стекла определяется составом стекла, температурой и временем плавки. Все указанные параметры варьировались в широких пределах с тем, чтобы определить влияние каждого из них с целью успешного подбора оптимальных соотношений между гидроокисью железа и флюсом различного состава. Состав стекла в дальнейшем изложении выражается наибольшим отношением веса порошка окислов железа к весу окислов присадки (SiO₂, Na₂O и др.). Соотношение окислов присадки характеризуется процентным их содержанием в плаве.

Поскольку технологические и аппаратуарные требования сводятся к понижению температуры и времени плавки, под оптимальным составом стекла подразумевается такой состав присадки и ее количества, который бы обеспечил высокую химическую стойкость стекла при относительно низкой температуре плавки.

Зависимость растворимости стекла от различных параметров показана на рисунках 1, 2 и 3.

Как видно из рисунков, во всех случаях химическая стойкость стекла резко увеличивается при повышении температуры плавки с 1100°С до 1200°С.
Растворимость стекла в 0,1 N HCl в зависимости от содержания SiO₂ при содержании Na₂O = 10%:
1 - 1100°C; 2 - 1200°C.
Время плавки 2 часа.

Увеличение химической стойкости стекла с повышением температуры связано с увеличением скорости силикатообразования как за счет ускорения самой реакции, так и за счет уменьшения вязкости системы.
Так, например, сравнение кривых 1, 2 и 3 на рис.2 показывает, что стекло, выплавленное в течение 6 часов при температуре 1100°C, обладает практически такой же растворимостью как и стекло, выплавленное в течение 2-х часов при температуре 1200°C.
Растворимость стекла в 0,1 N HCl в зависимости от содержания SiO₂ при содержании Na₂O 20%:
1 - 1100°С; 2 - 1200°С.
Время плавки 2 часа.

Из приведенных данных следует также, что при содержании SiO₂ в плаве менее 40% наступает резкое снижение химической стойкости, связанное с недостатком кремнезема необходимого для связывания железа в силикат. Увеличение содержания кремнезема от 50 до 65% заметно не оказывается на увеличении химической стойкости стекла, что объясняется тем, что с увеличением количества кремнезема, способствующего увеличению стойкости, значитель но увеличивается вязкость и уменьшается степень провара.

Таблица 1

ЗАВИСИМОСТЬ РАСТВОРИМОСТИ СТЕКЛА ОТ ВРЕМЕНИ ПЛАВЛЕНИЯ И ТЕМПЕРАТУРЫ

<table>
<thead>
<tr>
<th>№ плавки</th>
<th>Отношение порошок/присадка</th>
<th>% в плаве</th>
<th>Температура плавления, °С</th>
<th>Время плавки, час</th>
<th>Растворимость, % потеря</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>1:1,25</td>
<td>40</td>
<td>15</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>68</td>
<td>1:1,25</td>
<td>40</td>
<td>15</td>
<td>1100</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>1:1,25</td>
<td>40</td>
<td>15</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>1:1,5</td>
<td>45</td>
<td>15</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>69</td>
<td>1:1,5</td>
<td>45</td>
<td>15</td>
<td>1100</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>1:1,5</td>
<td>45</td>
<td>15</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>26</td>
<td>1:1,85</td>
<td>50</td>
<td>15</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>70</td>
<td>1:1,85</td>
<td>50</td>
<td>15</td>
<td>1100</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>1:1,85</td>
<td>50</td>
<td>15</td>
<td>1200</td>
<td>2</td>
</tr>
</tbody>
</table>
Влияние содержания Na₂O в плаве различно в зависимости от содержания в нем SiO₂. При малом содержании SiO₂ увеличение содержания Na₂O ухудшает химическую стойкость в силу связывания кремнезема окисью натрия. При содержании SiO₂ в плаве выше стехиометрического, увеличение количества Na₂O приводит к уменьшению вязкости плава и, соответственно, к более полному провару и, следовательно, к увеличению химической стойкости. Дальнейшее повышение количества Na₂O при высоком содержании SiO₂ приводит к образованию более щелочного и менее стойкого стекла.

Таким образом, при применении в качестве присадок песка и соды оптимальным составом стекла с точки зрения химической стойкости является стекло с соотношением между окислами железа и присадки = 1 : 1,85 и содержанием в нем SiO₂ = 50%; Na₂O = 15%, что соответствует составу присадки 77% SiO₂ и 23% Na₂O.

Изучение зависимости химической стойкости от температуры и времени плавки показало, что увеличение времени плавки с двух до шести часов при температуре 1100°C значительно повышает химическую стойкость и тем больше, чем выше содержание в плаве SiO₂.

Из этого следует, что химическая стойкость при заданном составе и температуре определяется кинетикой образования силикатов, т.е. временем и температурой плавки.

Повышение химической стойкости за счет присадок

Из литературных данных известно, что химическая стойкость стекол увеличивается при введении добавок таких окислов как Al₂O₃, TiO₂, ZrO₂, B₂O₃.

Результаты изучения действия указанных добавок приведены на рис. 4 и в табл. 1.

Из приведенных данных видно, что добавление указанных окислов не дает эффекта.

Это можно объяснить тем, что исследуемые стекла по сравнению с техническими содержат значительно большее количество окисла металла, и добавка других окислов приводит к непроизводительному расходу кремнезема. Надо полагать, что увеличение содержания SiO₂ в плаве дало бы положительный эффект, однако оно повлекло бы за собой, как следует из приведенных данных, нежелательное повышение температуры плавления, времени плавки и объема стекла.

Весьма существенным с точки зрения подбора материалов для аппаратурного оформления процесса плавки является снижение температуры плавления стекла.

Такое снижение может быть достигнуто двумя способами: 1) снижением содержания в плаве SiO₂ и соответствующим повышением содержания Na₂O или 2) добавкой к стеклу веществ, понижающих вязкость плава.

Из приведенных в табл. 1 данных видно, что добавление B₂O₃ за счет SiO₂ ухудшает стойкость из-за дефицита SiO₂. Поэтому до-
Влияние замещения $SiO_2$ окисью алюминия на растворимость:
1 - без $Al_2O_3$; 2 - добавка $Al_2O_3$.

Добавление $B_2O_3$ можно было вести за счет $Na_2O$. На рис. 5 приведены данные по растворимости стекла с добавкой $B_2O_3$ при $t = 1050^\circ C$ и времени 2 часа.

Как видно из приведенных данных замещение $Na_2O$ борным ангидридом значительно снижает температуру плавки без заметного снижения химической стойкости.

Для сравнения химической стойкости плава со стойкостью стекла марки "Дружная горка" было подвергнуто испытаниям стекло, в котором содержание $SiO_2$ составляло 56%; $Na_2O$ 10% и $B_2O_3$ 5%. Отношение окислов железа к окислам присадки составляло 1:1,85. Результаты испытаний приведены на рисунках 6, 7 и 8.

Из полученных данных была найдена среднесуточная скорость растворения стекол в различных средах, представленная в табл.3.

Из приведенных данных видно, что в воде химическая стойкость полученного стекла соизмерима со стойкостью стекла "Дружная горка", в кислоте она в 350 раз меньше, а в шелочи в 4 раза больше. Этот результат понятен, если учесть, что в плаве содержаться окислы металлов, хорошо растворимые в кислотах, в то время как действие кислоты на стекло "Дружная горка" приводит к образованию на его поверхности защитного слоя геля кремневой кислоты, замедляющего дальнейшее растворение стекла.

В щелочи защитный слой геля растворяется, что приводит к растворимости стекла "Дружная горка", в плаве же образуется защитный слой из трудно растворимой гидроокиси железа. Наконец, была исследована зависимость химической стойкости стекла от температуры хранения.

Зависимость химической стойкости стекла от температуры хранения

Из литературных данных [6] известно, что длительное выдерживание технических стекол при повышенных температурах приво-
Влияние добавок различных окислов на растворимость стекла при отношении порошок/присадка = 1:1,5, Na₂O = 15% (Температура плавления 1200°С, время плавления 2 часа.)

<table>
<thead>
<tr>
<th>№ плавки</th>
<th>Добавка</th>
<th>Cодержание в плаве, %</th>
<th>Растворимость, % потерь</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO₂ добавка</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>нет</td>
<td>45 0</td>
<td>0,2</td>
</tr>
<tr>
<td>47</td>
<td>Al₂O₃</td>
<td>44 1</td>
<td>2,0</td>
</tr>
<tr>
<td>48</td>
<td>Al₂O₃</td>
<td>42 3</td>
<td>3,3</td>
</tr>
<tr>
<td>49</td>
<td>Al₂O₃</td>
<td>40 5</td>
<td>6,4</td>
</tr>
<tr>
<td>43</td>
<td>ZrO₂</td>
<td>44 1</td>
<td>0,6</td>
</tr>
<tr>
<td>44</td>
<td>ZrO₂</td>
<td>42 3</td>
<td>1,1</td>
</tr>
<tr>
<td>45</td>
<td>ZrO₂</td>
<td>40 5</td>
<td>1,7</td>
</tr>
<tr>
<td>53</td>
<td>B₂O₃</td>
<td>44 1</td>
<td>2,1</td>
</tr>
<tr>
<td>54</td>
<td>B₂O₃</td>
<td>42 3</td>
<td>5,1</td>
</tr>
<tr>
<td>55</td>
<td>B₂O₃</td>
<td>40 5</td>
<td>6,0</td>
</tr>
<tr>
<td>56</td>
<td>TiO₂</td>
<td>44 1</td>
<td>0,5</td>
</tr>
<tr>
<td>57</td>
<td>TiO₂</td>
<td>42 3</td>
<td>0,9</td>
</tr>
<tr>
<td>58</td>
<td>TiO₂</td>
<td>40 5</td>
<td>1,2</td>
</tr>
</tbody>
</table>

дит к их расстекловыванию. Процесс кристаллизации, естественно, должен влиять и на химическую стойкость.

С целью проверки влияния расстекловывания стекла при повышенных температурах на химическую стойкость были проведены соответствующие опыты. Было показано, что нагрев стекла после плавки, приводит к уменьшению химической стойкости. При этом, как видно из табл. 4, по мере увеличения содержания SiO₂ влияние расстекловывания уменьшается.

Наличие радиоактивных продуктов деления в стекле, подлежащем длительному хранению, приводит к разогреву стекломассы за счет энергии радиоактивного распада.

Чтобы определить расчетным путем граничные размеры и условия хранения стекломассы, необходимо было найти ту минимальную
Зависимость растворимости стекла в 0,1 Н HCl от содержания борного ангидрида:
1 - 1050°С, время плавки 2 часа.
2 - 1000°С, время плавки 6 часов.

Сравнение растворимости плавки со стеклом марки "Дружная горка" в воде:
1 - плав; 2 - стекло "Дружная горка".

температуру хранения, при которой еще не происходит расстеклования и соответственно уменьшения химической стойкости. Для этого стекло подвергалось длительному отжигу (до 120 часов) при разных температурах, после чего проверялась его химическая стойкость.

Результаты исследования приведены на рис.9.
Из рисунка видно, что при температуре хранения стекла выше 350° химическая стойкость его сильно уменьшается с ростом температуры, причем значительное уменьшение химической стойкости происходит в первые двое-трое суток и преимущественно для образцов с отжигом при высоких температурах.
2. ИССЛЕДОВАНИЕ ЛЕТУЧЕСТИ РУТЕНИЯ И ЦЕЗИЯ

В процессе плавки стекла при повышенных температурах может наблюдаться летучесть некоторых продуктов деления, которые будут мигрировать из печи в сдувочные коммуникации. По литературным данным [2,7,8] из продуктов деления только рутений и це-
Таблица 3

СРАВНИТЕЛЬНЫЕ ДАННЫЕ СРЕДНЕСУТОЧНОЙ СКОРОСТИ РАСТВОРЕНИЯ ПЛАВА И СТЕКЛА МАРКИ "ДРУЖНАЯ ГОРКА"

<table>
<thead>
<tr>
<th>Сорт стекла</th>
<th>Среда</th>
<th>Скорость растворения, % потерь за сутки</th>
</tr>
</thead>
<tbody>
<tr>
<td>Плав</td>
<td>Вода</td>
<td>0,290</td>
</tr>
<tr>
<td>Стекло</td>
<td>Вода</td>
<td>0,068</td>
</tr>
<tr>
<td>Плав</td>
<td>0,1 N HCl</td>
<td>0,700</td>
</tr>
<tr>
<td>Стекло</td>
<td>0,1 N HCl</td>
<td>0,002</td>
</tr>
<tr>
<td>Плав</td>
<td>0,1 N NaOH</td>
<td>0,240</td>
</tr>
<tr>
<td>Стекло</td>
<td>0,1 N NaOH</td>
<td>1,030</td>
</tr>
</tbody>
</table>

Таблица 4

ВЛИЯНИЕ РАССТЕКЛОВЫВАНИЯ НА ХИМСТОЙКОСТЬ
(Отжиг 2 часа при температуре 1000°С.)

<table>
<thead>
<tr>
<th>№ плавки</th>
<th>Соотношение порошок/присадка</th>
<th>% в плаве</th>
<th>T-растворимость, °С</th>
<th>Время плавки, часы</th>
<th>Растворимость, до отжига, %</th>
<th>Растворимость, после отжига, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>1:1,25</td>
<td>40</td>
<td>1100</td>
<td>6</td>
<td>0,90</td>
<td>5,00</td>
</tr>
<tr>
<td>69</td>
<td>1:1,5</td>
<td>45</td>
<td>1100</td>
<td>6</td>
<td>0,30</td>
<td>3,60</td>
</tr>
<tr>
<td>70</td>
<td>1:1,85</td>
<td>50</td>
<td>1100</td>
<td>6</td>
<td>0,10</td>
<td>0,16</td>
</tr>
</tbody>
</table>

зий обладают заметной летучестью. Рутений является летучим в виде четырехокиси, образующейся при повышенной температуре в присутствии окислителей, в частности, нитратов при их разложении. Четырехокись рутения может быть уловлена адсорбентами в виде силикагеля, пропитанного солями железа, либо в скрубберах, орошаемых раствором азотной кислоты. Имеются данные о том, что четырехокись рутения восстанавливается до нелетучих форм на металлических поверхностях.

В соответствии с этим требовалось определить степень летучести рутения и условия подавления летучести с тем, чтобы избежать установки специальных поглотителей.

Летучесть цезия, определяемая значительной упругостью паров его окиси при повышенных температурах, изучалась также с целью
Зависимость растворимости стекла от температуры и времени отжига:
1 - 350°С; 2 - 500°С; 3 - 650°С; 4 - 800°С.

Таблица 5

ЛЕТУЧЕСТЬ РУТЕНИЯ В % ОТ ИСХОДНОГО В ТОКЕ ВОЗДУХА
(Время выдержки при каждой температуре 3 часа.
Скорость потока воздуха 100 мл/мин.)

<table>
<thead>
<tr>
<th>Температура, °C</th>
<th>Активность в отводящей трубке, (^{\mu})</th>
<th>Активность в поглотителях, (^{\mu})</th>
</tr>
</thead>
<tbody>
<tr>
<td>№ 1</td>
<td>№ 2</td>
<td>№ 1</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>0,45</td>
<td>0,40</td>
</tr>
<tr>
<td>500</td>
<td>3,50</td>
<td>3,10</td>
</tr>
<tr>
<td>600</td>
<td>1,30</td>
<td>1,30</td>
</tr>
<tr>
<td>700</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Всего:</td>
<td>5,25</td>
<td>4,80</td>
</tr>
</tbody>
</table>
выявления возможности предотвращения попадания радиоактивности в коммуникации и сдувочные линии.

Исследование летучести рутения

Исследование летучести рутения проводилось в аппарате, состоящем из стального стакана, в который помещался исследуемый образец и смесь поглотителей, в которых четырехокись рутения поглощалась в растворах соляной кислоты.

Стакан помещался в термостатированную печь и через всю систему пропускался ток воздуха или углекислого газа с определенной скоростью. Опыт продолжался в течение трех часов, после чего измерялась активность в поглотителях. Температура опытов варьировалась от 120 до 1100°С. Летучесть рутения измерялась в токе воздуха и токе углекислого газа. Последняя среда была взята в связи с тем, что при плавке за счет разложения соды выделяется углекислый газ.

Результаты серии опытов приведены в табл. 5 и 6.

Таблица 6

ЛЕТУЧЕСТЬ РУТЕНИЯ В % ОТ ИСХОДНОГО В ТОКЕ УГЛЕКИСЛОГО ГАЗА

(Время выдержки при каждой температуре 3 часа.
Скорость потока углекислого газа 100 мл/мин.)

<table>
<thead>
<tr>
<th>Температура, °С</th>
<th>Активность в отводящей трубке, %</th>
<th>Активность в поглотителях, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Опыты № 1</td>
<td>Опыты № 2</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1100</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Из приведенных данных видно, что летучесть рутения в токе воздуха не высока и составляет около 5%, в то время как в токе CO₂ она не наблюдается вовсе. Такое расхождение с литературными данными объясняется отсутствием в пульпе нитратов и, следовательно, окислов азота в газовой фазе. Отсутствие активности в поглотителях указывает на то, что четырехокись рутения, образовавшаяся в токе воздуха, полностью восстанавливается в холодной отводящей трубке.

Исследование летучести цезия

Летучесть цезия изучалась в кварцевом приборе, состоящем из стакана закрытого трубкой с притертой горловиной, который помещался в термостатируемую печь.

После выдерживания стакана в печи в течение 6 часов трубка снималась со стакана и ее радиоактивность измерялась по длине γ-счетчиком с узкой щелью. Предварительно счетчик градуировался и определялся коэффициент пересчета γ-активности в трубке к абсолютному содержанию цезия. Площадь, ограниченная кривой γ-активности и осью абсцисс (длина трубки), пропорциональна количеству цезия, сконденсированного на стенках трубки. Измеряя эту площадь и зная коэффициент пересчета от γ-активности к абсолютной, можно определить истинное количество цезия, осевшего на трубке. По указанной методике было проведено три серии опытов в интервале температур 200 - 1000°C.

Результаты этих опытов представлены на рисунках 10, 11 и 12.

Рис. 10

Летучесть цезия по γ-активности (серия № 1):
1 - после 700°C; 2 - после 800°C;
3 - после 900°C; 4 - после 1000°C.
Летучесть цезия по \(\gamma\)-активности (серия № 2):
1 - после 700°C; 2 - после 800°C;
3 - после 900°C; 4 - после 1000°C.

Из представленных графиков видно, что заметная летучесть цезия наступает с 700°C и растет с повышением температуры. Распределение \(\gamma\)-активности по длине трубки показывает, что с ростом температуры максимум кривой сдвигается в сторону крышки печи и в дальнейшем остается постоянным (кривые 3 и 4), что указывает на то, что цезий полностью конденсируется на холодной части трубки. Поскольку каждая кривая характеризует количество улетучившегося цезия за все предыдущие опыты, летучесть цезия при данной температуре пропорциональна разности площадей, ограниченных кривой при данной температуре предыдущего опыта. Для примера приводим расчетные данные по летучести цезия при разных температурах для одной серии опытов.
Полученные в этой и других сериях опытов данные по летучести цезия показывают, что она не превышает 1 - 2%. В условиях технологического процесса эта цифра снизится до десятых долей процента из-за того, что слой плава значительно больше, чем в указанных опытах и, соответственно, диффузия цезия к поверхности плава будет более затруднена.

**Таблица 7**

**ЛЕТУЧЕСТЬ ЦЕЗИЯ ПРИ РАЗНЫХ ТЕМПЕРАТУРАХ**

(Исходная активность: 65280000 имп/мин)

<table>
<thead>
<tr>
<th>Температура, °С</th>
<th>Суммарная площадь, см²</th>
<th>Площадь при данной температуре, см²</th>
<th>Активность улетучившегося цезия при данной температуре за 6 часов</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0,2</td>
<td>0,2</td>
<td>2200 0,003</td>
</tr>
<tr>
<td>400</td>
<td>1,8</td>
<td>1,6</td>
<td>17300 0,027</td>
</tr>
<tr>
<td>500</td>
<td>3,4</td>
<td>1,6</td>
<td>17300 0,027</td>
</tr>
<tr>
<td>600</td>
<td>5,4</td>
<td>2,0</td>
<td>21600 0,033</td>
</tr>
<tr>
<td>700</td>
<td>8,6</td>
<td>3,2</td>
<td>34500 0,053</td>
</tr>
<tr>
<td>800</td>
<td>14,4</td>
<td>5,8</td>
<td>62500 0,095</td>
</tr>
<tr>
<td>900</td>
<td>28,0</td>
<td>13,6</td>
<td>147000 0,225</td>
</tr>
<tr>
<td>1000</td>
<td>49,2</td>
<td>21,2</td>
<td>229000 0,350</td>
</tr>
<tr>
<td>Всего:</td>
<td></td>
<td></td>
<td>0,813</td>
</tr>
</tbody>
</table>

Исследование вымываемости цезия

Из всех продуктов деления цезий как щелочной металл обладает наибольшей вымываемостью из стекол из-за того, что он образует в водной среде хорошо растворимые соединения. В результате проведения серии опытов были получены данные, приведенные в табл. 8 и 9.

Из приведенных данных видно, что вымываемость цезия в течение 20 дней практически не зависит от времени и степени обмена среды и составляет для данных конкретных условий величину порядка 0,005%/сутки, что соответствует 0,4·10⁻⁵ кюри/м² сутки при активности стекла по цезию 1 кюри/л.

**РАСЧЕТ ТЕПЛОВЫДЕЛЕНИЯ**

Во время хранения остеклованных продуктов деления за счет β- и γ-радиации происходит выделение тепла, которое необходимо от-
Вымываемость цезия из стекла при ежедневной смене воды

Вес стекла 3 г.
Суммарная активность цезия в стекле 6 мкюр.
Объем воды 100 мл.
Температура среды 20°С.
Площадь поверхности стекла 60 см².

<table>
<thead>
<tr>
<th>Время, сутки</th>
<th>Активность воды, расп/мин·см³</th>
<th>Вымываемость цезия, % к исходной активн.</th>
<th>Примечание</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18 300</td>
<td>0,0135</td>
<td>Увеличение за счет пыли</td>
</tr>
<tr>
<td>2</td>
<td>7 500</td>
<td>0,0056</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9 500</td>
<td>0,0070</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7 100</td>
<td>0,0052</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6 900</td>
<td>0,0051</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>7 000</td>
<td>0,0052</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>11 100</td>
<td>0,0081</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6 500</td>
<td>0,0048</td>
<td></td>
</tr>
<tr>
<td>Среднее</td>
<td></td>
<td>0,0059 (сутки)</td>
<td></td>
</tr>
</tbody>
</table>

Чтобы определить общее тепловыделение, необходимо просуммировать выражение (1) по всем продуктам деления на основании данных изотопного состава сбросного раствора, подлежащего отверждению.

\[
E = \sum E_i \text{ Мэв/см}^3
\]
**Вымываемость цезия из стекла без смены воды**

Вес стекла 3 г.
Суммарная активность цезия в стекле 6 мкц ри.
Объем воды 100 мл.
Температура среды 20°С.
Площадь поверхности стекла 60 см².

<table>
<thead>
<tr>
<th>Время, сутки</th>
<th>Активность воды, расп/мин·см³</th>
<th>Вымываемость цезия, % к исход.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>за все время</td>
</tr>
<tr>
<td>1</td>
<td>14 000</td>
<td>0,0108</td>
</tr>
<tr>
<td>2</td>
<td>17 100</td>
<td>0,0131</td>
</tr>
<tr>
<td>3</td>
<td>21 070</td>
<td>0,0161</td>
</tr>
<tr>
<td>4</td>
<td>25 300</td>
<td>0,0195</td>
</tr>
<tr>
<td>5</td>
<td>35 400</td>
<td>0,0271</td>
</tr>
<tr>
<td>7</td>
<td>41 200</td>
<td>0,0316</td>
</tr>
<tr>
<td>8</td>
<td>43 500</td>
<td>0,0335</td>
</tr>
<tr>
<td>9</td>
<td>48 900</td>
<td>0,0376</td>
</tr>
<tr>
<td>10</td>
<td>59 000</td>
<td>0,0454</td>
</tr>
<tr>
<td>11</td>
<td>62 300</td>
<td>0,0480</td>
</tr>
<tr>
<td>13</td>
<td>73 000</td>
<td>0,0560</td>
</tr>
<tr>
<td>14</td>
<td>78 200</td>
<td>0,0600</td>
</tr>
<tr>
<td>15</td>
<td>87 700</td>
<td>0,0675</td>
</tr>
<tr>
<td>16</td>
<td>96 000</td>
<td>0,0740</td>
</tr>
<tr>
<td>17</td>
<td>105 400</td>
<td>0,0810</td>
</tr>
<tr>
<td>18</td>
<td>112 200</td>
<td>0,0860</td>
</tr>
<tr>
<td>20</td>
<td>133 400</td>
<td>0,1020</td>
</tr>
<tr>
<td>21</td>
<td>141 200</td>
<td>0,1080</td>
</tr>
<tr>
<td>22</td>
<td>146 100</td>
<td>0,1120</td>
</tr>
</tbody>
</table>

Среднее 0,0048

Величина $E$ представляет собой величину выделившейся энергии с момента захоронения до момента времени $t$ в 1 см³ стекла и определяет радиационную нагрузку стекла за время хранения.

Для определения общего количества энергии, выделяющегося из хранилища к моменту заполнения $t$ можно воспользоваться выражением:
\[ Q = E \cdot v \cdot \text{Mev} \text{ см}^3/\text{сек}, \quad (3) \]

где \( v \) - количество поступающего стекла в хранилище см\(^3\)/сек.

Помимо расчета общего тепловыделения из хранилища необходимо знать температурный режим хранения стекол, поскольку их химическая стойкость в значительной степени определяется температурой хранения.

Для шара, помещенного в среду, в которой теплоотвод не затруднен, например, при охлаждении слитков проточной водой с температурой \( T_0 \), температура внутри шарового слитка радиусом \( R \) после достижения стационарного состояния определяется выражением:

\[ T = T_0 + \frac{q}{6\lambda} (R^2 - r^2), \quad (4) \]

где \( q \) - количество тепла, выделяемого в 1 см\(^3\) стекла за 1 сек;

\( \lambda \) - коэффициент теплопроводности в кал/см.сек.град;

\( r \) - координата точки, в которой определяется температура.

Если шаровой слиток помещается в среду с коэффициентом теплопроводности, близким к стеклу, например, хранение в песчаном грунте, температура в любой точке внутри и вне слитка определяется выражениями:

\[ T = T_0 + \frac{q}{2\lambda} (R^2 - r^2) \quad \text{для области } r > R \quad (5) \]

и

\[ T = T_0 + \frac{1}{r} \frac{q R^2}{3\lambda} \quad \text{для области } r \leq R \quad (6) \]

где \( T_0 \) - температура среды при \( r \to \infty \).

Таким образом по известным значениям удельного тепловыделения \( q \), коэффициенту теплопроводности \( \lambda \) и максимально допустимого разогрева слитков определяются граничные размеры их для безопасного вечного хранения.

При этом следует учесть, что время достижения стационарного состояния \( t \) определяется выражением:

\[ t = \frac{c \rho R^2}{\lambda}, \]

где \( c \) - удельная теплоемкость стекла в кал/град;

\( \rho \) - плотность стекла г/см\(^3\).

Схема аппаратурного оформления

Как указывалось вначале, одним из основных принципов оформления процесса отверждения радиоактивных сбросов являлось уменьшение до минимума сбросных сдувочных газов, подлежащих очистке от аэрозолей и летучих радиоактивных компонент. В соответствии

...
с этим разработана схема аппаратного оформления, основанная на том, что практически вся масса газа-теплоносителя, циркулируя в замкнутой системе, исключает сброс большого количества газов в атмосферу.

Принципиальная схема процесса сушки представлена на рис.13.

К нагретому исходному азотнокислому раствору, подлежащему переработке, добавляются растворы азотнокислого железа (если его нет в исходном материале) и едкого натра. Выпавший осадок гидроокиси железа захватывает основную часть продуктов деления. Осветленный раствор направляется для осаждения цезия, а суспензии гидроокиси железа с добавкой осадка, содержащего цезий, направляются в распылительную сушилку. Высушивание суспензии до порошка происходит нагретым газом, засасываемым из калорифера. Распыление пульпы производится центробежным распылителем со скоростью на периметре распыляющего диска 90-100 м/сек. Сухой порошок вместе с газом проходит циклон, где происходит отделение 99% порошка, а газ с
1% порошка поступает в холодильник, где пары конденсируются и вместе с остатками твердых частиц стекают в отстойник.

Дополнительно очищенный при этом газ через ресивер и вентилятор направляется в калорифер. Осадок из отстойника поступает к исходной суспензии, а декантат направляется на очистку и сброс.

Сухой порошок смешивается с шихтой для плавки и поступает в плавильную печь с высокочастотным обогревом.

При варке стекла образуется углекислый газ и пары воды. Эти отходящие газы поступают в общий газовый цикл, где они очищаются на обеих ступенях и выбрасываются из системы после вентилятора. Количество выбрасываемых газов составляет 1/1000 от количества газа, необходимого на сушку суспензии. При этом очистка от твердой фазы на обеих ступенях (циклах) и холодильник составляет 99,99%, а со образующимися газами, поступающими на дополнительную очистку отходит ~10^-5 твердых частиц.

ВЫВОДЫ

Разработан метод отверждения радиоактивных сбросных растворов, основанный на сушке и остекловывании осадков гидроокиси железа, содержащих практически все продукты деления.

Варьированием состава присадок и их количеств установлены оптимальные условия получения химически стойкого стекла.

Показана возможность снижения температуры плавки на 150°С добавлением борного ангидрида за счет окиси натрия.

Показано снижение химической стойкости стекла, подвергшегося длительному температурному воздействию выше 300 - 350°С.

Изучена выплываемость радиоцезия из стекол. Исследовалась летучесть радиорутения и радиоцезия в процессе сушки и плавки. Показано, что в атмосфере углекислого газа летучесть рутения полностью подавляется.

Летучесть цезия в заметных количествах наступает при температуре 700°С и растет с дальнейшим повышением ее.

Показано, что улетучившийся цезий конденсируется на отводящих трубах при температуре ниже 400°С и легко смыывается с поверхностей слабым раствором азотной кислоты. Приведен расчет тепло-выделения радиоактивных стекол, показавший, что радиус шаровой отмывки стекла из высокоактивного материала ~ 10 к/г не должен превышать 25 см.

Приведена схема и аппаратное оформление процесса сушки и остекловывания радиоактивных пульп, основанная на использовании газа-теплоносителя в системе.

ЛИТЕРАТУРА

ДИСКУССИЯ

R. BONNIAUD: What you have in mind is the vitrification of concentrated solutions of fission products after previous precipitation of ferric ferrocyanide. Hence, it is the precipitate that you are vitrifying. This being the case, I would like to ask what decontamination factor was obtained during this precipitation and what treatment you plan to use for the supernatant liquid.

N. BREZHNeva: The decontamination factor obtained in the precipitation of iron hydroxide and ferrocyanide is determined by the decontamination factors for the individual radioisotopes (for the rare-earth elements, caesium, zirconium and niobium they are very high, for strontium they are about 100, for ruthenium up to 10). The purified solution is subjected to further decontamination and concentration by evaporation so as to reduce its volume. The activity of the distillate does not exceed the levels laid down in the health standards for open reservoirs, thereby permitting its discharge into the drainage system. The heels go into tanks for storage.

J. A. BUCKHAM: Could you indicate the scale on which your studies were conducted? For example, what was the size and throughput of the drying chamber, and what are the physical characteristics of the powder produced in the drying chamber?

N. BREZHNeva: The facility is a large laboratory-scale unit (approximately 5m × 5m × 6m), having a capacity of 5 liters of suspension per hour. As a result of drying in a dryer of this type, the power is obtained in monodisperse form, with a very high degree of dispersion. The monodispersion of the powder enables us to get a high degree of purification in the cyclone used in the system.

J. M. HOLMES: Could you tell us something about your construction materials? Also, could you indicate whether you intend to use a filter on the off-gas released from the process?
N. BREZHNEVA: The facility is entirely of stainless steel. It is planned to install a filter for the final purification of the gas emerging from the system, in an amount of about 1/1000 of the total gas volume.

D.W. CLELLAND: Would you confirm that your description of the glass-making procedure following an iron precipitation relates to highly active liquors and not liquors of medium activity?

N. BREZHNEVA: As indicated in the paper, what we are concerned with is the treatment of highly active solutions, having an activity of about 1 c/l of solution.

W. G. BELTER: Are your studies done in conjunction or co-operation with those of Professor Zimakov, and are they conducted at the same laboratory? Are any engineering-scale studies being conducted as a result of your laboratory work?

N. BREZHNEVA: Our vitrification activities are carried on at a number of laboratories. The work on which I reported is done in conjunction with that of the laboratory directed by Professor Zimakov, although a different technological process is involved. At present, an enlarged facility is available to us and we think that later on it can be used on a more extensive scale if the results obtained on the laboratory facility warrant this, as we expect that they will.

J. R. GROVER: If I understand your graphs correctly, they indicate solubilities of the order of 1%. These are surprisingly low for silicate glasses being about 1000 times greater than those which we have measured. Could you please comment?

N. BREZHNEVA: The graphs to which you refer are concerned with experiments in acids at a temperature of 90°C. As shown in the other graphs, the results obtained for water and room temperature are no different from those that you mention.

L. P. HATCH: The objectives which you outline at the beginning of the paper can be summarized as follows: (1) Simplicity and reliability of technical operations; (2) Suitability of process equipment for remote operation; (3) Keeping maintenance problems to a minimum. Do you consider that these objectives will be met in the development of the process as outlined?

N. BREZHNEVA: Future operation of the facility will show to what extent we were right. The individual units of the installation are simple as is also its overall arrangement. A closed system has great advantages, since it simplifies the procedure for purifying gases. We believe that we shall attain the goal we have set ourselves.

J. A. BUCKHAM: Have you made any studies which would indicate the advantages of the initial precipitation step (with its attendant complications of solid-liquid separation, reconcentration of supernatant solution and slurry handling) as compared with drying the concentrated solution directly?

N. BREZHNEVA: Experiments on the direct drying of high-activity nitrate solutions have not been done on an installation of this kind.
FIXATION OF RADIOACTIVE WASTE IN GLASS.
PART I. PILOT-PLANT EXPERIENCE AT HARWELL

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Abstract — Résumé — Аннотация — Resumen

FIXATION OF RADIOACTIVE WASTE IN GLASS. PART I. PILOT-PLANT EXPERIENCE AT HARWELL. The reasons for incorporating fission-product wastes into glass for long-term storage are outlined. The flow-sheet and operating cycle of the fixation process which has been developed at Harwell are described.

Two years of operation of an inactive pilot plant are surveyed to show how the present operating conditions have been evolved. Full-length runs under these conditions have confirmed the reliability and reproducibility of the process.

Engineering components suitable for an active plant have been developed and tested and the layout of the 1000-c pilot plant being commissioned at Harwell is illustrated in sketch form.

Factors that affect the scale-up of the process are discussed in relation to the needs of the developing United Kingdom power programme.

FIXATION DES DÉCHETS RADIOACTIFS DANS LE VERRE, PREMIÈRE PARTIE: L’USINE PILOTE DE HARWELL. Les auteurs exposent les raisons pour lesquelles on incorpore les déchets de produits de fission dans le verre en vue d’un stockage de longue durée. Ils donnent le diagramme d’opérations et le cycle du procédé de fixation mis au point à Harwell.

Ils décrivent les deux années de fonctionnement de l’usine pilote, sans produits radioactifs, pour montrer comment les conditions actuelles d’opérations ont été mises au point. Des cycles complets réalisés dans ces conditions ont confirmé la sécurité et la reproductibilité du processus.

L’appareillage approprié pour une usine de haute activité a été mis au point et essayé ; les auteurs décrivent les grandes lignes de l’usine pilote (activité de 1000 c) en construction à Harwell.

Les auteurs discutent les facteurs qui peuvent affecter le développement de ce processus à plus grande échelle, eu égard aux besoins du programme énergétique du Royaume-Uni.

ФИКСАЦИЯ РАДИОАКТИВНЫХ ОТХОДОВ В СТЕКЛЕ. ЧАСТЬ I. ПРОБНАЯ ОПЫТНАЯ УСТАНОВКА В ХАРУЭЛЛЕ. Доказывается необходимость остекловывания радиоактивных отходов с целью их длительного хранения. Описываются разработанные в Харуэлле технологическая схема и рабочий цикл процессов фиксации.

Дается обзор результатов двухгодичной работы экспериментальной нейтронной установки с целью показать процесс усовершенствования эксплуатационных характеристик. Полные циклы, проведенные в этих условиях, подтверждают надежность и воспроизводимость этого процесса.

Были разработаны и опробованы технологические узлы, необходимые для активной установки; дается схема пучковой в Харуэлле опытной установки на 1000 кэри.

Обсуждаются факторы, от которых зависит расширение масштабов применения этого метода в свете увеличения программ выработки электроэнергии в Соединенном Королевстве.

FIJACIÓN DE DESECHOS RADIACTIVOS EN VIDRIO. PARTE I: EXPERIENCIA ADQUIRIDA EN LA INSTALACIÓN PILOTO DE HARWELL. Los autores exponen las razones que aconsejan incorporar los desechos y productos de fisión a materiales vítreos para almacenarlos por tiempo largo. Describen el diagrama de circulación y el ciclo de operaciones que integran el proceso de fijación perfeccionado en Harwell.

Examinan luego los dos años de explotación de una instalación piloto inactiva, a fin de explicar cómo se han llegado a establecer las actuales condiciones de trabajo. El cumplimiento de ciclos de trabajo completos en estas condiciones ha demostrado que el procedimiento utilizado es seguro y susceptible de repetición.

Se han proyectado los elementos constructivos adecuados para una instalación activa, se los ha sometido a ensayo y los autores presentan el esquema de la instalación piloto de 1000 c que está por entrar en servicio en Harwell.

Analizan por último los factores que intervienen en la aplicación del proceso en mayor escala, teniendo en cuenta las necesidades del programa de energía nucleoeléctrica en vías de ejecución en el Reino Unido.
The work at Harwell on the incorporation into glass of the highly-active fission-product wastes which will arise in the United Kingdom was first described at the Idaho Falls Conference in September 1960 [1]. The process aims to convert the wastes to a leach-resistant glass in stainless-steel cylinders incorporating up to 40% of waste oxides. The cylinders form the basis of a storage system capable of lasting for centuries. Pilot-plant operation has demonstrated the practicability of the process in that many successful runs have now been completed producing 50-kg blocks of leach-resistant glass from low-activity simulated waste solution. This paper describes the problems that operating experience has revealed and the work that has been done to solve them. The next step is to operate with feed solutions that are sufficiently radioactive to enable decontamination factors to be measured for the important fission products and to prove the techniques of remote operation. A pilot plant to produce glass blocks containing 1000 c has been designed and built. The present scale of operation is not quite adequate for an industrial installation and a number of possible methods of increasing throughput are discussed. However, this would be done without altering the basic flow-sheet of the process which is described in the next section.

1.1. Flow-sheet

Figure 1 shows the general flow-sheet of the process. Three identical stainless-steel cylinders, each 6-in internal diam. × 5-ft long, are used in series. The first, the process vessel, is in a furnace and the other two, the filter vessels, in ovens which are held at 250°C to prevent condensation.

The waste solution and silica/borax slurry are mixed together in the correct proportions to give the required glass composition and pumped at the required flow-rate into the top of the cylinder in the furnace. Evaporation, denitrification, sintering and melting occur simultaneously over a narrow zone, which is termed the "working" zone, to form a bubble-free glass, the furnace-element temperature being controlled at 1050°C throughout. As the run progresses and the working zone moves up the cylinder, the power to the six independently controlled heating elements is adjusted to follow the evaporation. Each cylinder is filled with about 3½ ft of glass.

At this stage, the feed pipe is washed with water and the furnace is raised to melt the dust which has collected on the underside of the lid of the process cylinder.

The off-gases from the evaporation stage are passed through the second and third cylinders which contain a small primary and a large secondary filter respectively. These filters are packed with an adsorber for volatile ruthenium and are described in detail in Part III[3].

Most of the material carried over is trapped by the primary filter. At the end of the process cycle, the cylinder containing the glass is removed to storage and the cylinder in the second position containing the primary filter is put in the furnace. A new cylinder with a new filter is put in the first oven. Due to the small dust loading on the secondary filter, this is not moved through the process cycle and would not be used for glass making.
At the beginning of the next cycle of operations as the furnace temperature is raised, the spent filter drops into the bottom of the cylinder as the zinc weld connecting it to the lid is melted at 420°C.

The off-gases from the third cylinder pass directly to the condenser and the oxides of nitrogen are absorbed by the nitric-acid condensate in a packed column. A caustic scrubber removes traces of acid fumes before the effluent gas passes through a final absolute filter. The entire process equipment is maintained below atmospheric pressure by a vacuum ejector.

2. OPERATING EXPERIENCE

Although the basic concept of the process of forming the glass directly in disposable steel cylinders has been adhered to over the past two years, the operating conditions have been varied very considerably to develop the most reliable and reproducible process.

Engineering components, designed for the active pilot plant, have been tested under operating conditions. Where the results of such tests have implied modification of the operation of the process they are discussed in this section, but the engineering aspects will be described in section 3.

2.1. Feed system

For most of the runs, the silica, borax and mock fission-product solution were mixed together in the correct proportions before each run. A 'Kontak'
diaphragm metering pump was used to give deliveries from 20-150 ml/min with an accuracy ± 2%, the pulsations being damped out to give a steady flow.

With the comparatively low flow-rates of the process it was essential that the inlet to the process cylinder always ran full of feed, otherwise drying out and subsequent blockage occurred. Experiments with various pipe sizes indicated that 1⁄4-in internal diam. was the largest size that could be guaranteed to remain full provided that it was at least 3 in long. This is an important consideration which, when the vessel is used in the filter position, affects the pressure drop through the complete process equipment together with the prevention of blockages due to the dusty off-gas. It is discussed in detail in section 2.6.

It was realized that a combined slurry feed would present severe handling problems with active solutions so a dual-feed system was developed for the active plant. The silica/borax slurry was to be pumped separately from the active fission-product solution and the two streams mixed close to the inlet to the cylinder. Early mixing tests indicated that ferric hydroxide was precipitated on the surface of the slurry and unless this could be thoroughly mixed, blockages occurred. It was found, however, that if the silica/borax slurry was made up to a pH < 4 by adding nitric acid, no precipitation occurred on mixing.

The arrangement of the complete dual-feed system will be described in section 3.

2.2. Evaporation and glass formation

Early work on glasses suitable for the incorporation of fission products [2] had led to the choice of mix 279 as a suitable compromise between melting point, leach resistance and waste oxide content (see Part II [4] and Table I). 1150°C was considered a suitable maximum furnace operating temperature. The furnace elements were designed for continuous rating at 1300°C, so the lower temperature should ensure long life and the reliability necessary for a furnace which may ultimately be installed in an active cell.

To minimize scaling of the exterior surface of the stainless-steel cylinder at temperatures up to 1150°C, the furnace interior was purged with nitrogen. Between each of the process positions, combined pressure/vacuum gauges were fitted to measure the pressure drops and thermocouples were located as indicated on Fig. 1. Two longitudinal thermocouple pockets inside the process vessel enabled the internal temperature to be measured at any height.

The original intention was to carry out the evaporation and denitration under conditions which would suppress the ruthenium volatilization [3]. This meant carrying out the evaporation at 800°C and only when sinter had been produced and the high power input had been transferred to the next zone up the furnace would the element temperature be allowed to rise to 1150°C to melt the sinter. A number of runs in which sinter was produced at 800°C but not melted to glass were carried out successfully, with flow-rates in the range 80-150 ml/min. These were followed by two runs in which the
TABLE I

GLASS COMPOSITIONS USED FOR PILOT-PLANT WORK

<table>
<thead>
<tr>
<th>Mix No.</th>
<th>279</th>
<th>293</th>
<th>287</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition - % Waste oxides</td>
<td>30</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>% Silica</td>
<td>47</td>
<td>43</td>
<td>35</td>
</tr>
<tr>
<td>% Borax</td>
<td>23</td>
<td>32</td>
<td>40</td>
</tr>
<tr>
<td>Density g/cm³</td>
<td>2.65</td>
<td>2.58</td>
<td>2.37</td>
</tr>
<tr>
<td>Temperature at which oxides begin to sinter °C</td>
<td>700 - 750</td>
<td>600 - 650</td>
<td>500 - 550</td>
</tr>
<tr>
<td>Temperature at which sinter begins to melt °C(T₁)</td>
<td>1070</td>
<td>900</td>
<td>820</td>
</tr>
<tr>
<td>Melting point °C(T₂)</td>
<td>1110</td>
<td>1020</td>
<td>950</td>
</tr>
<tr>
<td>Maximum furnace temperature °C(T₃)</td>
<td>1150</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>T₂ - T₁</td>
<td>40</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>T₃ - T₂</td>
<td>40</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>T₃ - T₁</td>
<td>80</td>
<td>150</td>
<td>230</td>
</tr>
</tbody>
</table>

Full glass-making process was attempted. In the first, the initial flow-rate was 100 ml/min and the furnace-element temperatures were raised after the evaporation to 1130-1150°C. After 4½ hr running, a sudden surge of pressure occurred in the process vessel. Further pressure surges occurred during the 27 hr of the run, the magnitude ranging up to 30 lb/in² and the frequency being quite random. It was observed that the off-gas temperature rose markedly during a pressure surge.

The internal thermocouples indicated that a layer of cool sinter existed inside the vessel and slowly moved up as the run proceeded. When a pressure surge occurred, this cool zone dropped lower down the vessel.

At the beginning of the run, the working zone moved up the vessel at a rate which corresponded to the production of a sinter with extensive voids, equivalent to a bulk density ~ 1 g/cm³. As the temperature of the bottom element was raised to 1150°C the sinter below the evaporation zone melted to form glass and left a cavity due to the change of density (glass 2.65 g/cm³). At this stage the cool sinter produced a "bridge" across the inside of the vessel, sufficient temporarily to support its own weight. When, however, this bridge collapsed, the cool sinter fell on to the molten glass with a corresponding sudden increase in the rate of evaporation. Due to the resistance to flow through the filter, this increased gas flow could not be dissipated quickly enough and the pressure rose in the process vessel.

In the second run, the furnace-element temperatures were raised to 1150-1170°C earlier to melt the sinter more readily. Pressure surges again occurred randomly, but at no time did the magnitude exceed 16 lb/in². Most of the surges were 1-41 lb/in² and the increased gas flow could be accomm-
ated by temporarily increasing the vacuum beyond the condenser. By raising the temperature below the working zone earlier, the sinter had definitely melted more readily and the very large surges noticed in the first run had not occurred in the second run.

Severe external oxidation of the vessels had occurred in these two runs and it was obvious that the maximum operating temperature must be reduced to guarantee the integrity of the vessel against possible positive pressures. At the same time, the operating conditions must be modified to reduce or eliminate the pressure surges. Corrosion experiments of steel in air indicated that the maximum furnace operating temperature should be reduced to 1050°C. The second run had indicated that if the temperature difference between the furnace operating temperature and the glass melting-point was increased, the pressure surges would probably be reduced. Glass-mix 287 was chosen (see Table I) to increase this temperature difference from 40 to 100°C ($T_3 - T_2$ on Table I).

Seven runs were carried out of 1-4 hr duration with both the evaporation and melting taking place with the furnace at 1050°C. Severe deposition of sintered dust was observed in the outlet pipe from the process vessel which in some cases was almost a total obstruction. No pressure surges were observed during these runs, but they were of insufficient duration for a firm conclusion to be drawn regarding the effects of operating temperature on the occurrence of surges.

Further examination of the two-glass compositions indicated that there was a considerable difference in the way the sinter melted to glass [4]. With mix 279 the sinter began to drop under its own weight at 1070°C, i.e. 40°C below its melting point, whereas with mix 287 melting began at 820°C, 130°C below its melting point. ($T_2 - T_1$ on Table I). The temperature difference between the operating temperature and the temperature at which the sinter began to melt ($T_3 - T_1$) had been increased from 80 to 230°C. Although this had had a marked effect on the occurrence of pressure surges, a secondary problem of dust deposition had appeared.

A compromise glass composition (mix 293) was investigated and in 18 runs of between 4 and 12 hr duration, varying degrees of dust deposition were observed. Some pressure surges also occurred but their magnitude and frequency were lower than had been experienced with mix 279.

From these runs it became obvious that two factors were of prime importance:

1. The temperature of the gases leaving the process vessel must be controlled to prevent the deposition of sintered dust;
2. The evaporation and glass formation must be controlled to eliminate the tendency for a bed of cool sinter to build up, form a bridge and then collapse on to the molten glass below, giving rise to a pressure surge.

2.3. Control of off-gas temperature

Examination under the microscope of the dust which had deposited in the outlet pipes when using glass-mix 287 indicated that the oxide particles had begun to sinter. Laboratory measurements were made to find the tem-
perature at which the dried oxides began to sinter and stick together for mixes 279 and 287. This value was difficult to measure accurately but the temperature range over which the oxides just began to sinter together is indicated in Table I.

Measurement of the temperature of the gas at the outlet from the vessel was complicated due to pick up of dust on the measuring instrument and the radiation conditions near the outlet. However, a thermocouple 2 in under the lid in one of the longitudinal thermocouple pockets and one in the side of the outlet pipe indicated that the off-gas temperature was in the region of 500-600°C. It was not surprising, therefore, that when using mix 287 the dust particles were beginning to sinter, whereas with mix 279 there had been no signs of trouble.

When mix 293 was used, the dust deposition varied from almost total obstruction of the outlet pipe to trace amounts only.

Chemical analyses of the condensate from runs using all the mixes had indicated that there was a preferential carry-over of boron, probably as steam volatile boric acid [3]. It was thought this might have some effect in promoting the sintering of the oxides and causing the deposition. Samples of the deposited dust from 8 runs were analysed and the results are given in Table II, together with analyses of the dust collected on the filter and in the filter vessel. Although there was a considerable spread in the results, the dust carried over from the process vessel was not significantly rich in boron.

As has already been noted, when a pressure surge occurred, the off-gas temperature was observed to increase by an amount proportional to the magnitude of the surge. Although the off-gas temperature appeared to be the key to the deposition problem, it was not possible to tell whether the deposition occurred during normal running or only during a surge. However, it was obvious that the temperature of the gas leaving the process vessel must be considerably reduced. This was attempted by raising the vessel 4 in further out of the furnace so that the lid was now 6 in above the top of furnace. An air-cooling ring was placed round the top of the vessel to pro-

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**TABLE II**

CHEMICAL ANALYSES OF THE DUSTS CARRIED OVER USING MIX 293 (mg/g)

<table>
<thead>
<tr>
<th></th>
<th>( \text{U}_2\text{O}_3 )</th>
<th>( \text{F}_2\text{O}_3 )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{B}_2\text{O}_3 )</th>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{SiO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical feed</td>
<td>100</td>
<td>94</td>
<td>56</td>
<td>221</td>
<td>99</td>
<td>430</td>
</tr>
<tr>
<td>Blockages</td>
<td>103 ± 11</td>
<td>95 ± 23</td>
<td>65 ± 22</td>
<td>239 ± 29</td>
<td>105 ± 18</td>
<td>388 ± 21</td>
</tr>
<tr>
<td>Collected on filter</td>
<td>117 ± 11</td>
<td>94 ± 22</td>
<td>74 ± 19</td>
<td>242 ± 48</td>
<td>117 ± 31</td>
<td>355 ± 37</td>
</tr>
<tr>
<td>In filter vessel</td>
<td>105 ± 10</td>
<td>90 ± 19</td>
<td>68 ± 17</td>
<td>219 ± 34</td>
<td>89 ± 22</td>
<td>428 ± 37</td>
</tr>
</tbody>
</table>
vide extra cooling. This had the desired effect of reducing the normal off-gas temperature, but a large pressure surge could still raise the temperature enough to cause some deposition.

It was probable that more stable operation would be achieved if the depth of the cool sinter zone and the hold-up could be reduced. The feed flow-rate was reduced from 80 ml/min to 50 ml/min and this had the desired effect. Pressure surges became infrequent and rarely exceeded 1 lb/in² and it was possible to control the off-gas temperature at a steady value. Under these conditions it was possible to produce the required 3-ft 6-in depth of glass without deposition of sinter in the off-gas line.

2.4. Feed flow-rate and hold-up

In section 2.2 the occurrence of pressure surges was attributed to the collapse of a bed of cool damp sinter on to molten glass below. The evaporation occurs primarily from this sinter and some measure of the volatile liquid hold-up is desirable. This consists of free water and nitric acid and water of crystallization.
A graduated glass cylinder was inserted between the condenser and the condensate tank to measure the volume of condensate collected. The volume fed was obtained by multiplying the flow-rate according to the pump calibration by the elapsed time. The difference between these two values is the estimated hold-up after an allowance has been made for the volume change from feed to condensate, the normality of the condensate and the amount escaping to the scrubber. At the end of each run it was possible to measure the actual hold-up which was simply the condensate collected after feed was stopped and compare it with the value estimated by difference during the run.

Figure 2 shows two typical curves of the variation of hold-up with run duration for flow-rates of 50 and 80 ml/min. Individual errors in estimating the hold-up are cumulative, but if we assume a constant error, e.g. pump calibration bias, the dotted lines would represent the way in which the hold-up varied during the runs.

In all the runs the hold-up accumulated steadily over the first few hours of the run and then tended to drift up and down. Sudden falls in the hold-up occurred when a pressure surge occurred.

The actual values of hold-up obtained (average of 3-6 runs in each group) are given in Table III and although the hold-up is reduced from ~1 l at 80 ml/min to ~550 ml at 50 ml/min, there is no effect due to run duration.

<table>
<thead>
<tr>
<th>Table III</th>
</tr>
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<tbody>
<tr>
<td>VARIATION OF ACTUAL HOLD-UP WITH RUN DURATION AND FLOW-RATE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run Duration (hr)</th>
<th>Actual hold-up (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow-rate 50 ml/min</td>
</tr>
<tr>
<td>1-5</td>
<td>-</td>
</tr>
<tr>
<td>5-7</td>
<td>-</td>
</tr>
<tr>
<td>7-12</td>
<td>520 ±367</td>
</tr>
<tr>
<td>40-50</td>
<td>683 ±355</td>
</tr>
<tr>
<td>50-60</td>
<td>472 ±270</td>
</tr>
</tbody>
</table>

Figure 3 shows some typical curves of the estimated hold-up for full-length runs at 50 ml/min. Run 209 is an example of a run with a fairly constant cumulative error. Run 215, however, tends to drift up and down while the values from Run 207 indicate a negative hold-up for the first 17 hr of the run. Subsequent checks of the feed-pump delivery at the setting corresponding to 50 ml/min showed errors which could account for much of the difference between the observed and calculated hold-up.
2.5. Visual observations

For a number of the runs at both 80 and 50 ml/min a window was put on the lid of the vessel so that the evaporation could be observed visually. A detailed examination of the phenomenon occurring in the vessel was possible by using a cine camera at either 25 frames/sec for a few minutes or 2 frames/min over a period of hours.

At both flow-rates, the feed broke up into droplets which fell to the bottom of the vessel and formed a "puddle" of vigorously boiling liquid on the top of the sinter. At 80 ml/min the "puddle" covered 75-100% of the cross-section of the vessel. Melting of the sinter to glass continued below and the break-up of the crust of sinter released the liquid into the hot zone, giving rise to a pressure surge. At 50 ml/min the "puddle" generally occupied 25-50% of the cross-section and was contained within a crust of sinter. This crust tended to build up and then collapse, due to melting of the sinter below, so the visual impression over a long period was of a small "puddle" zone continually changing shape on top of the mass of sinter.

2.6. Carry-over

During the evaporation stage of the process, fine dust particles and volatile ruthenium tetroxide are carried over with the gas stream from the process vessel. The removal of these is discussed in another paper [3]. The layout of the piping between the process vessel and the filter vessel must allow for the free flow of the dust-laden gas without deposition of any dust, e.g. due to sudden change of direction. This form of deposition is not due to partial sintering but either impingement or settling.
We have already seen that the feed inlet must not be greater than \( \frac{3}{4} \)-in internal diam. over a 3-in length to maintain full flow conditions. This size of pipe must be on the filter vessel for it to be transferred to the process position each run. A large pipe size must be used for the remainder of the off-gas pipe lines to minimize the overall pressure drop through the equipment. To avoid a change of pipe size on the pipe line which will carry the dust-laden gas a \( \frac{3}{4} \)-in internal diam. section has been made at the outlet from the filter vessel.

A few runs at feed flow-rates of 80 ml/min were carried out to compare two sizes of off-gas pipe:

(a) \( \frac{1}{2} \)-in outer diam. 26 Standard wire gauge -0.464-in internal diam.

(b) \( \frac{3}{8} \)-in outer diam. 16 Standard wire gauge -0.934-in internal diam.

In the smaller pipe, where the Reynolds Number was \( \sim 5000 \), no deposition of dust was observed, but in the large pipe where the flow was almost streamline (Reynolds Number \( \sim 2500 \)) severe deposition of loose dust occurred. To maintain turbulent conditions with a feed flow-rate of 50 ml/min, the 0.464-in internal diam. pipe was found to be satisfactory (Reynolds Number \( \sim 3500 \)).

The total quantity of material carried over with the gases from the process vessel was measured for all the runs. Reducing the feed flow-rate from 80 ml/min to 50 ml/min led to an increase in the carry-over from 1.5±0.6% to 3.4±1.1%.

During the evaporation, all the pipes up to the condenser must be kept hot, not only to prevent condensation, but to prevent boric acid from crystallizing and causing a blockage. In practice, this deposition begins to occur below 200°C, so all the pipe lines are heated to 250°C to ensure freedom from trouble.

2.7 Present operating conditions

Having established satisfactory operating conditions, 12 full-length runs to make 3\( \frac{1}{2} \)-ft depth of glass have been carried out to:

(a) Prove the reliability and reproducibility of operation of the process;
(b) Test various filters under running conditions [3];
(c) Test items of engineering equipment before installation on the active pilot plant;
(d) Test the dual-feed system before installation on the active pilot plant.

Apart from small modifications for the above tests, the run conditions have been as follows:

(a) Feed flow-rate 50 ml/min ± 2 ml/min;
(b) Maximum furnace temperature 1050°C ± 10°C;
(c) Pressure at inlet to process vessel was kept steady at 1 to 2-in Hg below atmospheric. As the pressure drop built up across the filter, the main ejector was adjusted accordingly.

For seven of the twelve runs, filter dust from a previous run together with a mock filter were placed in the process vessel which was put in the
furnace with the top of the vessel 6 in above the furnace, and in one run the procedure of dropping a filter loaded in the previous run was successfully tested.

The furnace was heated to start-up temperatures with the lower two elements at 1050°C, the middle two elements at 700-800°C and the upper two elements at 500°C. (As the run progressed these were increased to 1050°C). One hour before the scheduled start-up the ovens and trace heating were switched on to bring them up to 250°C. A simple vacuum leak-test was applied. (A more rigorous leak test will be required before each active pilot-plant run).

Before the commencement of feed, air was drawn through the equipment from a point before the process vessel to preheat the pipe lines which could not be trace heated. This was followed by water at about 30 ml/min to cool the inlet pipe. Feed was then started and the flow-rate raised to 50 ml/min.

As a run progressed and the working zone moved up the vessel on top of the glass that was formed continuously, the power to the furnace-heating elements was adjusted to raise them in turn to 1050°C and to maintain them at this temperature for the duration of the run. The control of the process was by temperature, the power input being varied as the process demanded. The power requirements for each element were plotted during runs and showed a maximum demand steadily transferred from element to element as the working zone moved upwards. An illustration is given in Fig. 4. Any deviation from this pattern indicated malfunction.

![Fig. 4](image)

Power loading with glass level
The off-gas temperature was controlled by adjusting the cooling air to the top of the process vessel using the first thermocouple on the off-gas line as a guide.

At the end of the run the feed lines were flushed with water then a purge of air was maintained for two hours to remove the last traces of condensible gases and maintain all the pipes above 250°C. The furnace was raised to melt the dust on the lid of the vessel before all the heating was switched off to let the cylinder of glass cool down.

3. 1000-c PILOT PLANT

Figure 5 shows a general view of the pilot plant. The main concrete cell is built in the end of a pit which is 20 ft wide and 12 ft deep. A front and side wall of 3-ft thick concrete give an inner area 13 ft 9 in × 14 ft 3 in with a 3-ft wide access corridor on the right hand side. A 3-ft thick roof gives an internal height of 11 ft 3 in.

The pit area is served by a 50-t overhead crane which was used for the heavy constructional work and will be used for transferring the cylinders.
Three holes in the roof blocks line up with the fixed part of the remote joints and with the two ovens and the furnace inside the cell. A new cylinder with its lid, the disposable part of the remote joint and shielding plug is thoroughly tested and then loaded into one of the transfer coffins. This is moved to the top of the cell, positioned over the required roof hole and the cylinder is lowered from the coffin through the roof until the two parts of the remote joints engage.

Figure 6 and 7 show the details and photographs of the cylinder lid and the remote joint assembly which is located above the furnace.

The fixed part consists of the main support plate with four rollers top and bottom to guide the cylinder into and out of the furnace. Both the inlet
Photographs of cylinder-lid and remote-joint assembly

and outlet remote joints are opened and closed by an operating mechanism consisting of double-acting compressed air cylinders assisted by a spring to keep the joint closed if the compressed air fails.

Although the actual joint (see enlarged detail) is the same in both cases, the layout of the inlet and outlet joints is different.

The feed inlet pipe and water-wash pipe pass through a solid block into the permanent member of the joint. The block slides backwards and forwards in a housing through the main support plate to open and close the joint. The disposable member of the inlet joint is welded to the support ring.

The outlet joint works in reverse. The permanent member which is attached to a straight gas outlet pipe drops into a locating groove in the main support plate. The disposable member is attached to a shaft which transmits the forward movement of the operating mechanism to close the joint. A return spring is required to open the joint.

The complete joint assembly above the first oven is the mirror image of the one above the furnace so that the dust-laden gas passes through a straight pipe between the two positions. This pipe drops into position in the grooves in the main support plates and can be replaced remotely if required. The water-wash pipe is not fitted on the remote joint assemblies over the two ovens.

The disposable part of the remote joint is attached to the cylinder lid by two support rods. The gas outlet pipe finishes flush with the underside of the lid. The feed inlet pipe tapers near the lid and projects \( \frac{1}{4} \) in through
the underside, the lid thickness being reduced locally to \( \frac{1}{16} \) in to minimize conduction of heat to the feed. A short pipe connects a bursting disc carrier to the lid of the cylinder. Graphite discs are used which will burst at 20 lb/in\(^2\). (A view of the underside of the lid is shown in Fig. 5 of Ref.[3]. It must be remembered, however, that the inlet and outlet pipes are reversed between the process and filter positions).

When the furnace is raised at the end of the process cycle to fuse the dust on the underside of the lid, a plate resting on support pins through the support rods acts as a closure to the top aperture of the furnace.

Figure 8 shows a simplified layout of the dual-feed system.

The highly active fission products required to make up the 1000-c batches for each run will be transported in liquid transport coffins of 2.81 capacity. These coffins are put into an off-loading station on the top of the cell (see Fig. 9) and the active liquor is syphoned into a stock tank which is located in a small cell inside the main process cell. This inner feed liquor cell is shielded with 10-in lead sufficient to hold up to 10,000 c of active liquor. 300-ml aliquots of this stock liquor can be transferred by a meter-pot system into the feed tank. Inactive mock fission-product solution can

Fig. 8

Simplified layout of dual-feed system
be separately metered into the feed tank, so both the activity and chemical composition of the feed solution can be varied as required for each glass-making run. A drain tank completes the major equipment in the inner cell. Samplers are located in the access corridor to sample from the feed tank and drain tank. Control of the feed transfer etc. is from a control panel on the roof of the cell (see Fig. 9).

A 'Kontak' diaphragm pump is used to meter the active feed solution to the process, a small damping pot and weighted valve in series ensuring a steady, reproducible flow-rate. A transmitting rotameter in series gives a check on the flow-rate.

The slurry make-up equipment is located on the top of the cell. It consists of a hopper with a vibrating feeder to add the silica and borax to the nitric acid in the make-up tank. This tank has a paddle stirrer and the top is sealed with a perspex lid to prevent evaporation. The slurry is circulated in a closed loop by a 'Vanton' pump and a small by-pass line from the delivery side of this pump is used to give a positive slurry feed to a 'Watson Marlow' flow inducer which can be accurately speed-controlled to give the required flow-rate. A secondary flowmeter is used in series to check the flow-rate.

The fission-product feed is mixed with the slurry feed in a 'Y' piece close to the first remote joint.

The design of furnace is similar to that described earlier [1] and is illustrated in Fig. 10 together with the elevating stand and counter-balance
Fig. 10
Details of furnace and elevating stand
mechanism. Early designs called for a fixed bottom support inside the furnace with expansion bends on the pipes at the top of the vessel. This system has been abandoned in favour of a rigid top support to the cylinder and a counter-balance mechanism which will support the weight of the full cylinder and allow for the linear expansion at the same time.

The stand has a travel of 12 in and its position is indicated outside the concrete cell.

The ovens are 6 ft 1 in long and can be adjusted in height in relation to the remote joint assembly above. They are divided into three separate zones and are controlled at 250°C.

The off-gas pipes between the three positions and up to the condenser are wrapped with electric heating tapes, each zone being controlled.

Sufficiently high decontamination factors have been measured from inactive runs for the condenser and scrubber system to be located outside the main cell in the pit (see Fig.5). A scintillation counter monitors the condensate continuously to detect possible break-through of activity.

The cell itself is continuously ventilated and maintained at \( \frac{1}{2} \)-in water gauge below atmospheric pressure. Inlet air is filtered to remove dust and then drawn out of the cell through one of two absolute filters (at the rear of the roof of the cell) before exhausting to atmosphere above the building. The fan is rated at 1250 ft\(^3\)/min to remove the excess heat from inside the cell.

The main control panel can be seen in the pit area together with a small panel on the front wall of the cell. The complete operation, except for make-up of the feed, is from these panels.

Power supplies are all fed from the main panel and all the thermocouples throughout the entire plant are connected to a variety of recorders and indicators. In case of failure of thermocouples, duplicates are provided and can be connected to the instruments as required. The pressures between the various positions are measured by transducers which continuously transmit to a recorder. All flow-meters, alarms etc. are displayed on the panel.

Actual control of the furnace is manual, but the ovens and trace heating can be either manual or automatic.

4. FUTURE SCALE-UP OF THE PROCESS

The fixation process which has been described is designed to produce glass in stainless-steel cylinders which can be stored for the long periods necessary while the fission products decay. The size of cylinders and storage environment must be optimized so that in early periods, the decay heat can be removed and the maximum temperature of the glass controlled.

The heat generated will be transferred by conduction through the glass to the steel cylinder. The maximum temperature along the axis of the cylinder will depend upon the diameter of the cylinder, the quantity and activity of the fission products, the conductivity of the glass and the method of removal of the heat from the outside of the cylinder. The heat can be removed by a number of methods:

(a) By conduction, e.g. burial of the cylinders. In this case severe limitations will be imposed by the low rates of heat transfer in such a system.
(b) By water cooling. This would be the most efficient method of re­
moving the heat and keeping the temperature as low as possible.
However, it would only be required for the first few years of stor­
age and corrosion of the heat-treated cylinders would have to be
considered.
(c) By air cooling. This offers the safest and most reliable method
of removing the heat. The geometry of the storage system would
have to be optimized to obtain the maximum cooling capacity whilst
maintaining the glass at the required temperature.

The temperature difference through the glass, i.e. from the axis to
steel cylinder, is very sensitive to the percentage of waste oxides incor­
porated in the glass and to the cylinder diameter for cooling periods of less
than two years. Changes of reactor-fuel rating have a much smaller effect.
However, short-term storage of the waste solutions in tanks for up to 5 yr
before incorporation in glass will enable cylinders up to 12-in diam. to be
considered in the future.

The number of cylinders required to deal with the annual arising of
fission-product waste is simply related to cylinder diameter, length and
the percentage of waste oxides incorporated in the glass.

To obtain the required control of the off-gas temperature during the evapor­
ation stage of the process, a depth of about 18 in must be left at the top of
each cylinder. However, there is no process limitation on the length of
cylinder chosen and there are obvious advantages in using cylinders as long
as possible provided they can be handled. Both the number of cylinders and
the disposable remote joints would be reduced.

Future scale-up of the process to meet the increasing output of the
expanding United Kingdom Power Programme will require the installation
of a number of fixation units, the actual number depending upon the effects
of the large number of variables involved. For a given waste-solution flow­
rate and concentration factor, variation of the cylinder size and percentage
of waste oxides does not have a great effect on the number of fixation units
required. However, the biggest unknown factor in the scale-up of the pro­
cess is the flow-rate which can be obtained in larger diameter cylinders
whilst maintaining stable and reproducible operating conditions.

At low waste solution flow-rates the concentration factor of the solution
has a big effect on the number of fixation units. The process, in its present
form, is not an efficient evaporator, so

(a) The waste solutions must be concentrated as far as possible by
conventional means; and

(b) The addition of liquid with the glass-forming constituents (e.g. to
make a slurry) is wasteful.

New techniques of metering may be developed to overcome these limit­
ations.

With the present operating cycle, 60-65% of the time is taken up feeding
to the vessel and the remainder is required for heating and cooling, moving
the cylinders between each cycle, etc. A large potential gain is possible
if this percentage can be increased. If higher throughputs are possible in the
future and the time required to fill a cylinder with glass is correspondingly
reduced, it will become very important to reduce the time required for the remainder of each cycle.

Methods such as these discussed above should enable an increase in the throughput of the process sufficient to meet our future demands without altering the basic principle of the process.

5. CONCLUSIONS

A process for the incorporation of fission product wastes into glass has been developed and satisfactorily tested inactively. A pilot plant has been constructed to carry out the operations with up to 1000 c of fission products per cylinder of glass. Further development of techniques for obtaining high decontamination factors will be possible, along with the engineering equipment required for a full production plant.

Further scale-up of the process is desirable in the future but it could form the basis for a production plant to handle the fission product arisings in the United Kingdom.

ACKNOWLEDGEMENTS

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REFERENCES


DISCUSSION

E. GLUECKAUF: I would like to add a few comments on how the technique of using glass blocks, described by Mr. Grover, would operate in large-scale practice.

In the case of a fuel with a burn-up of 3000 MWD/t and a rating of 4 MW/t, the waste oxide will develop, after one year, about 140 W/kg of heat. Each glass block, measuring 6 in in diam. and 3 ½ ft in length, will contain 20 kg of waste oxide and therefore release 900 000 c or 2.8 kW after one year.
Various possibilities of storage and disposal have been considered and it appears that the safest and most economical one is storage in underground tunnels located in an escarpment with good drainage. The cylinder blocks would be cooled by air, the necessary circulation being affected by the natural draft of the heated air up a shaft from the panels to the surface of the escarpment. The British arisings up to 1985 could be put into a single storage block of this kind, involving a storage area of less than 1000 m². The planned arrangement of the tunnels is that shown in the Figure and it would accommodate the 10 000 - 13 000 glass blocks accumulating up to 1980-85. Even after 50 yr, such a storage system would produce about 1 MW of heat. The necessary power for the automatic air circulation is therefore assured for centuries.

Moreover, the heat developed makes it effectively impossible for any water to get near the glass blocks with their stainless-steel cladding, so that the question of leaching does not arise for the first few centuries. However, as all this waste up to 1985 could also be kept as solution in a space about one-fifth of the size of this room, it is quite clear that storage as glass is less economical than storage in solution. But solid storage is no doubt safer, since it requires no servicing, and the paper we are discussing is an indication that we in the UKAEA are rapidly pressing ahead in this direction.

Fig.

Arrangement of tunnels for 30 000 tonnes uranium capacity, with entrance tunnel.

R. BONNIAUD: Could Mr. Grover indicate the rate at which the pot is filled after vitrification?

J. R. GROVER (on behalf of M. N. ELLIOTT et al.): The active waste liquor and glass-making constituents are fed continuously to the process vessel until it is about three-quarters filled with glass.

R. BONNIAUD: Wouldn't there be, at the upper part of the pot, a calcine dust from scattering which would not be vitrified because the temperature in that part of the pot is too low?

J. R. GROVER: At the end of the filling cycle, the feed is stopped, the feed pipe washed with water (to bring the remaining active feed into the pot) and the furnace raised round the lid of the vessel to convert the oxide dust
on the underside of the lid of the vessel to glass. This is to minimize the possible leaching of activity in storage. The vessel is then cooled and removed to storage. After transfer of the vessels as described in the paper, a new filling cycle commences in the vessel containing the spent filter from the previous cycle.

J. A. McBRIEDE: Do you plan to seal the pots and, if so, how?

J. R. GROVER: A number of factors must be considered before we decide whether we should seal the vessels with glass in storage. While a seal would prevent access of water to the glass, the chance of water entering the area is small. At present we do not know whether there will be sufficient gas evolution in storage to warrant pressurization of the vessel. It would not be a difficult remote operation to cut off the remote joint assembly from the lid of the vessel so that any gas evolved could escape. Access of water, however, would be very difficult.
FIXATION OF RADIOACTIVE WASTE IN GLASS. PART III. THE REMOVAL OF RUTHENIUM AND DUST FROM NITRIC-ACID VAPOURS

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Abstract — Résumé — Аннотация — Resumen

FIXATION OF RADIOACTIVE WASTE IN GLASS. PART III. THE REMOVAL OF RUTHENIUM AND DUST FROM NITRIC-ACID VAPOURS. The off-gas from the glass-fixation process contains volatile and particulate radioactive materials. To avoid a secondary effluent problem these are trapped on a filter/absorber and prevented from passing into the nitric-acid condensate. The filter/absorber with its radioactive burden is incorporated in glass as it is formed in the next cycle of operation in the process vessel.

The major volatile constituent is ruthenium as the tetroxide, and its formation has been studied over a range of operating temperatures and feed flow-rates. Various materials suitable for the removal of ruthenium tetroxide from the off-gas have been examined and the effects of the operating variables on the decontamination factor have been tested for the more promising materials.

The volatility of caesium, molybdenum and boron during the process has also been studied.

Methods and equipment for the removal of dust particles from gases have been surveyed. Tests have been carried out on a range of filter materials, for use as pre-filters and high efficiency absolute filters. The design of a compact, disposable, filter/absorber unit which can be incorporated into the cylinders of glass is described, together with the results of some full-scale tests.

FIXATION DES DÉCHETS RADIOACTIFS DANS LE VERRE, TROISIÈME PARTIE: EXTRACTION DU RUTHÉNIUM ET DES POUSSIÈRES PRÉSENTES DANS LES VAPEURS D’ACIDE NITRIQUE. Les gaz s’échappant au cours du processus de fixation de déchets radioactifs dans le verre contiennent des matières radioactives volatiles et sous forme de particules. Pour éviter le traitement secondaire des effluents, ces matières sont piégées dans un filtre absorbant de sorte qu’elles ne peuvent passer dans le condensat d’acide nitrique. Le filtre absorbant ainsi que sa charge radioactive sont incorporés dans le verre au fur et à mesure de sa formation au stade de fabrication suivant dans la cuve de traitement.

Le ruthénium se présentant sous la forme de tétroxyde est l’élément volatile principal; sa formation a été étudiée pour une vaste gamme de températures de fonctionnement et de débit d’alimentation. Les auteurs ont examiné diverses matières convenant à l’extraction du tétroxyde présent dans les gaz d’échappement; ils ont étudié l’influence des variables de fonctionnement sur les facteurs de contamination pour les matériaux présentant le plus d’intérêt.

La volatilité du césium, du molybdène et du bore au cours de ce processus a également été étudiée.

Les auteurs ont aussi examiné les méthodes et le matériel d’extraction des particules de poussières présentes dans les gaz. Des essais ont été faits pour un certain nombre de matières filtrantes pouvant être employées comme pré-filtres et comme filtres absorbants de haute efficacité. Les auteurs décrivent un filtre absorbant compact et maniable qui peut être incorporé aux cylindres de verre, ainsi que les résultats de quelques essais à grande échelle.

ФИКСАЦИЯ РАДИОАКТИВНЫХ ОТХОДОВ В СТЕКЛЕ. ЧАСТЬ III. ИЗЛУЧЕНИЕ РУТЯ И УДАЛЕНИЕ ПЫЛИ ИЗ ПАРОВ АЗОТНОЙ КИСЛОТЫ. Газ, образующийся в процессе осаждения радиоактивных отходов, содержит летучие радиоактивные материалы и их частицы. Чтобы избежать вторичных жидких отходов, эти вещества улавливаются фильтр-поглотителем, и таким образом предотвращается их попадание в конденсат азотной кислоты. Фильтр-поглотитель вместе с поглощёнными радиоактивными частицами осаждается в следующем цикле операций в специальном сосуде, служащем для такой обработки.

Главной составной частью летучих веществ является рутевый в виде четверехокиси; образование его было изучено в широком диапазоне рабочих температур и скоростей подачи обрабатываемого материала. Были изучены разнообразные материалы, пригодные для удаления четверехокиси рутения из

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выходящих газов; для более перспективных материалов было испытано влияние изменений эксплуатационных условий на степень дезактивации.

Была изучена также летучесть цезия, молибдена и бора в условиях переработки.

Дается обзор методов и оборудования, применяемых для удаления из газов частиц пыли. Были проведены испытания на целом ряде фильтровальных материалов для использования последних в качестве предварительных фильтров и абсолютных фильтров высокой эффективности. Описывается конструкция компактного фильтровально-поглощающего устройства, которое может быть превращено в стеклянное цилиндрическое бочка; приводятся также результаты испытаний в технологических масштабах.

FIJACIÓN DE DESECHOS RADIACTIVOS EN VIDRIO. PARTE III: ELIMINACIÓN DEL RUTENIO Y DEL POLVO DE LOS VAPORES DE ÁCIDO NÍTRICO. El gas que se desprende en el proceso de fijación en vidrio contiene sustancias radiactivas volátiles y en forma de partículas. Para no tener que tratar un efluente secundario, esas sustancias se retienen en un sistema filtro/absorbedor, impidiéndose así que pasen al condensado de ácido nítrico. El filtro/absorbedor, con su carga radiactiva, se incorpora al vidrio a medida que éste se forma durante el ciclo de trabajo siguiente en el recipiente de tratamiento.

El principal componente volátil es el rutenio, en forma de tetraóxido, y los autores estudiaron su formación a diversas temperaturas de trabajo y caudales de alimentación. Examinaron la posibilidad de utilizar una serie de materiales que se prestan para eliminar el tetraóxido de rutenio del gas que se desprende y probaron los efectos de condiciones de trabajo variables sobre el factor de descontaminación, para aquellos materiales que parecían ofrecer las mayores posibilidades.

También estudiaron la volatilidad del cesio, del molibdeno y del boro en el curso de la operación. Examinaron asimismo los métodos y los equipos para aliminar las partículas de polvo de los gases. Efectuaron ensayos con una serie de materiales filtrantes, destinados a servir como elementos prefiltrantes y como filtros absolutos de elevado rendimiento. En la memoria describen por último el diseño de un dispositivo filtro/absorbedor compacto, que puede descartarse una vez usado, incorporándose a los cilindros de vidrio, y exponen los resultados de algunos ensayos realizados en escala industrial.

1. INTRODUCTION

The glass-fixation process has been described in my previous paper [16], and it was shown that an appreciable amount (between 1 and 5%) of the total solids fed to the cylinder was carried off in the process gases (oxygen, water vapour, oxides of nitrogen). In addition, certain of the fission products, notably ruthenium and caesium, are known to have appreciable volatilities at temperatures similar to those used in the Harwell process [1, 2, 3].

The object of the glass-fixation process is the conversion of a highly radioactive liquid into a stable, leach-resistant solid, if possible without the production of a secondary radioactive liquid effluent. The concept differs from that of other workers where the emphasis has been placed on a high calcination rate with a recycle of radioactive effluent. The production of a substantially inactive effluent implies a highly efficient gas cleaning system, and an overall decontamination factor (DF) of $10^8$ was set as the design target. This DF is defined as the ratio: 

\[
\frac{\text{activity in the feed}}{\text{activity in the condensate}}
\]

A further requirement of the gas cleaning system was that it should be disposable with the final glass block.

The problems which required study fell into two categories:

(a) The behaviour and removal of volatiles, and

(b) The behaviour and removal of particulate material.

2. THE BEHAVIOUR OF VOLATILE CONSTITUENTS

Studies of the behaviour of volatile constituents of the waste were made using tracers, on a small rig, shown diagrammatically in Fig. 1. Evapor-
REMOVAL OF RUTHENIUM AND DUST FROM NITRIC-ACID VAPOURS

![Flow diagram of small-scale fixation rig](image)

ation, denitration and glass-making were carried out in a stainless-steel cylinder 20 in long by $4\frac{1}{2}$ in internal diam. The top was flanged and a lid carrying connections for feed inlet and off-gas outlet was fitted. The off-gas was passed through heated lines to a filter, then to a condenser and a scrubber. The condensate was passed through a counting cell, so that a continuous measure of the specific activity present was obtained.

After each run the equipment was decontaminated and the liquids counted to obtain a measure of the total activity which had left the vessel. The results were expressed as a series of decontamination factors defined as:

\[
\text{pot DF} = \frac{\text{activity fed to the vessel}}{\text{activity leaving the vessel}}
\]

\[
\text{filter DF} = \frac{\text{activity leaving the vessel}}{\text{activity passing through the filter}}
\]

\[
\text{overall DF} = \text{pot DF} \times \text{filter DF}
\]

\[
= \frac{\text{activity fed to the vessel}}{\text{activity present in the condensate}}
\]

The condensate monitoring system, therefore, gave a continuous measure of the overall decontamination factor.

2.1 Ruthenium volatilization

The ruthenium species present in fuel-element dissolver solutions have been shown by FLETCHER et al. [4] to consist of nitro and nitrato complexes of nitrosylruthenium, together with uncomplexed compounds. The equilibrium of the complexes can be expressed as:

\[
\text{Ru(NO)} \text{ nitrato complexes} \xrightleftharpoons{\text{HNO}_2} \text{Ru(NO) nitro complexes}
\]
The nitro complexes are considerably more stable than the nitrato complexes.

The evaporation of dissolver solutions has been shown to be accompanied by a loss of ruthenium, probably by oxidation to the volatile compound RuO₄ [5]. An increase in nitric-acid normality and a long distillation time both gave enhanced volatilization rates whilst the presence of reducing agents suppressed the volatilization. This suggested that if the processes of evaporation and denitration could be carried out rapidly, loss of ruthenium from the fixation process would be reduced. There was some evidence [6, 7] of an increased volatility of ruthenium at temperatures above 1000°C, and denitration was not complete at temperatures below 800°C. It was, therefore, decided to operate the process as an evaporation and denitration at 800°C, followed by melting of the sinter (see Ref. [16]). It was thought that little volatilization would then occur during the melting stage.

In order to examine the effect of evaporation rate on ruthenium volatility, a series of runs were carried out at 800°C in which the feed flow-rate was varied. The feed consisted of a simulated waste solution to which tracer and carrier ruthenium were added. The tracer, Ru¹⁰⁶, was added as the nitrosyl nitrate. Inactive ruthenium trichloride was converted to nitrosylruthenium hydroxide (Ru(NO)(OH)₃), using the method described by FLETCHER et al. [8], and stored under acetone. This was then refluxed in nitric acid with tracer as required. The nitrato complex was used for the experiments since this was thought to be the species most susceptible to oxidation.

Ruthenium tended to plate on stainless-steel pipework, and it was found that the pipework and filter had an appreciable capacity for the removal of ruthenium. Once this had been exceeded, however, the specific activity reaching the condensate increased rapidly until it reached a steady value. This latter value was used in calculating the decontamination factor at a given condition.

Figure 2 shows the variation of DFRu with flow-rate for the series of runs at 800°C. These were repeated at 1050°C using a glass melting at 1020°C (mix 293, see Ref. [16]), and the results are shown in Fig. 3. Both curves show a trend of decreasing DFRu as the flow-rate is increased and in addition the DFRu is decreased at a given flow-rate as the temperature is increased.

The liquid hold-up occurring in the system is described in Ref. [16] and the variation of hold-up with flow-rate for runs at 1050°C is shown in Fig. 3. This shows how the hold-up increases as the flow-rate is increased. Heat transfer in the system occurs largely by conduction through sinter containing evaporating liquid, and at a given flow-rate the hold-up of liquid will increase by percolating through the sinter until the area contacted is such that the rate of evaporation becomes equal to the flow-rate. Thus, at higher flow-rates the residence time of liquid within the system is increased, with a corresponding increase in the formation of RuO₄.

The results at 800°C show a large scatter. These runs were taken to the stage at which sintered material was building up in the process vessel, and it was extremely difficult to obtain exactly reproducible conditions of heat input. This resulted in a variation in the hold-up of liquid between runs carried out at the same flow-rate, and the anomalously low DFRu values pre-
Fig. 2
Variation of decontamination factor with flow-rate at 800°C.

Fig. 3
Variation of decontamination factor and hold-up with flow-rate at 1050°C.
sumably correspond to large volumes of liquid hold-up. At the extremes of flow-rate, it became easier to obtain reproducible results.

Figures 2 and 3 show a marked difference between the volatility of ruthenium at 800°C and at 1050°C. Runs at 800°C were taken to the sinter stage only, whereas runs at 1050°C included the melting stage. WELCH et al. [9] have shown that evaporation followed by fusion with sodium nitrate of a solution containing fission product ruthenium produced the ruthenate which was readily oxidized to RuO_4. A reaction of this nature occurring during the glass-making stage may be the reason for the enhanced volatility. Alternatively, it may be a function of the increased temperature, and a reaction:

\[ \text{RuO}_2 + O_2 \rightarrow \text{RuO}_4 \]  

or \[ 2\text{RuO}_2 \rightarrow \text{RuO}_4 + \text{Ru} \]  

may be occurring. The ruthenium not initially converted to the volatile species would then form the dioxide which could undergo air oxidation or disproportionation. SCHRÄFER et al. [6] have shown that reaction (1) occurs in oxygen at temperatures above 800°C, and MELLOR [7] refers to the decomposition of RuO_2, reaction (2), at temperatures above 1000°C.

When the experiments were started it was hoped that operating conditions could be chosen which corresponded to minimum ruthenium volatilization. Other considerations, (see Ref. [16]) ultimately dictated the choice, however. A volatilization of approximately 30% of the ruthenium fed to the process vessel would be anticipated under present operating conditions.

2.2 Caesium volatilization

The volatility of caesium was measured for the operating conditions described in Ref. [16] when a glass melting at 1110°C (Mix 279) was used. An overall decontamination factor of \( > 10^3 \) was then measured [10].

The measurement was repeated under the modified operating conditions using a glass melting at 1020°C (Mix 293). A feed containing Cs\(^{137}\) tracer was metered into a vessel heated to 1050°C, and a decontamination factor from feed to condensate of \( > 5 \times 10^5 \) was measured.

The caesium decontamination factors measured in these runs correspond closely to those of non volatile constituents (iron, uranium) and suggest that the caesium was carried from the vessel in particulate form with the other oxides. The volatilization of \( \sim 2\% \) of the caesium during the melting stage of the nepheline syenite process reported by BANCROFT et al. [1] is no doubt a function of the higher operating temperature (1350°C).

2.3 Molybdenum volatilization

Molybdenum trioxide has a relatively high vapour pressure (0.76 mm Hg at 782°C) which is increased by the presence of water vapour [11]. Molybdenum is a major constituent of a high burn-up waste, and although radioactive decay will be complete before incorporation into glass, volatilization followed by deposition in cooler off-gas lines could form a blockage.

A run at 1050°C using a feed containing Mo\(^{99}\) and carrier showed that loss of molybdenum would not constitute a problem. A decontamination factor from feed to condensate of \( > 5 \times 10^3 \) was measured.
TABLE I
MEAN BORON DECONTAMINATION FACTORS (FEED TO CONDENSATE)

<table>
<thead>
<tr>
<th>Run conditions</th>
<th>Mean Boron DF</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C, sinter formation only</td>
<td>9.5 ± 4.5</td>
</tr>
<tr>
<td>small rig</td>
<td></td>
</tr>
<tr>
<td>950°C, sinter formation only</td>
<td>8.8 ± 2.7</td>
</tr>
<tr>
<td>small rig</td>
<td></td>
</tr>
<tr>
<td>1050°C, glass formation</td>
<td>38 ± 5.7</td>
</tr>
<tr>
<td>small rig</td>
<td></td>
</tr>
<tr>
<td>1050°C, glass formation</td>
<td>46 ± 10.4</td>
</tr>
<tr>
<td>large rig</td>
<td></td>
</tr>
</tbody>
</table>

2.4. Boron volatilization

During runs producing sinter or glass, appreciable quantities of boron have been carried from the process vessel into the condensate, probably by steam distillation of boric acid. The percentage volatilized appears to be independent of flow-rate and temperature, but is markedly reduced under glass-making conditions. Table I shows mean boron decontamination factors from feed to condensate obtained from runs on the large and small-scale equipment.

The presence of boric acid in the process gas does not constitute a problem unless the temperature is allowed to fall to ~ 170°C. At or below this temperature a crystalline deposit of boric acid is formed on the cool surface, which could lead to a pipe blockage.

3. RUTHERNIOIUS ADSORPTION

Approximately 30% of the ruthenium present in the feed is expected to be carried from the process vessel. This must be removed from the gas stream to prevent contamination of the condensate and adsorption on a solid. The problem had been studied elsewhere, and ferric oxide supported on firebrick had been selected at Chalk River [1], where large quantities of gas were to be handled, and silica gel at the ICPP [12] where the bed was regenerated with hot water. For the Harwell process an adsorbent was required which could be accommodated within a filter vessel, and ideally be disposable with the final glass block. Because of the limited space available a high capacity and removal efficiency was required.

To test possible materials, ruthenium tetroxide was generated by metering a nitric acid solution of Ru$^{106}$ and carrier, both as the nitrosyl nitrate, into a stainless-steel vessel heated to 600°C. The off-gas (water vapour, oxides of nitrogen, oxygen and ruthenium tetroxide) was passed downwards through a heated glass column containing the adsorbent and then to a condenser and caustic scrubber system. The condensate was passed through
a counting cell to obtain a continuous record of the activity passing through the column. The gas was diverted at intervals during a run and absorbed in sodium hydroxide solution. The solution was counted and the rate of flow of ruthenium determined. The gas flow-rate through the column was calculated from the liquid flow-rate. The rig was decontaminated after each run and the ruthenium balance and decontamination factor calculated. The decontamination factor was based on the quantity of ruthenium passing to the column and that reaching the condensate.

A 16N nitric-acid feed was used for the preliminary tests, since it was suggested by WILSON [5] that high acid strength favoured the formation of ruthenium tetroxide. Other details and the results of the tests, are shown in Table II.

**Table II**

**SELECTION OF A SUITABLE ADSORBENT**

<table>
<thead>
<tr>
<th>Material</th>
<th>Run Duration (hr)</th>
<th>Overall DF</th>
<th>Capacity (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric oxide</td>
<td>29</td>
<td>1.21 x 10²</td>
<td>&gt;2 x 10⁻²</td>
</tr>
<tr>
<td>Kaolin</td>
<td>26</td>
<td>160</td>
<td>&gt;2 x 10⁻²</td>
</tr>
<tr>
<td>Silica gel</td>
<td>30</td>
<td>72</td>
<td>&gt;2 x 10⁻²</td>
</tr>
<tr>
<td>Fuller earth</td>
<td>5</td>
<td>72</td>
<td>&gt;3 x 10⁻³</td>
</tr>
<tr>
<td>Molecular sieve</td>
<td>4</td>
<td>5</td>
<td>&gt;2 x 10⁻³</td>
</tr>
<tr>
<td>&quot;Stillite&quot;</td>
<td>1.5</td>
<td>1</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

The capacity is based on the total volume of the bed.

**CONDITIONS**

- Adsorber size: -18 +25 mesh
- Bed depth: 5 cm
- Superficial gas velocity: 0.3 ft/sec
- Bed temperature: 150°C
- Feed solution: Ru(NO)(NO₃)₂ in 16N HNO₃

From these tests, ferric oxide was selected as the most suitable material. It was prepared in granular form from calcined ferric oxide using a hydrolysable organic silicate. The method was similar to that developed by GROVER [13] and was as follows: A mixture containing 400 ml of ethyl orthosilicate, 100 ml ethyl alcohol, 60 ml water and 4 ml concentrated hydrochloric acid was prepared. The organic silicate hydrolysed and when this was complete a kilogram of ferric oxide was added to the mixture. Water was added to produce a smooth paste which was dried at 200°C for 24 hr. The solid was then fired at 350°C for one hour to produce a granular material which was crushed and sieved.
The variation of decontamination factor and capacity with operating conditions was studied. Variables studied were: bed temperature, gas velocity, off-gas composition and bed depth.

No effect of temperature was noted between runs at a bed temperature of 150°C and runs at 250°C.

Figure 4 shows the variation of decontamination factor with superficial gas velocity (based on the empty column cross-section). A 5-cm depth of -18+25 mesh material was used and the bed temperature was 150°C. At low velocities break-through of the bed had not occurred after 65 hr of operation and capacities are, therefore, expressed as 'greater than' values. A capacity of $4 \times 10^{-2}$ g Ru/cm$^3$ of bed was obtained at a superficial gas velocity of 0.3 ft/sec. At a velocity of 0.6 ft/sec, break-through occurred at a loading of $6.5 \times 10^{-3}$ g Ru/cm$^3$, and at higher velocities (between 0.8 and 1.7 ft/sec), the effluent activity rose to a value near to that of the feed within minutes of starting a run.

**Fig. 4**

Variation of decontamination factor with gas velocity for ferric oxide.
Similar values of decontamination factor were obtained when runs were repeated using a 2-cm bed depth. At low gas velocities the break-point was again not-reached. The loading at which breakthrough occurred was reduced by a factor of 3 to 4 at a velocity of 0.6 ft/sec.

The composition of the gas produced by a 16N acid feed differed considerably from that of the process gas. Table III shows calculated gas compositions for feeds of 16N and 5N nitric acid and for a full fission-product feed. This shows that a 5N acid feed produces a gas of very similar composition to that produced by the full feed. No variation in behaviour of the adsorber was noted when 16N and 5N acid feeds were used.

**TABLE III**

**GAS COMPOSITIONS**

<table>
<thead>
<tr>
<th>Feed solution</th>
<th>Gas composition (% vol./vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td>16N HNO₃</td>
<td>60.8</td>
</tr>
<tr>
<td>5N HNO₃</td>
<td>88.9</td>
</tr>
<tr>
<td>Full fission-product</td>
<td>90</td>
</tr>
</tbody>
</table>

* This assumes no dissociation of NO₂=NO + ½O₂

The ruthenium was deposited on the adsorber as a black solid which was identified by X-ray examination as ruthenium dioxide. At low gas velocities deposition occurred on the upper surface of the bed, forming a layer of solid which increased in depth as a run proceeded. As the velocity increased, deposition occurred to a greater extent within the bed. At the beginning of a run, a surge of activity passed through the bed, the decontamination factor then improving as RuO₂ was deposited.

It appears that the presence of RuO₂ improves the efficiency of a bed for the removal of RuO₄ from the gas stream, probably acting as a catalyst for decomposition of the tetroxide.

4. DUST REMOVAL

The dust carried from the process vessel is a mixture of approximately spherical particles and crystalline material. Some of the spherical particles have the hollow form associated with spray-dried material, while others have a refractive index similar to that of the final glass. Ferric oxide, sodium nitrate and boric acid have been identified in the dust.

Early ideas on dust removal were that a cyclone could be used to remove the bulk of the dust, followed by a high efficiency filter. Cyclones were tested, but a low efficiency was obtained and it proved difficult to incorporate a cyclone into the design concept of disposable vessels. It appeared that an advantage might be gained by allowing the coarse material to form a cake on the filter, rather than allow the fines alone to pass to the filter and possibly produce clogging. As a result, work was concentrated on the develop-
ment of a filter of high efficiency with an acceptable pressure drop at high dust loadings.

The removal of particles from gas streams occurs essentially by impingement on to the fibres of the filter medium for all but the finest particles; for these diffusion towards the fibres becomes controlling at low gas velocities. For the maximum efficiency, fine fibres are required and the filter must not be allowed to become partially choked otherwise local velocities through the filter are increased and particles may be re-entrained from the fibres [14].

A cylindrical filter element was required which could fit into a process vessel. Since it would operate at a temperature of about 250°C, a glass-fibre paper was selected as the main filter medium. A commercially available filter of this type was tested, but although decontamination factors \( \sim 10^6 \) across the filter were measured using a Pr\(^{142}\) tracer in a liquid feed, the pressure drop increased rapidly during runs and often limited run length. Glass fibre papers were available of the required efficiency, provided the design gas velocity was used, but there was a need for the development of a pre-filter which would prevent clogging of the paper.

Three classes of pre-filter material were tested: glass fabrics, "Stillite" (a mineral wool material used for insulation) and glass-fibre mat. Cylindrical filters were made incorporating these materials and air laden with a silica test dust passed at the correct velocity to the filters. The pressure drop was measured as a function of the weight of dust passed to the filter. The pressure drop across a filter containing a woven glass cloth pre-filter varied from 12 to 14 in of Hg when loaded with dust, the pressure drop varying with the cloth used. These pressure drops were the highest obtained, and probably resulted from penetration of dust to the paper, causing clogging. Pressure drops ranging from 7 to 11 in of Hg were obtained with a glass-fibre mat. The pressure drop decreased as the rigidity of the glass fibre was increased. Thus the pressure drop of 11 in of Hg corresponded to an unbonded material, whilst that of 7 in of Hg corresponded to a rigid glass-fibre material similar to that used for thermal insulation. The less rigid material tended to compress as the dust loading and pressure drop increased, giving a rapid increase in pressure drop. Pressure drops of 5 to 9 in of Hg were measured with "Stillite".

Since a "Stillite" pre-filter proved more bulky than the others, and a material capable of incorporation into the final glass block was required, the glass-fibre pre-filter has been selected.

5. DESIGN OF A FILTER AND ADSORBER

5.1 Filter design and testing

The pressure drop measured during tests with silica dust was found to be much higher (by a factor of 2 to 3) than that obtained during runs on the full-scale rig. Thus although the tests described in section 4 enabled comparisons to be made, absolute values of pressure drop were not relevant to the practical case. A series of filters were, therefore, prepared and tested during full-length runs. A sodium flame test was applied before and
after each run to measure the penetration and overall decontamination factors from feed to condensate were calculated. The pressure drop was measured throughout a run.

Each filter was attached to the underside of a process vessel lid. The inside diameter of the vessel was ~6 in, and since a dust cake of approximately ½ in depth was formed, the outer diameter of the filter was limited to 4 in to provide sufficient clearance. The diameter of the filter frame was then 3½ in and the thickness of filter material ¼ in. Since the filter would ultimately be destroyed it was made as short as possible, the length of filtration surface being 9 in. The face velocity at the filter paper was then 8 ft/min, corresponding to the operating conditions of 50 ml/min flow-rate and a pressure of 20-in Hg absolute (the paper was rated at a penetration of 0.001% at 11.5 ft/min).

The ruthenium adsorber was packed into the interior of the filter canister, so that it too was disposable. In order to obtain the minimum gas velocity, the bed was made an annulus.

The construction of the filter is shown in Fig. 5. The filter medium is supported by a mild steel cylinder 3½-in outer diam. which is perforated over the filtration area. A ½-in outer diam. gauze cylinder is supported from a top plate and forms the gas outlet. Adsorber is packed into the annulus formed by the two cylinders and a bottom cap is then welded into position. Filter paper is tightly wound on to the outer cylinder and sealed with an inorganic cement. The glass fibre is then wound on and an open-mesh wire cage fitted which compresses the pre-filter to a predetermined value. The filter medium is pinched against sealing ridges provided at the ends of the filter.

The filter is attached to a skirt provided on the underside of the vessel lid. A zinc welding technique developed by WALL and WHITE [15] is used. The zinc weld melts when heated to 420°C allowing the filter assembly to fall into the vessel after use.

Filters constructed in this way were tested during full-length runs as described above. A variety of glass-fibre pre-filters were used, and the results are summarized in Table IV. The penetration test was used to detect faults in manufacture of the filters, but since it was not possible to test at the correct face velocity, this does not represent the efficiency during operation. This is measured by the DF across the filter, uranium being readily determined analytically. To obtain the overall DF from feed to condensate the above value must be multiplied by the DF corresponding to the percentage of solid carried from the vessel (1 to 5% DF 100 to 20).

The pressure-drop values measured with glass-fibre pre-filters were acceptable, but the low-efficiency paper proved less suitable. It is likely that penetration of dust to the backing filter occurred in this case.

5.2 Adsorber design

It was shown in section 3 that ruthenium decontamination factors increased at low gas velocities, and that at the low velocities adsorption occurred largely at the surface of the bed. For the annular bed described above, superficial gas velocities based on the outer and inner diameters are 0.13
Fig. 5

Filter assembly.
## TABLE IV

### FILTER TEST RESULTS

<table>
<thead>
<tr>
<th>Pre-filter material</th>
<th>Fibre size $(\mu)$</th>
<th>Density $(\text{lb/ft}^3)$</th>
<th>Sodium flame penetration $\text{DF (Uranium)}^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Uncompressed</td>
<td>Compressed</td>
</tr>
<tr>
<td>Superfine, unbonded glass Fibre mat</td>
<td>2.5 - 3.8</td>
<td>0.5</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>2.5 - 3.8</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Bonded glass-fibre mat</td>
<td>6 - 7</td>
<td>1.0</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>6 - 7</td>
<td>1.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Low-efficiency (10%) glass-fibre paper</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* In all cases the pressure drop across the clean filter was 0.5 - 1.0-in Hg

** All filters contained a high-efficiency glass-fibre paper
and 0.88 ft/sec respectively at a feed flow-rate of 50 ml/min. The mean velocity of 0.5 ft/sec corresponds to a residence time of 0.33 sec. If the adsorption occurs largely at the outer surface of the bed, then a DF of $10^3$ to $10^4$ would be expected, but since the velocity gradient across the bed is large, it was difficult to predict behaviour of the annular bed from results obtained from columns.

Annular beds were tested using a feed similar to that used for ruthenium volatility experiments. The off-gas from the process vessel was passed through a filter to the annular bed, then to the condenser and scrubber system described in section 2. The ratio of the superficial gas velocities was as on the full-scale filter, although it was not possible to obtain the same residence time.

Results of the tests are shown in Table V. The residence time is based on the mean of the inner and outer velocities. The results have been plotted on Fig. 4 as a function of residence time. The values of $\text{DF}_\text{Ru}$ obtained with annular beds are larger than corresponding values obtained from column experiments, but are less than would be expected if the outer velocity were the important parameter. No bed was taken to the break point, so that absolute values of capacity were not obtained. The loading obtained during run 89 is greater than anticipated for a full-scale run using a low burn-up waste ($2 \times 10^{-3}$ g Ru/cm$^3$ of bed).

From the scale tests, a $\text{DF}_\text{Ru}$ across the adsorber $\sim 5 \times 10^2$ is anticipated, which combined with a $\text{DF}_\text{Ru}$ across the process vessel of $\sim 3$ will yield an overall $\text{DF}_\text{Ru}$ of $\sim 10^3$.

5.3 Disposal of filter/adsorber

The disposal of the spent filter unit has been tested during a full-length run. During the preliminary heating stage the zinc weld melted at a temperature of 420°C and the filter fell to the bottom of the process vessel. A normal start-up procedure as described in Ref. [16] was then followed. After the run the bottom 12-in length of the vessel which had contained the filter was cut into 3-in sections and the glass examined. The filter medium and the adsorber had been incorporated into the glass, together with the mild steel filter frame except for the sealing cap at the base. This was, in fact, in contact with the bottom of the vessel. Figures 6 and 7 show the upper and lower faces respectively of the section taken from the base of the vessel. It can be seen that nothing remains of the filter at a height of 3 in from the base (Fig. 6), and the sealing cap can be seen in Fig. 7.

Glass incorporating the filter has been leached, and the results are discussed in Ref. [17].

5.4. Secondary filter/absorber

Limitations of geometry have largely governed the size of the disposable filter unit described above, and the decontamination factors measured fall short of the target of $10^8$. It is planned, therefore, to provide a secondary filter in series with the disposable unit. This will be contained within a conventional process vessel, but will almost completely fill the interior.
## TABLE V

TESTS OF ANNULAR BEDS OF FERRIC OXIDE

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Adsorber type</th>
<th>Superficial gas velocity (ft/sec)</th>
<th>Residence time (sec)</th>
<th>Decontamination factor</th>
<th>Capacity (g Ru/cm³ adsorber)</th>
<th>Duration (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>Annular bed</td>
<td>0.15 0.90 0.52 0.10</td>
<td></td>
<td>30</td>
<td>&gt; 7 x 10⁻⁸</td>
<td>4</td>
</tr>
<tr>
<td>88</td>
<td>Annular bed</td>
<td>0.11 0.64 0.37 0.14</td>
<td></td>
<td>10</td>
<td>&gt; 3 x 10⁻³</td>
<td>2.5</td>
</tr>
<tr>
<td>89</td>
<td>Annular bed</td>
<td>0.06 0.38 0.22 0.28</td>
<td></td>
<td>220</td>
<td>&gt; 7 x 10⁻³</td>
<td>10.5</td>
</tr>
<tr>
<td>92</td>
<td>Annular bed</td>
<td>0.065 0.39 0.23 0.26</td>
<td></td>
<td>310</td>
<td>&gt; 2 x 10⁻⁸</td>
<td>3</td>
</tr>
</tbody>
</table>
The decrease in gas velocity should be accompanied by a high efficiency for the removal of dust and ruthenium. The filter will handle low quantities of dust and will have a long service life. It will provide a safeguard should the disposable filter fail. If the overall DF is still less than that thought desirable, the low-activity nitric-acid condensate produced can easily be accommodated by recycling to the fuel-reprocessing dissolvers.
5. CONCLUSIONS

The effects of flow-rate and temperature on ruthenium volatilization have been studied. The amount volatilized increased as the flow-rate and operating temperature increased. It has not proved possible to choose operating conditions which would yield minimum volatilization, and an overall decontamination factor of only 3 to 5 for the glass-making stage is anticipated during full-scale operation. Other possible volatile materials do not constitute a problem in the process.

Ferric oxide was selected as adsorbent for ruthenium and the effects of operating variables on decontamination factor studied. A high efficiency, compact filter has been developed, incorporating a ruthenium adsorber. This is ultimately incorporated in the glass block for disposal.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Mr. D. Auty, Mr. B. Sammons and Mr. T. Jordan with experimental work and Mr. T. Hodge for filter tests, and of the analytical team for their services.

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VITRIFICATION DES SOLUTIONS CONCENTRÉES DE PRODUITS DE FISSION: ÉTUDES TECHNOLOGIQUES

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Abstract — Résumé — Аннотация — Resumen

VITRIFICATION OF CONCENTRATED SOLUTIONS OF FISSION PRODUCTS: TECHNOLOGICAL STUDIES.

Vitrification in crucibles has a number of advantages including simplicity of operation and low activity loss in firing. On the other hand, the installations needed for a given output take up considerable room and the mass left to be stored is fairly large.

Two processes have been developed which can give a sizeable output with installations taking up little space. One makes possible continuous vitrification, and the other semi-continuous vitrification by the method known as the pot process.

The continuous vitrification installation tried out can treat about 100 l/d of solution. It consists of a rotary calcinator coupled to a continuous fusion furnace made up of an overflow crucible heated by a resistance furnace in super-kanthal.

The original overflow crucible, in regular silicon aluminium, has been replaced by one in cast zirconium silicate to be proof against the corrosive action of phosphate glasses.

Operation of the installation has been by runs of about 100 hr, with a “tracer” activity of about 10 mc/d.

Two important problems are to be noted: (a) entrained dust rate - a bubble plate tower (cascade) recycles the dust left in the calcinator; (b) its efficiency is of the order of 90%; and ruthenium volatility, which is still high.

The pot-vitrification installation is a process coming between that described above and the crucible process. After glass frit and gelling clay have been added, the active solution is poured continuously into a pot at 500°C until filling is complete. Calcination and feeding go on together. The filling level is determined by measurement of internal temperatures.

After the full charge is calcinated, the glass is melted and tapped through the lower end of the pot, which can thus be re-used.

The pot itself, in inconel, has a cross-section of 20 cm in diam, and a height of 1 m. Items studied include composition of the mixture, optimum feed flow-rates, possibility of separate feeding of active solution and glass frit with no prior mixing, glass tapping conditions.

Work is in progress on an installation having an induction-heated pot of 2 m high and some 20 cm in diam.

VITRIFICATION DES SOLUTIONS CONCENTRÉES DE PRODUITS DE FISSION: ÉTUDES TECHNOLOGIQUES. La vitrification en creusets présente un certain nombre d’avantages: simplicité opératoire, perte faible d’activité à la cuisson; en revanche, pour une production donnée, l’encombrement des installations est considérable et la masse à stocker reste relativement importante.

Deux procédés capables d’assurer une production importante avec un faible volume d’appareillages ont été développés. L’un permet la vitrification en continu, l’autre est un procédé de vitrification semi-continu dit "en pot".

L’installation de vitrification en continu expérimentée a une capacité de production d’environ 100 l de solution par jour. Elle est composée d’un calcinateur rotatif relié à un four de fusion continue constitué par un creuset à trop plein chauffé par un four à résistances en super-kanthal.

Ce creuset à trop plein, qui était à l’origine en silico-alumineux ordinaire, a été remplacé par un creuset en silicate de zirconium électrofondu pour résister à l’action corrosive des verres phosphatés.

L’installation a fonctionné par campagnes d’environ 100 heures avec une activité "tracer" d’une dizaine de millicuries par jour.

Deux problèmes importants sont à noter: a) Le taux de poussières entraînées; un ensemble de barboteurs en cascade recycle les poussières dans le calcinateur; son efficacité est de l’ordre de 90%. b) La volatilité du ruthénium qui est encore importante.

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VITRIFICACIÓN DE SOLUCIONES CONCENTRADAS DE PRODUCTOS DE FISIÓN: ESTUDIOS TECNOLÓGICOS. La vitrificación en crisol ofrece ciertas ventajas, a saber: a) la simplicidad de las operaciones, y b) la baja pérdida de actividad durante la cocción.

Sin embargo, para una producción determinada, se requiere una instalación complicada y la masa que es preciso almacenar sigue siendo relativamente grande.

Se han ideado dos procedimientos capaces de asegurar una gran producción con instalaciones compactas. Uno de ellos permite lograr una vitrificación continua, mientras que el otro constituye un procedimiento semicontinuo, llamado "de cuba".

Se ha ensayado la instalación de vitrificación continua, cuya capacidad de producción diaria asciende a 100 l de solución, aproximadamente. Se compone de un calcinador giratorio unido a un horno de fusión continuo constituido por un crisol de aliviadero, calentado mediante un horno de resistencia de super-kanthal.

El crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplazado por un crisol de aliviadero, que en un principio era de sílice 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de aliviadero, que en un principio era de sílice aluminosa ordinaria, ha sido reemplaza...
un crisol de silicato de circonio, fundido eléctricamente para resistir la acción corrosiva de los vidrios fosforados.

La instalación ha funcionado por turnos de unas 100 h, con una actividad marcadora del orden de una decena de milicuries por día.

Es preciso señalar dos problemas importantes: a) la cantidad de sustancias pulverulentas arrastradas: mediante un conjunto de burbujeadores en cascada se hacen recircular esas sustancias pulverulentas en el calcinador; su rendimiento es del orden del 90%, y b) la volatilidad del rutenio, que sigue siendo apreciable.

En cuanto a la instalación de vitrificación "de cuba", se trata de un procedimiento intermedio entre el que se acaba de describir y el de los críosoles. Luego de añadirle vidrio sinterizado y arcilla gelificante, la solución activa se cuele continuamente en una cuba que se mantiene a 500°C hasta colmarla. La calcinación y la alimentación son simultáneas. El nivel a que llega la masa se determina midiendo las temperaturas internas.

Después de calcinar la carga completa, el vidrio se funde y cuele por la extremidad inferior de la cuba, que puede así volver a utilizarse.

La cuba actualmente utilizada, que es de inconel, tiene una sección de 20 cm de diámetro y una altura de 1 m. Se han estudiado los siguientes aspectos: composición de la mezcla; caudal de alimentación óptimo; posibilidad de efectuar una alimentación separada de la solución activa y del vidrio sinterizado, sin mezcla previa; y condiciones de la colada del vidrio.

Se está construyendo una instalación formada por una cuba de 2 m de altura y de unos 20 cm de diámetro, calentada por inducción.

I. INTRODUCTION ET GÉNÉRALITÉS

Le traitement, par vitrification, des solutions concentrées de produits de fission se ramène toujours à trois opérations correspondant à l'évaporation, la calcination et la fusion de la masse.

Trois techniques ont été étudiées et sont expérimentées en France pour réaliser ce traitement.

- La première consiste à effectuer les trois opérations précitées, successivement, après avoir gelifié la masse à vitrifier. Il s'agit donc d'une technique discontinue.

- La seconde est, au contraire, une technique continue, où toutes les opérations sont réalisées simultanément. Le procédé adopté consiste à utiliser un calcinateur rotatif associé à un four de fusion continu.

- La troisième technique, que l'on peut considérer comme semi-continue, permet d'évaporer et de calciner simultanément dans un pot métallique et d'effectuer ensuite la fusion.

Chaque procédé présente des avantages et des inconvénients. La vitrification, après gelification de la masse, nécessite, à production égale, une installation plus importante et donne lieu à un volume à stocker plus grand, surtout si l'opération a été réalisée en creuset. Par contre, le procédé conduit à une perte d'activité minime en cours de cuisson.

Les difficultés inhérentes au procédé continu proviennent d'une part d'un entraînement de poussières radioactives et d'une volatilité plus importante que précédemment, nécessitant un appareillage plus complexe d'épuration des gaz, d'autre part d'un ensemble mécanique plus fragile. En compensation, la production est grande malgré un volume réduit d'installations. Le procédé de vitrification en pot est un procédé intermédiaire entre les deux procédés précédents. Il présente l'avantage d'un appareillage simplifié, le taux de poussières et de produits volatils entraînés inférieur au procédé continu.
Nous nous attacherons plus particulièrement aux techniques continue et semi-continue. Nous rappellerons brièvement le principe de procédé de gélification. La solution de produits de fission est additionnée d'une charge comprenant une argile gélifiante en milieu acide et d'une fritte verrée complémentaire, l'ensemble reconstituant la formule du verre envisagé. Le mélange est coulé, encore fluide, dans un creuset avant gélification complète. La prise s'effectue rapidement, en donnant une masse dure et compacte qui sera évaporée, puis fondu.

Le procédé nous a servi à tester les verres [1]; des activités spécifiques de 0,3 à 1 c/cm$^3$ de verre ont été obtenues. La perte d'activité au cours de la cuisson, y compris l'activité fixée sur l'appareillage, ne se limite qu'à 0,15% environ de l'activité totale, et se compose presque exclusivement de$^{106}$Ru et$^{137}$Cs. Le facteur de réduction de volume entre le verre et la solution de départ est voisin de 3 [2].

Une installation fournissant des blocs de verre de 10 000 c environ est en cours d'étude et de réalisation.

Pour une unité de production, il serait concevable de monter en parallèle une série de fours, et de les associer à un seul ensemble d'épuration et d'absorption des gaz.

II. INSTALLATION DE VITRIFICATION CONTINUE

L'installation de vitrification continue expérimentée a une capacité de production d'environ 100 l de solution par jour. Elle a été étudiée et expérimentée en collaboration avec la Société potasse et engrais chimiques et la Société carbonisation, entreprise et céramiques. La solution de produits de fission est évaporée et calcinée dans un calcinateur rotatif; le calcinat obtenu se déverse dans un four de fusion continue où sont introduits les adjuvants inactifs nécessaires à la vitrification. Le verre, après affinage, se coule par un trop-plein à la base du four [3, 4].

L'appareillage est disposé dans deux cellules en plexiglass maintenues en légère dépression dont l'une contient le matériel de vitrification tandis que l'autre contient l'ensemble d'épuration des gaz de cuisson.

L'installation a fonctionné en inactif pendant plusieurs campagnes et a été testée avec une activité traceur correspondant à 15 mc environ de produit de fission, au cours d'essais d'une durée de 100 h.

1. Description de l'installation

1.1 Alimentation en solution (figure 1)

La solution synthétique de produits de fission est préparée et activée dans un bac de stockage de 150 l, puis est introduite dans un récipient d'alimentation de forme aplatie, relié directement par un siphon à l'extrémité supérieure du calcinateur.

L'appareillage d'alimentation comprend en outre deux bacs superposés et étanches, l'un initialement rempli d'eau, l'autre vide. Le bas supérieur est relié au récipient d'alimentation. Une pompe doseuse injecte, à débit constant, l'eau du bac inférieur dans le bac supérieur. Le déplacement d'air
ainsi provoqué déplace à son tour un volume de solution active peu différent du volume d'eau injectée, étant donné la forme aplatie du récipient.

Le débit est évidemment fonction de l'état de remplissage du récipient d'alimentation, cependant l'écart entre les volumes écoulés ne dépasse pas 4%.

1.2 Calcination

La calcination s'effectue dans un tube tournant de 12 cm de diamètre et 160 cm de long, en acier inoxydable NS 22 S; sa pente est de 7%, sa vitesse de 70 t/min. Il est chauffé par un four concentrique de 13 kW formant deux coquilles. La partie chauffée est divisée en deux zones indépendantes:
- une zone d'évaporation en amont où la température est d'environ 160-200°, et où les 2/3 de la puissance sont dissipés,
- une zone de calcination où la température atteint progressivement 450-500°.

Le calcinat est muni, dans son dernier tiers inférieur, d'une gorge de rétention destinée à éviter une éventuelle entrée de solution dans le four de fusion, à la suite d'une alimentation trop brutale ou d'une défaillance des circuits de chauffage. De plus, si la zone d'évaporation s'étend dans la zone de calcination, un dispositif de sécurité, commandé par les thermocouples internes au calcinat, coupe automatiquement l'alimentation en solution.

Le calcinat est équipé de deux barres libres de 155 cm de longueur en acier inoxydable, qui favorisent le décollage du calcinat et permettent
d'éviter la formation de blocs. L'extrémité basse du tube tournant est munie de lumières formant un crible, et ne laisse passer que des particules inférieures à 5 mm.

L'étanchéité à la rotation est obtenue par des joints à bagues de graphite; une entrée contrôlée d'air ou de vapeur est possible. Une dépression légère est maintenue en permanence par les pompes de fin de circuit.

1.3 Fusion

Le four est équipé d'un creuset de fusion, soit en sillimanite et monobloc, soit en silicate de zirconium électrofondu. Dans ce dernier cas, il est réalisé en deux parties distinctes qui sont accolées au montage par un coulis d'alumineux (figure 2).

Le creuset en sillimanite a une capacité utile de 4 kg de verre, le creuset en silicate de zirconium une capacité de 12 kg de verre, permettant ainsi de prolonger la durée d'affinage. Un tube de trop-plein de 16 mm de dia-

Figure 2
Partie inférieure du creuset de fusion.
mètre intérieur est aménagé dans la partie inférieure, un dôme de protec-
tion évite le passage direct des produits solides par le trou de coulée.

Le calcinat s'écoule dans le creuset par un tube de liaison en acier réfractaire muni d'ailerettes de refroidissement ; l'étanchéité entre le creuset et le tube de liaison est assurée par un joint liquide de verre fusible, déposé dans une gorge circulaire à la partie supérieure du creuset.

Les matières premières complémentaires, sous forme de fritte vitri-
fiée, sont introduites par un distributeur automatique dans le tube de liaison.

Le four, équipé d'éléments chauffants en super Kauthal, a une puissance de 14 kW. Il est muni d'un tunnel de chargement et d'évacuation des godets récepteurs de verre. Ces godets sont actuellement de petite capacité pour permettre plus aisément un contrôle du débit de verre. Leur progression est assurée par vérin, dès que la charge de verre atteint 1 kg.

1.4 Traitement des gaz

Les gaz de cuisson, composés de vapeur d'eau, oxydes d'azote et air, sont aspirés à l'extrémité supérieure du calcinateur. Leur température est alors voisine de 200°.

Le système d'épuration comprend une série de trois barboteurs en cas-
cade dans lesquels les poussières sont arrêtées et entraînées par un flux
d'acide nitrique dilué circulant à contre courant. Cet acide se déverse en-
suite dans le calcinateur par un trop-plein. Ce système a été préféré aux
cyclones classiques à cause de la facilité de recyclage.

Les gaz, réchauffés par une épingle chauffante, passent ensuite dans
un filtre destiné à fixer le $^{106}$Ru. La charge du filtre peut être soit du sili-
cagel, soit des granulés ferrugineux de même composition que le verre,
qui, une fois saturés, peuvent être fondues. Il faut cependant signaler que
la température des gaz était trop faible à ce niveau pour que ce dernier
filtre travaillé dans des conditions optima.

Le circuit d'absorption des oxydes d'azote se compose d'un condenseur
en pyrex et de trois colonnes d'arrosage garnies d'anneaux de Raschig, la
première est arrosée par une partie du condensat, les deux suivantes par
une solution sodique. Un filtre à laine de verre complète le circuit.

L'ensemble du circuit est maintenu en dépression ; au niveau du tube
de liaison, la dépression est de 3 mm à 5 mm d'eau.

2. Expérimentation et résultats

L'installation continue de vitrification a été étudiée pour traiter soit
des solutions concentrées provenant de la dissolution de barreaux d'uranium
non alliés, soit des solutions provenant d'alliage uranium-molybdène.

Dans le premier cas, la solution synthétique à vitrifier avait la com-
position suivante :

<table>
<thead>
<tr>
<th>Ions</th>
<th>Sous forme nitrate</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>10 g/l</td>
<td></td>
</tr>
<tr>
<td>Fe⁵⁺</td>
<td>5 g/l</td>
<td></td>
</tr>
<tr>
<td>U⁶⁺</td>
<td>10 g/l</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>2 M</td>
<td></td>
</tr>
<tr>
<td>Al³⁺</td>
<td>10,8 g/l (rajouté à la composition pour éviter l'adhérence du calcinat).</td>
<td></td>
</tr>
</tbody>
</table>
Dans le second cas, nous avons utilisé, pour des essais de calcination, la composition phosphomolybdique suivante:

<table>
<thead>
<tr>
<th></th>
<th>Sous forme</th>
<th>Quantité (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo^{5+}</td>
<td>MoO₃</td>
<td>100</td>
</tr>
<tr>
<td>P</td>
<td>H₃PO₄</td>
<td>6,4</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Nitrate</td>
<td>2</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>Nitrate</td>
<td>5</td>
</tr>
<tr>
<td>HNO₃</td>
<td></td>
<td>2 M</td>
</tr>
</tbody>
</table>

La vitrification du calcinat molybdénique n'a pas encore été expérimentée, la composition du verre correspondant n'étant pas encore totalement définie.

2.1 Calcination

a) Conditions de calcination

La calcination des solutions brutes provenant des barreaux uranium non alliés s'est avérée difficile par suite de la forte proportion de nitrate de sodium. Ce sel, au point de fusion voisin de 300°, tend à former avec les autres composants une pâte semi-fondue, qui se prend en masse par refroidissement à la sortie du calcinateur et obstrue les lucarnes. Pour solidifier le calcinat et éviter son adhésion à la paroi du tube tournant, un constituant jouant le rôle de charge et se décomposant à basse température a dû être ajouté à la solution. Le nitrate d'aluminium a été utilisé, l'alumine étant un constituant du verre. Les essais ont montré qu'il fallait introduire dans la solution un poids d'élément Al au moins égal à la teneur en élément Na. Dans ces conditions 12% des oxydes du verre proviennent du liquide à calciner : un litre de solution traitée donne naissance à 420 g de verre, correspondant à un facteur de réduction de volume voisin de 6.

La calcination des solutions provenant de la dissolution des barreaux uranium-molybdène, donne un produit dont l'aspect et le comportement dépendent de la teneur en H₃PO₄. Pour un rapport molaire H₃PO₄/MoO₃ voisin de 1/6, le calcinat s'écoule facilement sans collage dans le calcinateur. Lorsque le rapport précédent atteint 1/3, la proportion trop forte d'acides ortho-et méthaphosphoriques dans le solide provoque l'apparition d'une phase pâteuse contre laquelle les barres de broyage sont inefficaces. Pour un rapport molaire H₃PO₄/MoO₃ # 2/3, on observe un blocage systématique du tube tournant. Bien que les rapports molaïres envisagés soient voisins de 1/7, il pourrait s'avérer utile également, surtout si la teneur en ions sodiques pouvait varier, d'introduire dans les solutions molybdéiques une charge évitant l'agglomération en blocs.

Au cours de la calcination des solutions molybdéniques, on observe en outre une volatilisation du MoO₃ pour une température de calcination moyenne de 480°. La teneur en MoO₃ du calcinat atteint 80% contre 85% pour une température de 350°.

L'aspect du calcinat dépend également du débit d'alimentation. Celui-ci est conditionné par le gradient de température dans le calcinateur. La figure 3 donne la répartition des températures dans les deux zones de chauffage. Pour un débit d'alimentation inférieur à 2,5 l/h, la zone d'évaporation
Répartition des températures dans le tube tournant.

se limite à l'extrémité supérieure du tube tournant et la solution arrive directement sur une paroi chauffée au-dessus de 100°. Si, au contraire, le débit est supérieur à 7 l/h, la zone d'évaporation s'étend sur une partie de la zone de calcination. Le produit est imparfaitement calciné, des collages et des bouchages sont possibles. Les meilleures conditions correspondent à un débit de 3 l/h à 5 l/h. La durée de passage dans le calcinateur pour un débit de 3 l/h est d'environ 18 min, et les gaz au niveau de la conduite de départ sont à une température d'environ 200°.

Il faut cependant remarquer que le solide s'écoulant du calcinateur est incomplètement calciné. On note une perte au feu à 900° d'environ 30% pour le calcinat alumineux, calciné à 450° et une perte au feu à 450° de 5 à 10% pour le calcinat molybdénique calciné à 400°.

Malgré l'inconvénient d'une production de fines, la présence des deux barres métalliques est indispensable pour éviter un engorgement du crible. La granulométrie du calcinat se situe aux environs des chiffres suivants, correspondant à un échantillon moyen :

- granulés supérieurs à 3 mm  19,7%
- granulés compris entre 3 et 1,6 mm  20,5%
- granulés compris entre 1,6 et 0,45 mm  29,5%
- granulés compris entre 0,45 et 0,197 mm  15,2%
- granulés inférieurs à 0,197 mm  15,1%.

b) Problèmes soulevés par la calcination

Les difficultés principales de la calcination sont d'une part l'étanchéité du calcinateur, d'autre part les colmatages du tube de liaison calcinateur-creuset.
Le calcinateur utilisé pour les essais préliminaires ne comportait pas de joints tournants, mais un ensemble de chicanes destinées à éviter la sortie éventuelle du calcinat, et par lesquelles un certain volume d'air pénètre. Le tube étant maintenu en dépression, le débit d'air atteignait 10 à 15 m$^3$/h.

Le calcinateur a, en conséquence, été muni de bagues en graphite « Morganite », montées par frettage sur un support relié par une membrane déformable inoxydable au tube tournant. Le rôle de la membrane est d'éviter l'éclatement des bagues sous l'effort de dilatation des pièces métalliques (figure 4).

![Figure 4](image)

Figure 4
Principe de l'étanchéité du calcinateur.

Un soufflet inoxydable assure l'étanchéité entre la portée de frottement et le corps du capot de liaison. Un léger balayage d'air ou de vapeur est cependant indispensable pour protéger les joints tournants contre les poussières abrasives de calcinat, mais ce débit reste faible et contrôlable. Pour un débit de balayage d'air de 70 l/h, l'écart entre les dépressions à l'entrée du calcinateur, et au capot du tube de liaison n'est que de 1 mm d'eau.

Le débit d'incondensable, préalablement de 15 m$^3$/h, a aussi pu être ramené à moins de 2 m$^3$/h, malgré une entrée d'air observée au niveau du joint liquide à la base du tube de liaison, due à l'insuffisance de la profondeur de la gorge du creuset.

En ce qui concerne le colmatage du tube de liaison, le problème est plus difficilement contrôlable. Il est dû au fait que des particules de fritte et de calcinat s'accrochent sur la paroi du tube de liaison, dont la température, surtout à la base, est supérieure à la température de calcination. Le produit commence à fondre en partie, entraînant un bouchage du tube.

Des améliorations ont été apportées :
- d'une part en munissant le tube de liaison d'ailettes de refroidissement.
  Une lunette composée d'un prisme à réflexion totale a été montée sur le capot du tube pour suivre la descente du calcinat et de la fritte.
- d'autre part, en éliminant les fines de la fritte de verre. La fritte actuellement utilisée est calibrée entre 1,5 et 4 mm. Sa descente provoque de plus un certain ramonage favorable au décollage du calcinat.
2.2 Fusion du verre

Le verre fabriqué a la composition suivante :

- SiO₂ .................. 65,11
- Al₂O₃ .................. 4,86
- Na₂O .................. 15,47
- FeO ................... 11,75
- U₃O₈ .................. 2,81

Sa viscosité à 1100° est voisine de 12 000 P.

Les problèmes essentiels sont : l'affinage et la coulée du verre.

Les examens microscopiques d'échantillons de verre ont montré qu'un verre ayant un temps d'affinage de 4 h présentait encore des particules non digérées de calcinat, pour un temps d'affinage de 6 h, le produit est parfaitement verré. Dans ces conditions, la capacité utile du creuset est passée de 4 kg à 12 kg de verre. En outre, cet accroissement de capacité permettra de travailler à un débit d'alimentation supérieur à 3 l/h, ce qui favorisera la coulée de verre.

La température du verre doit être suffisante pour assurer une parfaite fluidité nécessaire à la coulée, d'autant plus que le débit de verre est faible, environ 1,3 kg/h pour une alimentation moyenne de 3 l/h.

En dessous d'une température de four de 1200° le verre s'écoule en gros fils sans napper dans le creuset de réception. À la température de 1250°, la surface de verre coulée est encore bulleée au fond du creuset de réception. Le nappage devient par contre satisfaisant à 1300°. On peut donc considérer cette température comme limite inférieure.

2.3 Traitement des gaz - Bilan des pertes d'activités

Trois essais de 100 heures ont été réalisés avec une activité traceur, en utilisant le calcinateur préliminaire à chicanes. La solution active contenait 2% 106Ru et 14% 137Cs.

Les entraînements d'activité sont dus, d'une part aux poussières du calcinat s'échappant du calcinateur, d'autre part à la volatilité propre de certains éléments.

Le taux de fines entraînées par les gaz et recyclées au calcinateur par la batterie de barboteurs atteint 7% environ du calcinat. Ces barboteurs ont donné un rendement de rétention supérieur à 90%. La partie s'échappant se trouve arrêtée par les premières couches du filtre à ruthénium qui joue alors le rôle de filtre à choc. Néanmoins, il a été retrouvé dans le condensat des fines particules correspondant à un extrait sec de 40 µg/l.

Les activités retrouvées dans l'appareillage d'épuration des gaz sont résumées sur le tableau I.

Il apparaît que la perte d'activité, et notamment la perte en 106Ru est importante. Il faut cependant noter que les essais ont été réalisés avec un calcinateur non étanche, et que la forte entrée d'air favorise l'entraînement d'activité.

Cette entrée d'air explique également les rendements très faibles de rétention du 106Ru dans le filtre destiné à le piéger : le silicagel n'a donné
R. BONNIAUD et P. RANÇON

**TABLEAU I**

**BILANS DES PERTES D'ACTIVITÉ AU COURS DES ESSAIS DE LONGUE DUREÉE**

<table>
<thead>
<tr>
<th>Essais de longue durée</th>
<th>Volume de solution traité</th>
<th>Volume moyen d'incondensable</th>
<th>Perte d'activité en % de l'activité totale introduite</th>
<th>Teneur en $^{106}$Ru</th>
<th>Perte en $^{106}$Ru par rapport au Ru total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>296 l</td>
<td>10 m³/h</td>
<td>Condensat élaboré 0,02%</td>
<td>60%</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Condensat recyclé 0,47%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Colonnes d'absorption 0,02%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Piège à ruthénium 0,29%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(silicagel)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Perte globale mesurée environ 1,4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>298 l</td>
<td>15 m³/h</td>
<td>Condensat élaboré 0,55%</td>
<td>83,4%</td>
<td>84%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Condensat recyclé 1,46%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Colonnes d'absorption 0,14%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Piège à ruthénium 0,08%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(granulés ferrugineux)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Incondensables avant filtration 0,008%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Perte globale mesurée environ 2,24%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>288 l</td>
<td>15 m³/h</td>
<td>Condensat élaboré 0,74%</td>
<td>70%</td>
<td>73,5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Condensat recyclé 1,43%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Colonnes d'absorption 0,18%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Incondensables avant filtration 0,02%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Perte globale mesurée environ 2,37%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

qu'un rendement de 20%, le filtre à granulés ferrugineux un rendement minimum de 3%. Le temps de contact des gaz dans ces filtres était trop faible, de plus, pour les granulés ferrugineux, la température de fonctionnement n'a pas dépassé 200°.

La perte d'activité s'est d'ailleurs trouvée abaissée lorsque le débit gazeux est passé de 15 à 10 m³/h, mais ce débit est une limite pour obtenir une dépression acceptable au niveau du tube de liaison.

Il faut cependant penser que les entraînements d'activité seront considérablement réduits par diminution du volume d'air de balayage, lors des essais avec le calcinateur étanche.

Les analyses de $^{106}$Ru effectuées sur le calcinat et le verre au cours de l'essai n°3 ont permis d'évaluer à 43% le $^{106}$Ru s'échappant au cours de la calcination et à 34% celui s'échappant du verre en fusion, soit un total de perte de 77% en concordance avec l'activité retrouvée dans le circuit d'absorption (9,5%).

Au cours de calcinations de solutions phosphomolybdéniques, une activité correspondant à 2,1% de l'activité totale s'est trouvée arrêtée par le système de recyclage des poussières. Par contre, dans les mêmes con-
ditions, avec du $^{99}$Mo comme traceur, l’activité mesurée correspondait à 4\% de l’activité totale, ce qui confirme une certaine volatilité propre à l’anhydride molybdique.

III. INSTALLATION DE VITRIFICATION EN POT

Le principe de la méthode consiste à alimenter un pot métallique porté à température moyenne par la solution à vitrifier et les adjuvants complémentaires du verre. L’alimentation, l’évaporation et la calcination sont des opérations continues et simultanées jusqu’au remplissage du pot. Le calcinit est alors fondu à plus haute température. On distingue donc deux phases, l’une de calcination, l’autre de vitrification [2].

Un pot en inconel de 1 m de hauteur et de 20 cm de diamètre est actuellement utilisé. Une installation équipée d’un pot de 2 m de hauteur et 18 cm de diamètre est en cours d’exécution en collaboration avec la Société Saint-Gobain nucléaire.

Pour limiter l’évaporation brutale et un entraînement de poussières, la température de calcination de 500° a été choisie. En outre, afin de réduire le volume au stockage et abaisser le prix de revient du procédé, nous avons cherché à évacuer par coulée le verre formé dans le pot. Cette technique nécessite une température plus haute d’élaboration. Le pot pourrait ainsi être réutilisé pour un certain nombre d’opérations avant d’être stocké définitivement.

1. Description de l’installation de vitrification en pot

L’appareillage est équipé d’un pot en inconel de 1 m de haut, 20 cm de diamètre, 2 mm d’épaisseur. Il est terminé à sa partie inférieure par une partie conique, munie d’un tube de coulée de 15 mm de diamètre intérieur (figure 5).

Le tube de coulée est entouré d’une couronne concentrique de refroidissement, à l’intérieur de laquelle peut circuler de l’air comprimé. Le dispositif permet de maintenir pendant la fusion un bouchon solide de verre dans la buse de coulée.

Le pot comporte sur sa bride supérieure trois conduites, l’une refroidie, centrale, réservée à l’alimentation, une autre pour le départ des gaz, une troisième, branchée sur une garde hydraulique, joue le rôle de soupape de sécurité.

Cinq thermocouples placés le long du pot dans des doigts latéraux, et distants les uns des autres de 10 cm, permettent l’enregistrement des températures de cinq niveaux différents. Les températures sont prises à 5 cm de la paroi interne.

Le pot est chauffé par un four tubulaire à éléments super-Kauthal de 30 kW.

Un dispositif de levage permet d’introduire le récipient de réception du verre sous le pot, soit à l’extérieur, soit à l’intérieur du four. Dans le premier cas, la coulée du verre se fait dans un récipient froid, dans le deuxième cas, le récipient de réception est lui-même à 800° environ.
Figure 5
Vitrification en pot.
La solution d'alimentation est injectée dans le pot, par une pompe Sigma motor. Les adjuvants du verre sont mélangés, préalablement à la solution synthétique, ou introduits séparément dans le pot sans mélange préalable.

Le circuit d'absorption des gaz se compose d'un condenseur en pyrex et de deux colonnes d'arrosage à la soude. L'ensemble du circuit et du pot est maintenu en légère dépression.

2. Phase de calcination

a) Techniques d'alimentation

La solution synthétique d'essai est une solution nitrique 2N contenant 8,5 g Na/l sous forme nitrate. Les adjuvants complémentaires du verre sont introduits sous forme de fritte verrée broyée et tamisée au tamis 100, maille tyler.

Deux techniques d'alimentation ont été testées :

La première consiste à effectuer un mélange préalable des adjuvants. L'agent de suspension utilisé, pour éviter la décantation rapide de la fritte de verre est l'argile SA 938 de la Société carbonisation et charbon actif. Ce produit possède des propriétés gélifiantes en milieu acide. Pour des quantités relatives de solution, d'argile et fritte déterminées, il est possible d'obtenir une composition de mélange peu décantable, mais restant suffisamment fluide pour s'écouler sans bouclage. La conduite d'alimentation est cependant refroidie par un water jacket.

Rapportée au litre de solution, la composition utilisée est la suivante :

\[
\begin{align*}
1 \text{ l de solution synthétique} & \\
66,7 \text{ g d'Argile SA 938} & \\
376 \text{ g de fritte.} &
\end{align*}
\]

Elle correspond à un facteur de réduction de volume de 5,4.

Le volume de solution injectable dans le pot par opération dépend de l'aptitude du mélange à diminuer de volume au cours de la calcination. Un mélange trop riche en substance gélifiante aura une meilleure tenue à la décantation, mais présentera à la calcination une diminution de volume trop faible. Un mélange, par exemple, totalement gélifié ne donne aucune diminution de volume à la calcination. Le produit obtenu reste poreux ; cette porosité est nuisible car elle favorise les infiltrations de liquide vers les zones à température plus élevée.

La composition retenue, dans le cas d'un mélange préalable, donne un facteur de réduction de volume à la calcination d'environ 2,2. Dans ces conditions, pour le pot actuel de 1 m de hauteur, il est possible de vitrifier 40 l de solution concentrée de produits de fission.

La seconde technique d'alimentation expérimentée consiste à charger séparément le pot, en solution à vitrifier d'une part, et en adjuvants du verre d'autre part, préalablement mélangés à l'agent de suspension et à une petite quantité d'acide nitrique N/13; on obtient ainsi une boue facilement manipulable qui est injectée dans la conduite d'alimentation en solution.
En utilisant la même composition minéralogique que précédemment, on obtient, par suite de l’absence totale de gélification, un facteur de réduction de volume à la calcination voisin de 4. Il devient alors possible de vitrifier, par opération, 75 l de solution. En modifiant la composition minéralogique, c’est-à-dire la proportion d’adjuvant du verre par rapport à la solution active, le volume introduit pourrait être double sans difficulté.

Il apparaît donc qu’il serait plus rentable de travailler par double alimentation : le mélange préalable actif est supprimé, le volume d’effluent vitrifiable par opération est accru. Cependant, le choix définitif est fonction de l’entraînement d’activité au cours de la calcination. Ce taux risque d’être plus fort pour la technique de double alimentation.

b) Débit d’alimentation

L’alimentation et la calcination étant simultanées, une phase aqueuse se maintient dans le pot pendant toute la durée de l’opération. La progression de cette nappe aqueuse, déterminée par les thermocouples, nous renseigne sur le niveau du remplissage. La reproduction de l’enregistrement graphique de la figure 6, représente l’évolution de la calcination et du remplissage du pot au cours d’un essai.

Il est intéressant de limiter cette phase aqueuse au minimum. Elle est due à un certain retard à la condensation. Le volume condensé par unité de temps est inférieur au volume introduit. Ce retard dépend de nombreux facteurs parmi lesquels la température de chauffage et le débit d’alimentation.

Le tableau II donne les retards moyens à la condensation rapportés au litre de solution dans différentes conditions opératoires. Les débits préconisés pour l’appareillage actuel exprimés en liquide de départ sont d’environ 50 cc/min (correspondant à 60 cc/min du mélange solution-adjuvants) pour l’alimentation à mélange préalable et 70 cc/min pour la double alimentation.

La figure 7 représente les courbes d’alimentation et de condensation obtenues dans le cas d’une alimentation unique, à la température de 500° et pour un débit moyen de 70,5 cc/min et dans le cas d’une double alimentation, à la même température et un débit peu différent de 66,5 cc/min.

Il est à noter que la détermination des niveaux par mesure de température pourrait se faire par une série de thermocouples fixés sur la paroi externe. La courbe de la figure 8 montre l’évolution de la température du point 2 situé à l’intérieur du pot à 20 cm du fond, et du point A situé au même niveau sur la paroi externe.

On note l’apparition de la phase aqueuse sur les deux courbes, la température du point A évolue ensuite plus rapidement par suite de l’évaporation plus rapide au contact de la paroi. Ce dispositif présenterait l’avantage de préserver les couples du foisonnement éventuel du verre au cours de la fusion.
Figure 6

Evolution des températures à différents niveaux au cours de l'alimentation du pot.
Figure 7

Courbes d'alimentation et de condensation.

(1) MÉLANGE PRÉALABLE DÉBIT MOYEN 70,5 cc/m
(2) DOUBLE ALIMENTATION DÉBIT MOYEN 66,5 cc/m

Figure 8

Evolution de la température dans le pot et contre la paroi.
TABLEAU II

INFLUENCE DU DÉBIT ET DU MODE D'ALIMENTATION SUR LE RETARD MOYEN A LA CONDENSATION

<table>
<thead>
<tr>
<th>Technique opératoire</th>
<th>Débit moyen d'alimentation en boue</th>
<th>Débit moyen d'alimentation en liquide correspondant</th>
<th>Retard moyen à la condensation par litre de solution</th>
<th>Température de calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple alimentation</td>
<td>98,4 cc/min</td>
<td>83,5 cc/min</td>
<td>0,30 l/l</td>
<td>500°</td>
</tr>
<tr>
<td>Simple alimentation</td>
<td>83,5 cc/min</td>
<td>70,5 cc/min</td>
<td>0,23 l/l</td>
<td>500°</td>
</tr>
<tr>
<td>Simple alimentation</td>
<td>62,5 cc/min</td>
<td>53,0 cc/min</td>
<td>0,13 l/l</td>
<td>500°</td>
</tr>
<tr>
<td>Simple alimentation</td>
<td>47,5 cc/min</td>
<td>40,5 cc/min</td>
<td>0,12 l/l</td>
<td>500°</td>
</tr>
<tr>
<td>Simple alimentation</td>
<td>32,2 cc/min</td>
<td>27,3 cc/min</td>
<td>0,10 l/l</td>
<td>500°</td>
</tr>
<tr>
<td>Double alimentation</td>
<td>66,5 cc/min</td>
<td>64,0 cc/min</td>
<td>0,08 l/l</td>
<td>500°</td>
</tr>
</tbody>
</table>

3. Phase de fusion et coulée de verre

Le verre fabriqué a la composition et les caractéristiques suivantes :

- SiO₂ ........................................ 64%  
- Al₂O₃ ........................................ 4,7%  
- Fe₂O₃ ........................................ 9,7%  
- Na₂O ........................................ 15,1%  
- K₂O .......................................... 0,8%  
- B₂O₃ ........................................ 4,76%  
- CaO ......................................... 0,87%  
- divers MgO ................................ 0,07%  
- Viscosité 1000° ............................ 2800 P  
- Viscosité 1100° ............................ 800 P

Dans les conditions de remplissage maximum : pour une alimentation à mélange préalable, le volume de verre après fusion ne représente que 26% du volume total utile.

La coulée du verre permet de recycler un certain nombre de fois le pot. Pendant la montée en température et l'affinage, un bouchon de verre obtenu par refroidissement local obstrue le tube de coulée. Après vitrification de la masse l'arrêt du refroidissement entraîne la fusion du bouchon de verre et la coulée. Le verre doit alors être suffisamment fluide pour napper correctement dans un récipient. Le débit de coulée dépend de la charge et de la température du pot. Ils atteignent les valeurs suivantes :
Pour une charge = 7 kg

1,6 kg/h pour une température de 1100° au four
4,4 kg/h pour une température de 1150° au four
9,5 kg/h pour une température de 1250° au four

Pour une charge = 17 kg

20 kg/h pour une température au four de 1200° (1250° en fin de coulée)
13 kg/h pour une température au four de 1150°.

Ces températures sont notées au niveau des résistances, les températures internes sont inférieures d’environ 50°.

Au début de la coulée, les débits sont grands (figure 9), mais décroissent rapidement. Le jet continu de verre s’interrompt, faisant place à des gouttes ou des fils.

Pour une température du four de 1200° minimum, le nappage en récipient froid est en général correct, sauf en fin de coulée, où 200 à 300 g de verre s’écoulant en gouttes forment des stalagmites au-dessus de la surface du verre.

Pour une température du four de 1150°, le débit de verre est insuffisant pour assurer un nappage correct dans les mêmes conditions. Le récipient récepteur est alors introduit à la base du four et maintenu à 800°. Dans ces conditions, le nappage est excellent même en fin de coulée.

Le choix de la technique de coulée de verre dépendra essentiellement des pertes en Ru observées et de la tenue du pot à haute température.

Figure 9
Courbes de coulée de verre.
Le pot actuel a subi vingt-cinq cycles répétés. Seuls les doigts latéraux de prises de température ont souffert par suite d'un foisonnement de la masse au cours de la fusion.

Les micrographies effectuées sur le métal du pot ayant subi dix cycles, n'ont pas décelé, en dehors du grossissement du grain, de corrosion profonde en surface, ni de corrosion intergranulaire.

Les macrographies ont fait apparaître quelques criques aux soudures, pouvant provenir de soudures irrégulières. Les essais de traction montrent une baisse assez sensible de la charge de rupture 49,7 kg/mm$^2$ au lieu de 67,6 kg/mm$^2$ pour le témoin; mais ceci peut être relié au grossissement du grain et ne semble pas alarmant.

4. Développement futur

Une installation complète utilisant un pot de 2 m de hauteur et 180 mm de diamètre en inconel est en préparation. Elle sera équipée d'un four à induction à plusieurs niveaux de chauffage. La coulée du verre sera démarrée par réchauffage du tube de coulée, grâce à un enroulement inducteur complémentaire, pouvant être mis en circuit au moment opportun.

L'appareillage comportera deux filtres, destinés à piéger les éléments volatils.

L'installation est destinée à fonctionner, après une série d'essais inactifs, avec une activité faible; elle sera de ce fait placée dans une enceinte d'étanchéité en plexiglass et éventuellement protégée par 5 cm de plomb.

IV. CONCLUSION

Les trois procédés précédemment définis, gélification, calcination et vitrification en pot métallique, fusion et calcination continues, sont actuellement en cours d'expérimentation.

Ils ne sont pas obligatoirement destinés à se concurrencer, le domaine d'application de chacun d'eux pouvant être bien distinct.

Deux éléments peuvent intervenir dans le choix du traitement:

a) d'une part, le volume d'effluents concentrés à vitrifier. On aura intérêt, plutôt que de transporter des solutions très actives vers une unité centrale de solidification, à concevoir plusieurs installations de moyenne production associées aux ateliers de traitement des barreaux d'uranium et étudiées pour un type de solution défini.

Un ensemble de vitrification discontinue après gélification pourrait être une installation de secours, lorsque la production est limitée; par exemple, pour compléter un atelier de séparation de $^{137}$Cs ou $^{90}$Sr.

b) d'autre part, la composition des solutions à vitrifier. Dans l'état actuel des études, par exemple, les eaux mères dérivées des barreaux uranium molybdène, s'adaptant mal au procédé de vitrification en pot métallique par suite de la corrosion importante du verre correspondant.

De toute façon, le problème commun essentiel reste l'entraînement de poussières et d'éléments volatils au cours de la cuisson. Il faut limiter
cette perte afin de réduire les installations d'épuration des gaz, et d'éviter les traitements complémentaires des solutions d'absorption.

Ce problème n'est pas encore parfaitement résolu pour l'installation continue de vitrification, et n'a pas fait l'objet d'études pour le procédé de fusion en pot.

Les nouvelles installations prévues sont spécialement destinées à résoudre ce problème. Après cette étape seulement, une sélection éventuelle sera possible.

RÉFÉRENCES


DISCUSSION

J. R. GROVER: I have two questions which refer to both the rotary calciner and the pot calciner that you used. First, can you give any indication of how they might maintain or replace the high-temperature furnaces and calcination vessels? Second, is there any escape of volatile activity, such as caesium, when the glass is fed from the furnace to the final receiver pot?

R. BONNIAUD: In answer to your first question, there is provision for changing the rotary calciner and its furnace by remote control. For this purpose, three tubes have to be disconnected: the solution inlet tube, the gas outlet tube and the connecting tube. This disconnection is effected by means of a remote-controlled coupling. At present, the calcining furnace and the calciner are removed by a monorail.

As regards the second question, it is indeed possible that we lose some Cs\(^{137}\) during the pouring of the glass. This is something that still needs verification and we plan to check on it shortly. If it proves to be true, it will be sufficient to evacuate these volatile products in the direction of the firing-gas purification circuit.

W. H. HARDWICK: I would like to know what you consider to be the advantages of separate calcination and fusion. It is obvious that you do not have confidence in the calcined product as a final storage medium, and I would agree with you here, since a calcine may have trapped gas cavities and local overheating when fission products are incorporated. However, it seems to me that it is much more sensible to go directly to glass, as we do in the United Kingdom, rather than go through an intermediate calcining stage.

R. BONNIAUD: We do indeed believe that the vitrification alternative affords greater security in the treatment of concentrated solutions of fission
products. We are obliged, however, to go through a calcination phase. The reason why, when working with a continuous vitrification installation, we carry out the vitrification in a separate unit is the apparent difficulty in vitrifying the mass and refining the glass directly in the rotating furnace. In the pot installation, our preliminary tests have shown that an attempt to carry out the calcination and vitrification operations simultaneously resulted in the formation of cavities between the melted part and the calcined mass. As has been pointed out by Mr. Grover, these cavities are responsible for the pressure jumps in the pot. Moreover, the temperature gradient between the melted phase and the phase during calcination is very considerable, and the risks of violent boiling and entrainment of dust are very great. In these circumstances, it seemed preferable not to undertake the calcining and vitrification operations simultaneously.
ULTIMATE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTES - FIXATION IN PHOSPHATE GLASS WITH EMPHASIS ON THE CONTINUOUS MODE OF PLANT OPERATION

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Abstract — Résumé — Аннотация — Resumen

ULTIMATE DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTES - FIXATION IN PHOSPHATE GLASS WITH EMPHASIS ON THE CONTINUOUS MODE OF PLANT OPERATION. In the study of ultimate disposal of high-level radioactive wastes at Brookhaven National Laboratory emphasis is being placed on the formation of phosphate glasses as a means of incorporating the fission products in stable media. Of primary interest here is the development of a process in which the entire conversion from the raw aqueous wastes to the final glass product would be carried out in an all-liquid system. The phosphate-glass method offers a number of important advantages in this respect and, in particular, lends itself to the development of a continuous process in which the liquid medium would be readily transferable from one process step to another.

The paper presents the results of bench-scale studies on the production of phosphate glasses, with the continuous mode of operation, utilizing various types of aqueous wastes. The studies have been in progress for some 20 months and were carried out to determine essential operating parameters with particular attention paid to corrosion resistance and physical integrity of the high-temperature crucible. In addition, the paper discusses flow-sheet development together with the design and results of operation of an engineering-scale plant having a capacity of 0.5 ft³ of glass per day with a continuous feed of simulated non-radioactive wastes.

ÉLIMINATION DÉFINITIVE DE DÉCHETS DE HAUTE ACTIVITÉ - FIXATION DANS DU VERRE AU PHOSPHATE EN VUE D'UNE EXPLOITATION DE L'INSTALLATION EN CONTINU. Dans l'étude des méthodes d'élimination définitive des déchets de haute activité, le Laboratoire national de Brookhaven attache une grande importance aux verres au phosphate pour la fixation des produits de fission dans un milieu stable. On s'efforce essentiellement de mettre au point un processus dans lequel la transformation, depuis le déchet liquide à l'état brut jusqu'au produit vitreux final, s'opérerait entièrement en phase liquide. A cet égard, le verre au phosphate présente un grand nombre d'avantages importants; en particulier, il se prête à la mise au point d'un processus continu dans lequel le milieu liquide pourrait facilement passer d'un stade au stade suivant.

Les auteurs exposent les résultats d'études en laboratoire sur la production de verres au phosphate, suivant un processus continu, avec différents types de déchets liquides. Ces études, qui sont en cours depuis une vingtaine de mois, ont pour objet de déterminer les paramètres de fonctionnement essentiels, en tenant compte notamment de la résistance à la corrosion et de l'intégrité physique du creuset à haute température. Les auteurs commentent aussi le diagramme de circulation ainsi que les plans et le fonctionnement d'une installation expérimentale pouvant produire 14 dm³ de verre par jour en étant alimentée de manière continue avec des déchets simulés.

ОКОНЧАТЕЛЬНОЕ УДАЛЕНИЕ ВЫСОКОАКТИВНЫХ ОТХОДОВ - ФИКСАЦИЯ В ФОСФАТИЧЕСКОМ СТЕКЛЕ НА НЕПРЕРЫВНО РАБОТАЮЩЕЙ УСТАНОВКЕ. При изучении методов окончательного удаления высокоактивных отходов в Брукхейвенской национальной лаборатории особое внимание уделяется получению фосфатных стекол как способу включения продуктов деления в устойчивую среду. Главный интерес представляет разработка процесса, при котором водные отходы превращались бы в окончательный стекловидный продукт в полностью жидкой системе. Метод получения фосфатного стекла представляет собой ряд важных аспектов в этом отношении преимуществ и, в частности, дает возможность разработать непрерывный процесс, в котором жидкая среда может легко направляться из одной стадии процесса в другую.

В докладе приводятся результаты проводимых в лаборатории работ исследований по непрерывному получению фосфатных стекол с использованием разного рода водных отходов. Эти исследования продолжались в течение около 20 месяцев, их целью было определение важнейших рабочих параметров, причем особое внимание уделялось коррозионной стойкости и физической сохранности тигля,
рабочего при высокой температуре. Помимо этого, в докладе обсуждается разработка технологической схемы, а также конструкция и результаты работы промышленной установки с производительностью в 0,5 кубических футов отхода в сутки при непрерывной подаче нерадиоактивного раствора, имитирующего отход.

EVACUACIÓN DEFINITIVA DE DESECHOS DE ELEVADA RADIACTIVIDAD. FIJACIÓN EN VIDRIO AL FOSFATO ATENDIENDO PARTICULARMENTE A LA CONTINUIDAD DE LA MARCHA DE LA INSTALACIÓN. En el estudio de los métodos para la evacuación definitiva de desechos de elevada radiactividad, que se realiza en el Brookhaven National Laboratory, se viene prestando particular atención a la formación de vidrios al fosfato como recurso para incorporar los productos de fisión a un medio estable. Interesa principalmente encontrar un proceso con arreglo al cual la conversión, desde los desechos acuosos en bruto hasta el producto vítreo final, pueda efectuarse enteramente en fase líquida. En este sentido, el método del vidrio al fosfato ofrece una serie de importantes ventajas y, en particular, se presta para el desarrollo de un proceso continuo en cuyo curso el medio líquido puede pasar fácilmente de una operación a otra.

El autor expone los resultados de estudios de laboratorio sobre la obtención de vidrios al fosfato, con arreglo a un procedimiento continuo con distintos tipos de desechos acuosos. Estos estudios se vienen realizando desde unos veinte meses atrás y su propósito es determinar los parámetros funcionales básicos, prestando particular atención a la resistencia a la corrosión y a la integridad física del crisol de alta temperatura. Además, se examina en la memoria el trazado del diagrama de circulación, juntamente con el cálculo y los resultados obtenidos en la explotación de una instalación experimental de una capacidad de elaboración de 0,5 pies\(^3\) (14 dm\(^3\)) de vidrio por día, con alimentación continua de desechos inactivos simulados.

Over the past decade, extensive investigations have been carried out on a number of different processes for the fixation of high-level radioactive wastes in stable solids as a means of ultimate disposal. Calcination of high salt-content wastes, adsorption of fission products on minerals, and incorporation of fission products into glasses and ceramic bodies form the bases of many of these processes. Each method of achieving fixation presents its own particular set of advantages but it is notable that comparative evaluations of the various methods often tend to emphasize engineering design and plant operations features to a much greater extent than quality of product as determined by actual degree of fixation in a stable solid. The long-term integrity of physical containers for storing waste-bearing solids and, more importantly, the isolation protection offered by certain natural storage environments, as represented by man-made cavities in salt formations, therefore, may in some cases be regarded as the major factors in insuring safe and permanent disposal.

During the past three years a process for incorporating fission products in phosphate glass has been under development at Brookhaven National Laboratory which is designed to bring together a highly desirable set of advantages through such features as simplicity of plant layout and operation, relatively high degree of fixation in a stable solid and the continuous mode of plant operation. The phosphate-glass process was selected for study and development largely because it offered a means of carrying out the entire conversion from the raw aqueous waste to the molten-glass product in an all-liquid system. Thus, problems associated with heat input, removal of decomposition gases, mixing of ingredients and general handling and transport of process media would tend to be minimized. Phosphoric acid appears to be highly suitable for the purpose in that the raw waste may be mixed directly with the acid, and an initial evaporation and denitration step carried out in the boiling-liquid medium at temperatures up to 200°C, after which the product is pumped directly to a high-temperature crucible where it is
transformed to a homogeneous green glass at 1100°C. The denitration step is carried out smoothly without any interference which otherwise would result from formation or precipitation of solids or from stratification of ingredients. The glass is free of bubbles and has a density of about 2.9 (see Fig. 1). Off-gases from the high-temperature step contain the remainder of the nitrate together with a large proportion of the sulphate and small amounts of phosphate. The behaviour of the fission products in the system has not been investigated quantitatively although there is ample evidence to show that ruthenium will be a major contributor to the radioactive contamination of the off-gases from the high-temperature crucible. Present plans call for treatment of these off-gases by condensation and subsequent distillation with a view to obtaining a reasonably decontaminated effluent from the plant and returning the still bottoms to the system to be incorporated into the glass.

The types of aqueous wastes which appear to be most suitable for incorporation into phosphate glasses are those of relatively low salt content such as Purex and Darex, although, with slightly higher temperatures and added amounts of \( \text{H}_3\text{PO}_4 \), the process appears to be readily applicable to high-salt-content Redox waste as well. Studies to date, however, have been centred on the processing of Purex-type solutions with varying concentrations of iron, phosphate and sodium. The composition of a typical Purex waste is shown in Table I. The feed solution, made up in the proportion of 200 ml of 85% phosphoric acid per liter of simulated Purex waste, previously concentrated through evaporation by a factor of 10, is fed to the
TABLE I

<table>
<thead>
<tr>
<th>Equivalents (metal ion)</th>
<th>Gram molecular weight</th>
<th>(M)</th>
<th>(g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺NO₃</td>
<td>1.0</td>
<td>1.0</td>
<td>85</td>
</tr>
<tr>
<td>Fe(NO₃)₃</td>
<td>0.70</td>
<td>2.1</td>
<td>404</td>
</tr>
<tr>
<td>Mo(NO₃)₆H₂O</td>
<td>0.01</td>
<td>0.2</td>
<td>290</td>
</tr>
<tr>
<td>Cr(NO₃)₃</td>
<td>0.02</td>
<td>0.06</td>
<td>400</td>
</tr>
<tr>
<td>AK(NO₃)₃</td>
<td>0.1</td>
<td>0.3</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>37.5</td>
</tr>
<tr>
<td>HNO₃</td>
<td>7.0</td>
<td>7.0(3.51 needed)</td>
<td>63</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>1.1</td>
<td>2.2</td>
<td>98</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>0.01</td>
<td>0.03</td>
<td>98</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>0.02</td>
<td>0.04</td>
<td>284.2</td>
</tr>
<tr>
<td>H⁺</td>
<td>5.8</td>
<td></td>
<td>5.16</td>
</tr>
<tr>
<td>Sr(NO₃)₂</td>
<td>2.3 x 10⁻²</td>
<td>4.6 x 10⁻³</td>
<td>211</td>
</tr>
<tr>
<td>CsNO₃</td>
<td>3.6 x 10⁻⁸</td>
<td>7.2 x 10⁻⁴</td>
<td>194</td>
</tr>
<tr>
<td>Y(NO₃)₃</td>
<td>1.3 x 10⁻³</td>
<td>3.9 x 10⁻¹</td>
<td>383</td>
</tr>
<tr>
<td>Ba(NO₃)₃</td>
<td>1.72 x 10⁻⁴</td>
<td>3.4 x 10⁻¹</td>
<td>261</td>
</tr>
<tr>
<td>Ce(NO₃)₄·6H₂O</td>
<td>3.7 x 10⁻⁵</td>
<td>1.1 x 10⁻¹</td>
<td>434</td>
</tr>
<tr>
<td>La(NO₃)₃·6H₂O</td>
<td>1.6 x 10⁻⁸</td>
<td>4.8 x 10⁻¹</td>
<td>433</td>
</tr>
<tr>
<td>Pr(NO₃)₃</td>
<td>1.7 x 10⁻⁸</td>
<td>5.1 x 10⁻¹</td>
<td>327</td>
</tr>
<tr>
<td>Nd(NO₃)₃</td>
<td>3.8 x 10⁻⁹</td>
<td>1.4 x 10⁻¹</td>
<td>438</td>
</tr>
<tr>
<td>Na₂MeO₂(2H₂O)</td>
<td>4.7 x 10⁻²</td>
<td></td>
<td>241</td>
</tr>
<tr>
<td>ZrO(NO₃)₂(2H₂O)</td>
<td>4.85 x 10⁻³</td>
<td>9.7 x 10⁻³</td>
<td>268</td>
</tr>
</tbody>
</table>

The removal of a large fraction of the nitrate in the low-temperature step of the process contributes to the subsequent smooth conversion of the solution to a glass at 1100°C. At this point there is a further reduction in volume by a factor of about 2.2, thus making the over-all reduction in volume from that of the raw waste by a factor of 125.
An extensive series of bench-scale experiments on the production of Purex-phosphate glass, with the continuous mode of operation, have been carried out during the past year. The apparatus, shown in Fig. 2, consists of a mixing vessel, a combined flash evaporator and denitrator, a high-temperature furnace containing a platinum crucible, and an off-gas condenser and scrubber train. The crucible is a simple cylindrical vessel 2 in in diam. and 6 in high and is equipped with an overflow tube with the upper opening at the 4-in level and extending through and welded to the bottom of the vessel. The tube serves to maintain a constant level of the molten glass in the crucible and, in conjunction with a loose-fitting baffle tube, provides for a substantial and uniform retention period for glass formation. Molten glass flows out of the crucible by displacement, therefore, as the denitrated solution is fed to the crucible. A major objective in carrying out these experiments was to investigate performance characteristics in the continuous operations system and, in particular, to determine the corrosion resistance of platinum under actual glass-forming conditions wherein it would be exposed not only to the molten glass but also to volatile sulphates and other products of decomposition. Platinum was selected as the material of construction for the crucible on the basis of corrosion tests on a number of metals and on a variety of ceramics. Coupons of platinum and platinum alloys of rhenium, gold, and iridium were exposed at 1100°C to molten Purex-phosphate glass for 3000 hr and to Redox-phosphate glass for 700 hr. Under the conditions of the tests all specimens showed high resistance to corrosion and no evidence of attack was found at the air-glass interface. Platinum
crucibles are used commercially in the production of optical glasses and the high unit cost of platinum does not rule out its use as a practical crucible material for phosphate glass production in full plant-scale waste-disposal operations.

The bench-scale apparatus has been operated under a variety of conditions during the past year but on an intermittent basis and usually for periods of 6-8 hr at a time. With this irregular schedule it is estimated that the platinum has been exposed to the molten glass under conditions which may be considered reasonably representative of full-scale plant operation for some 500 hr. Additional exposure to the molten phosphate of some 3000 hr was incurred with the feed turned off but with the crucible and glass contents held at 1000°C. No evidence of corrosion of the platinum has been found. Actually, the main difficulties encountered in the operation of the system have so far been of a minor nature such as those associated with the feeding of the denitrated solution to the high-temperature crucible under the rather cramped conditions imposed by its small (2 in) diameter. With the low flow-rates and drop-wise addition to the crucible there was a tendency for splattering on the walls of the entrance tube which is located just above the crucible. The 2-in-diam. crucible has recently been replaced with a somewhat larger crucible (3 in in diam. and 10 in high) and the problem of splattering and residue accumulation on the walls appears to be minimal. Moreover, a new type of feeder is being constructed which features a cooling jacket around the central feed tube and an insulator jacket on the outside. The purpose is to convey the feed solution to a point near the surface of the molten glass without boiling or splattering, using gas-flow for cooling and to avoid condensation and reflux on the outside feeder surface. A brief trial test was made with a temporary feeder, which was cooled by means of a water jacket, with good results. Overheating of the phosphate solution was prevented up to the time it emerged from the feeder at a point about 1 in above the surface of the molten-glass pool. Glass production with both the 2-in and 3-in crucibles has averaged out to be equivalent to about two crucible volumes in 8 hr. With the previously noted volume reduction by a factor of 125 from the raw Purex waste to the solidified glass product, a plant designed to process 1000 gal/d of waste would require a crucible of less than 0.2 ft³ capacity.

As stated previously, it is planned to treat the off-gases from the high-temperature step by condensation, which separates out a large proportion of the constituents, and then by distillation of the condensate to remove as much of the sulphate as possible in a decontaminated state before cycling the residual liquid back to the system. A series of experiments has been carried out to determine general characteristics in processing the off-gases from the Purex-phosphate process but only two experiments included sampling for chemical analyses of the various portions.

In the first of these experiments 10 l of simulated Purex waste, already concentrated by a factor of 10, were mixed with 2 l of 85% H₃PO₄ and the solution processed by boiling without reflux to a temperature of 130°C. At this point the volume of the solution had been reduced by a factor of 3.8. The off-gas constituents were recovered by condensation and analyses of the condensate show that 92% of the nitrate was recovered along with 0.0075%
of the phosphate and 1.92% of the ruthenium. The solution was then pumped to the platinum crucible for glass formation at 1100°C. Off-gases from the crucible were condensed and analyses of the condensate showed the following percentages of the various constituents in terms of the original amounts, i.e. HNO$_3$ - 2.5%, H$_3$PO$_4$ - 0.3%, H$_2$SO$_4$ - 86.0%, Ru - 6.6%, Fe - 0.006%, Na - 0.008%, Cs* - 0.007%, Mo - 0.29%, Zr - not detectable.

In the second experiment a 400-ml aliquot of the condensate from the previous experiment was distilled to a temperature of 340°C. At this point the volume reduction was by a factor of 12, and 73.7% of the sulphate had been carried over along with 0.61% of the phosphate. The liquid residue was then further distilled to a temperature of 350°C where it was reduced in volume by an additional factor of 2.3 and found to contain 8.8% of the sulphate and 99.3% of the phosphate based on the amounts originally present in the aliquot. The over-all volume reduction, therefore, was by a factor of 28 and the final residue still remained in the clear liquid state upon cooling. The residue was found to be readily converted to a glass without further additives. It is planned to carry out an extensive study on the off-gas system to determine the extent of decontamination of the high sulphate effluent from the plant. Analysis of the Purex-phosphate glass itself showed no detectable nitrate or sulphate but a ruthenium content of 87% of the amount added to the waste.

Concurrent with the development of a process for forming phosphate glass from Purex waste, a number of experiments were carried out with simulated aluminium-nitrate (Redox wastes). Several satisfactory appearing glasses have been made at 1100°C with suitable adjustment in the relative amounts of aluminium, iron, sodium and phosphate. The volume of Redox phosphate glass is about 1.5 times the bulk volume of the aluminium oxide which would be produced by direct calcination of the same amount of aluminium nitrate involved. This small disadvantage in volume reduction might well be compensated for, with respect to over-all storage-space requirements, simply through the higher thermal conductivity of the glass as compared with that of the bulk aluminium oxide. No tests have been made on the leachability of Redox-phosphate glasses as yet but they should be essentially non-leachable as compared with the highly leachable product from calcined aluminium nitrate. It is planned to carry out a programme of study directed toward the development of a Redox-phosphate glass process in conjunction with the development of a Purex-phosphate glass process. Darex-type wastes would also seem to fit readily into this development programme. Bench-scale experiments, with simulated Redox waste, using the apparatus shown in Fig. 2 and the continuous mode of operation, were carried out for a total of 85 hr. Fe and PO$_4$ were added to the waste in amounts to give mole ratios for Al$_2$O$_3$ : Fe$_2$O$_3$ : P$_2$O$_5$ : Na$_2$O of 1.0 : 0.63 : 4.1 : 0.25.

A variety of phosphate-glass compositions have been studied experimentally with particular attention to devitrification and leachability. Since the leachability of fission products from the glass is somewhat proportional to the exposed surface area, it is desirable that the glass remain vitrous...
and free from cracks. The triangular plot Fig. 3 shows some of the compositions which were studied. The iron to sodium ratio along the line starting at the point marked IWW is the same as would be found in a typical Purex waste. The triangular diagram permitted the plotting of only two variables in addition to the $P_2O_5$, however, the experiments involved a full complement of cations representative of Purex waste. Since Fe and Na are normally present in concentrations appreciably exceeding those of the other cations this choice of variables is indicated. Glasses free of any devitrified areas resulted when the mol percent of $P_2O_5$, considering the three components only, was in the neighbourhood of 70. The black dots in the diagram indicate the starting compositions and the lengths of the arrows represent the loss of $P_2O_5$ from the original feed as determined by analysis of the glass produced. Glasses of almost identical composition were made starting with solutions made up with different ratios of $H_3PO_4$ to Purex salts. This indicates that the excess $P_2O_5$ was removed. Similar studies were carried out with respect to Redox-phosphate glass, see Fig. 4.

Up to this point, studies on the phosphate glasses have emphasized the elements of simplicity in carrying out the process steps for the entire
glass-forming operation rather than the quality of high stability in the final product. Stability of product, however, must be considered a matter of first importance if we are to adhere to the principle of ultimate disposal by fixation in solids. The results of leach tests obtained with phosphate glasses made from a Purex-type waste are shown in Tables II and III. The leach rates compare favourably with those obtained from studies on other types of glasses. More extensive leaching experiments with a wider range of Fe$_2$O$_3$ : NaO : P$_2$O$_5$ values are at present underway.

The radiation stability of phosphate glasses is a matter for future study since only a few low-level experiments have been carried out in this area. Purex-phosphate glass samples periodically withdrawn from the gamma facility thus far have shown no signs of devitrification, upon examination by X-ray defraction, after a total exposure of 4.8 X 10$^8$ r. Polished samples of these glasses after the same exposure period, showed no deterioration upon visual inspection.

In order to investigate the problems of phosphate-glass production on a more realistic operations level, an engineering scale plant was designed and constructed this past year. A diagramatic flow-sheet for the plant is shown in Fig. 5 and a photograph of the plant in Fig. 6. As in the case of the bench-scale apparatus, the plant consists essentially of a feed mixing tank, a combined evaporator and denitrator, a high-temperature furnace.
### TABLE II

**LEACHING RATES FOR PUREX-TYPE PHOSPHATE GLASS CONTAINING Ce\textsuperscript{144} AS A TRACER**

<table>
<thead>
<tr>
<th></th>
<th>L* in cm/week</th>
<th>pH = 4 HNO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H\textsubscript{2}O</td>
<td></td>
</tr>
<tr>
<td>1st week</td>
<td>8.80 x 10^{-7}</td>
<td>9.80 x 10^{-7}</td>
</tr>
<tr>
<td>2nd week</td>
<td>1.29 x 10^{-6}</td>
<td>2.22 x 10^{-6}</td>
</tr>
<tr>
<td>4th week</td>
<td>2.30 x 10^{-6}</td>
<td>2.89 x 10^{-6}</td>
</tr>
<tr>
<td>5th week</td>
<td>2.45 x 10^{-6}</td>
<td>4.65 x 10^{-6}</td>
</tr>
<tr>
<td>7th week</td>
<td>2.63 x 10^{-6}</td>
<td>4.68 x 10^{-6}</td>
</tr>
<tr>
<td>8th week</td>
<td>2.24 x 10^{-6}</td>
<td>3.20 x 10^{-6}</td>
</tr>
</tbody>
</table>

L* = C\textsubscript{1}/C\textsubscript{2}DS

\nC\textsubscript{1} = activity leached per gram of glass in one week

\nC\textsubscript{2} = initial activity per gram of glass

D = density in g/cm\textsuperscript{3}

S = surface area in cm\textsuperscript{2}/g

Glass-particle size: 35/45

### TABLE III

**LEACHING RATES FOR PUREX-TYPE PHOSPHATE GLASS CONTAINING Sr\textsuperscript{90} AS A TRACER**

<table>
<thead>
<tr>
<th></th>
<th>L* in cm/week</th>
<th>pH = 4 HNO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H\textsubscript{2}O</td>
<td></td>
</tr>
<tr>
<td>1st week</td>
<td>4.78 x 10^{-7}</td>
<td>4.90 x 10^{-7}</td>
</tr>
<tr>
<td>2nd week</td>
<td>5.45 x 10^{-7}</td>
<td>1.37 x 10^{-6}</td>
</tr>
<tr>
<td>4th week</td>
<td>1.00 x 10^{-6}</td>
<td>2.27 x 10^{-6}</td>
</tr>
<tr>
<td>5th week</td>
<td>1.94 x 10^{-6}</td>
<td>3.70 x 10^{-6}</td>
</tr>
<tr>
<td>7th week</td>
<td>1.59 x 10^{-6}</td>
<td>3.90 x 10^{-6}</td>
</tr>
<tr>
<td>8th week</td>
<td>1.51 x 10^{-6}</td>
<td>2.50 x 10^{-6}</td>
</tr>
</tbody>
</table>

L* = C\textsubscript{1}/C\textsubscript{2}DS

\nC\textsubscript{1} = activity leached per gram of glass in one week

\nC\textsubscript{2} = initial activity per gram of glass

D = density in g/cm\textsuperscript{3}

S = surface area in cm\textsuperscript{2}/g

Glass-particle size: 35/45 mesh
Fig. 5

Flow diagram - phosphate glass plant
Phosphate glass pilot plant

and platinum-lined crucible and an off-gas condenser and scrubber system. The plant has not been operated as a unit as yet because of delays in procuring the platinum crucible. For initial test purposes an evaporator-denittrator unit was made up from a 6-in internal-diam. glass pipe, 40 in long, with two 1.2-kW cartridge immersion heaters sheathed in Carpenter 20 pipe. The unit, which was connected with the plant water-coil condenser, was operated for several weeks at controlled temperatures ranging between 130°C and 180°C. Volume reductions up to a factor of 6 were obtained when the temperature was held at 130°C; the solution maintained the consistency of a medium syrup without any formation of solids when held at this temperature for several days. With the higher temperature, in the neighbourhood of 180°C, solids formed on standing overnight. For service in this range of temperatures it had been found that Carpenter 20 showed good resistance to corrosion.

The high-temperature crucible is 8 in in diam. and 24 in high and made up of a liner of platinum 0.040 in in thickness supported by an outer vessel constructed of Inconel 600. An aluminium oxide layer deposited on the platinum serves to separate the two metals and prevent migration from the alloy into the platinum. An overflow tube, the outlet of which is equipped with a freeze valve, is positioned so as to maintain the level of the molten glass 12 in above the bottom. A baffle is provided to prevent short-circuiting and to insure uniform retention for glass formation. With the hold-up volume of 2.6 gal, it is estimated that the crucible and, therefore, the entire plant will have a capacity for producing 1 kg/d of glass. The quantity of raw Purex waste thus processed would be roughly 1000 gal.
О ТЕПЛОВЫДЕЛЕНИИ ВЫСОКОРАДИОАКТИВНЫХ ТВЕРДЫХ ПРЕПАРАТОВ В СВЯЗИ С ПРОБЛЕМАМИ ИХ ЗАХОРОНЕНИЯ И ИСПОЛЬЗОВАНИЯ

П.В. ЗИМАКОВ, Б.С. КОЛЫЧЕВ, В.В. КУЛИЧЕНКО, Ю.П. МАРТЫНОВ
СССР

Abstract — Résumé — Аннотация — Resumen

THE HEAT RELEASE FROM HIGH-ACTIVITY SOLID SUBSTANCES IN RELATION TO THE PROBLEM OF THEIR BURIAL AND USE. Heat release is of special significance when transforming high-activity liquid wastes into solid substances and especially when these solids are buried. The author considers possible ways of taking off and using the heat in the melting of glass-forming mixtures. This method makes it possible to keep temperature increases in the burial grounds within given limits, without resorting to external cooling. In the long run, this method may provide means for the safe disposal of high-activity substances for an indefinite period.

LE DÉGAGEMENT DE CHALEUR DES PRÉPARATIONS SOLIDES FORTEMENT RADIOACTIVES ET LES PROBLÈMES QU’IL POSE POUR LEUR ENFOUISSEMENT ET LEUR UTILISATION. Dans la transformation des déchets liquides fortement radioactifs en produits solides, et plus particulièrement dans l’enfouissement de ces derniê­res, le dégagement de chaleur joue un rôle important. Les auteurs examinent certaines considérations dont on peut s’inspirer pour le choix des éléments constitutifs du mélange vitreux et des procédés de fusion de ce mélange. La méthode indiquée permet d’empêcher que la température dans l’entrepôt souterrain s’élève au-dessus de la température prévue, sans qu’il soit besoin de recourir à un refroidissement par des agents extérieurs. Elle permet, en dernière analyse, de créer les conditions nécessaires pour assurer, en toute sécurité, l’enfouissement à demeure des produits fortement radioactifs.

О ТЕПЛОВЫДЕЛЕНИИ ВЫСОКОРАДИОАКТИВНЫХ ТВЕРДЫХ ПРЕПАРАТОВ В СВЯЗИ С ПРОБЛЕМАМИ ИХ ЗАХОРОНЕНИЯ И ИСПОЛЬЗОВАНИЯ. В процессе переработки жидких радиоактивных отходов в твердые продукты, и особенно при захоронении последних, особое место занимает тепловыделение. Рассматриваются одно из возможных направлений отбора и использования тепла в процессе плавления стеклообразующей миши. Этот прием позволяет предотвратить повышение температуры в могильнике выше заданной, не прибегая к охлаждению внешними агентами. В конечном результате этот метод может позволить создать условия для обеспечения безопасного захоронения высокоактивных продуктов на вечные времена.

DESPRENDIMIENTO DE CALOR POR RESIDUOS SÓLIDOS DE ELEVADA ACTIVIDAD Y PROBLEMAS CONÉCTICOS DE EVACUACIÓN Y APROVECHAMIENTO. En la transformación de los desechos líquidos de elevada actividad en productos sólidos, y en particular al enterrar estos últimos, el desprendimiento de calor asume gran importancia. Los autores examinan una de las posibles formas de disipar y aprovechar ese calor en el proceso de fusión de mezclas vitreas. El método permite evitar la elevación de temperatura en el depósito subterráneo sin recurrir a agentes externos de enfriamiento. Es posible que perfeccionando el procedimiento se logren crear las condiciones requeridas para enterrar permanentemente y sin riesgos los desechos de elevada actividad.

Неизменным спутником любых продуктов, содержащих радиоизотопы, является саморазогрев за счет тепла, выделяющегося при радиоактивном распаде. У радиоактивных отходов атомных производств, благодаря наличию долгоживущих осколочных изотопов, генерация тепла наблюдается в течение многих лет [1].

В процессе переработки жидких высокоактивных отходов в твердые плавленные препараты и, тем более, в процессе захоронения последних вопросы тепловыделения занимают особое место [2,3].
При переработке радиоактивных отходов естественно стремление к концентрированию осколочных изотопов в минимальных объемах, что приводит к созданию плавленных препаратов с высокой удельной активностью и, соответственно, высоким удельным тепловыделением (табл.1). Это приводит к значительному саморазогреву препаратов, подлежащих вечному захоронению.

Таблица 1

УДЕЛЬНОЕ ТЕПЛОВЫДЕЛЕНИЕ ПЛАВЛЕННОГО КОНЦЕНТРАТА ОСКОЛОЧНЫХ ИЗОТОПОВ ккал/л·час
(ЗА СЧЕТ $\gamma + \beta$ ИЗЛУЧЕНИЯ)

<table>
<thead>
<tr>
<th>Возраст осколков</th>
<th>Удельная первоначальная активность препарата, кюри/л</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3000</td>
</tr>
<tr>
<td>120 дней</td>
<td>10,0</td>
</tr>
<tr>
<td>1 год</td>
<td>2,20</td>
</tr>
<tr>
<td>2 года</td>
<td>0,78</td>
</tr>
<tr>
<td>5 лет</td>
<td>0,14</td>
</tr>
</tbody>
</table>

Величина саморазогрева зависит от количества выделяющегося тепла и условий его отдачи в окружающую среду. Из расчетных данных, приведенных в табл.2, видно, что регулирование температуры одиночного блока возможно путем ограничения его размеров (в случае цилиндрической формы - радиуса цилиндра).

Однако даже при ограничении размеров блоков их большое скопление в могильнике потребует специального теплосъема.

В табл.3 приводятся некоторые характеристики могильников высокоактивных плавленых препаратов, с применением различных систем теплоотвода, обеспечивающих температуру в могильнике не выше заданной.

При захоронении в могильниках скапливаются блоки, общая активность которых достигает миллионов кюри, а тепловыделение за период хранения достигает миллионов килокалорий (табл.4). Этот факт приводит к задаче использовать выделяющееся тепло для полезных целей одновременно с решением вопроса поддержания определенной температуры блоков.

Одним из возможных путей регулирования температуры в могильнике является проведение в нем эндоэтермического процесса. Таким процессом может быть процесс плавления.

С целью определения принципиальных условий использования плавления стеклообразующей шихты для поддержания на заданном
ЗАВИСИМОСТЬ СТАЦИОНАРНОЙ ТЕМПЕРАТУРЫ ВЫСОКОРАДИАКТИВНОГО БЛОКА ОТ УДЕЛЬНОЙ АКТИВНОСТИ И РАЗМЕРОВ (БЕЗ ПРИНУДИТЕЛЬНОГО ОХЛАЖДЕНИЯ, НА ВОЗДУХЕ)

<table>
<thead>
<tr>
<th>Удельная активность, кюри/л</th>
<th>Температура в центре препарата, °С для цилиндров диаметром</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 см</td>
</tr>
<tr>
<td>125 ООО</td>
<td>42 ООО*</td>
</tr>
<tr>
<td>25 ООО</td>
<td>8 400*</td>
</tr>
<tr>
<td>10 ООО</td>
<td>3 400*</td>
</tr>
</tbody>
</table>

* Учитывая, что термостойкость плавленных препаратов не превышает 1200°С, существование подобных блоков практически невозможно.

уровне температуры в могильнике высокоактивных блоков были поставлены опыты с электромоделированием. Задачей этих опытов являлось определение зависимости температуры в могильнике от количества и удельной активности блоков, количества стеклозающей шихты и необходимой скорости засыпки и некоторых других факторов. Эти же опыты должны были привести к получению необходимых исходных данных для проектирования и сооружения могильников высокоактивных блоков.

Созданная для проведения опытов установка состояла из емкости объемом около куб.метра из шамотного кирпича, окруженной слоем изоляции с наружными габаритами 1,10 x 1,40 м. В качестве изоляции был использован ультралегковес с весьма малым коэффициентом теплопроводности...
<table>
<thead>
<tr>
<th>Тип могильника</th>
<th>Пути регулирования температуры в могильнике</th>
<th>Недостатки</th>
</tr>
</thead>
<tbody>
<tr>
<td>Вертикальные скважины в почве, диаметр которых равен диаметру блоков</td>
<td>Расстояние между скважинами около 3 м; отвод тепла в почву</td>
<td>Сложность загрузки; большая площадь могильника</td>
</tr>
<tr>
<td>Расположение блоков &quot;навалом&quot; в яме без охлаждения</td>
<td>Постепенное заполнение могильника в течение 5 - 10 лет, высота слоя не более 1 - 2 блоков в год</td>
<td>Большая площадь могильника; загрузка не простая</td>
</tr>
<tr>
<td>Расположение блоков &quot;навалом&quot; в яме с принудительным охлаждением воздухом</td>
<td>Большая скорость воздушного потока, продуваемого через навал блоков</td>
<td>Установка фильтров на выходе воздуха; расход электроэнергии для обеспечения работы воздуховодов</td>
</tr>
<tr>
<td>Вертикальные металлические трубы с охлаждением воздушным потоком</td>
<td>Необходимая скорость воздушного потока достигается установкой вытяжной трубы определенного размера (диаметра и высоты)</td>
<td>Сложность загрузки блоков в могильник</td>
</tr>
</tbody>
</table>

Таблица 3
ОБРАЗУЮЩАЯ ШИХТА, РАСПЛАВЛЯЮЩАЯСЯ ПРИ ТЕМПЕРАТУРЕ ОКОЛО 800°С. ШИХТА ЧЕРЕЗ ОПРЕДЕЛЕННОЕ ВРЕМЯ ПЛАВИЛАСЬ, И РАСПЛАВ СЛИВАЛСЯ ЧЕРЕЗ ОТВЕРСТИЕ В ДНЕ ЕМКОСТИ.

При проведении опытов на модельном могильнике было показано, что "производительность" могильника по плавлению стеклообразующей шихты составляет в среднем 2 кг шихты в час на каждый киловатт мощности сверх необходимой для поддержания температуры расплавления шихты. Определенная в результате опытов зависимость количеств выплавляемой шихты от величин удельных активностей блоков приведена в табл. 5.

**Таблица 5**

**КОЛИЧЕСТВО РАСПЛАВЛЯЕМОЙ ШИХТЫ В МОДЕЛЬНОМ МОГИЛЬНИКЕ ОБЪЕМОМ 1 м³, СОДЕРЖАЩЕМ 240 Л ПРЕПАРАТА, ИМИТИРУЮЩЕГО ВЫСОКОАКТИВНЫЙ ПЛАВ РАЗЛИЧНОЙ УДЕЛЬНОЙ АКТИВНОСТИ**

<table>
<thead>
<tr>
<th>Удельная активность кюри/л</th>
<th>6600*</th>
<th>7500*</th>
<th>15 000**</th>
<th>30 000**</th>
</tr>
</thead>
<tbody>
<tr>
<td>кг/час</td>
<td>4,4</td>
<td>6,0</td>
<td>18,7</td>
<td>44</td>
</tr>
<tr>
<td>кг/сутки</td>
<td>105</td>
<td>144</td>
<td>450</td>
<td>1050</td>
</tr>
<tr>
<td>тонна/месяц</td>
<td>3,1</td>
<td>4,3</td>
<td>13,5</td>
<td>31,5</td>
</tr>
</tbody>
</table>

* Достигнуто путем подведения соответствующей электрической мощности.
** Расчетные данные
П.В. ЗИМАКОВ и др.

За длительное время (40) дней проведения опытов в модельном могильнике при различных модельных удельных активностях "захороненных" блоков (от 2,5 до 10 килокюри/л) путем периодической засыпки в могильник стеклообразующей шихты удалось поддерживать температуру в могильнике в пределах 800 - 900°С, причем уровень температуры в этих пределах можно было регулировать количеством подаваемой шихты.

Вышеизложенная система регулирования уровня температуры в могильниках высокорадиоактивных блоков за счет расплавления в них стеклообразующей шихты неизбежно приводит к увеличению общего объема могильника. Однако следует принять во внимание, что наряду с высокоактивными отходами в результате работы атомных заводов образуются жидкие отходы средней и низкой активности, объем которых значительно превышает объем высокорадиоактивных отходов. В качестве стеклообразующей шихты можно использовать такую шихту, получаемую при смещении с соответствующими плавами сухого остатка от кальцинирования менее активных отходов. Такая шихта должна расплавляться до 900°C во избежание расплавления самых высокоактивных блоков.

Вышеуказанный прием позволяет, наряду с поддержанием температуры в могильнике высокоактивных блоков на заданном уровне, превращать в расплав большие объемы маломощных кальцинированных отходов, избегнув необходимости создания для них плавильных агрегатов.

Однако нельзя ограничивать использование высокоактивных концентратов только для этих целей. Свойства плавленого осколочного концентрата, подлежащего захоронению (большая удельная активность, высокая степень локализации радиоизотопов, термическая и радиационная устойчивость) позволили рекомендовать его в качестве мощных источников ионизирующих излучений [4,5]. Интенсивное энерговыделение позволяет использовать такие препараты в качестве тепловых источников для различных целей. В частности, плавленые препараты, полученные при переработке высокорадиоактивных отходов, могут быть использованы в качестве изотопных источников электроэнергии. Такие источники тока в настоящее время привлекают к себе большее внимание.

Приведенные в табл. 6 данные обосновывают возможность использования подобных препаратов для тех случаев, когда вес и объем генератора не очень ограничиваются.

Для сравнительно мощных источников кратковременного действия (3 - 5 месяцев) наиболее целесообразно использовать препарат с возрастом осколков 120 - 180 дней. Для источников небольшой мощности, но продолжительной службы, целесообразно использовать препараты с возрастом 2 года.

Из вышеизложенного видно, что тепловыделение плавленых осколочных препаратов, получаемых при переработке высокоактивных отходов атомных производств, создает трудности при организации могильников. Однако, можно подобрать конструкцию могильника, при которой тепловыделение может быть использовано для расплавления шихты из низкоактивных отходов. В таком могильнике после осты-
Тепловыделение высокорадиоактивных препаратов

Таблица 6

Мощность тепловыделения осколочных концентратов в зависимости от активности и возраста радиоизотопов

<table>
<thead>
<tr>
<th>Возраст осколков</th>
<th>Удельная активность кюри/л</th>
<th>Мощность тепловыделения с учетом полного поглощения γ и β излучения, вт/л</th>
<th>Мощность тепловыделения без учета поглощения γ-излучения, вт/л</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 дней</td>
<td>8,1·10⁴</td>
<td>290</td>
<td>88</td>
</tr>
<tr>
<td>180 дней</td>
<td>5,3·10⁴</td>
<td>190</td>
<td>60</td>
</tr>
<tr>
<td>2 года</td>
<td>1,3·10⁴</td>
<td>43</td>
<td>13</td>
</tr>
<tr>
<td>5 лет</td>
<td>0,3·10⁴</td>
<td>8</td>
<td>3</td>
</tr>
</tbody>
</table>

вания блоки высокоактивных препаратов оказываются заключенными в монолитный блок из стекла, что создает условия для их безопасного вечного захоронения.

Литература


Обсуждение

E. GLUECKAUF: I considered the possibility of utilizing the heating capacity of mixed fission-product waste a long time ago, but came to the conclusion that the utilisable heat was equivalent to less than 1 per cent of the electric power obtainable by fission. Hence, any utilization would seem to be quite uneconomical, particularly as new investments would have to be made to obtain the heat in a utilisable form.
B. KOLYCHEV (Chairman): The point is that we obtain this heat free. Moreover, in using this heat, we can regulate the temperature of the buried blocks without having to provide any additional cooling systems, such as air cooling or other methods. I certainly did not wish to imply that this process is the only possible solution; it is just one of many possible solutions, and needs to be discussed further. Nevertheless, we are carrying on this work and our group hopes that it may be of interest to engineers as a solution to the problem of burial-ground design.
SOLIDIFICATION AND FIXATION OF LIQUIDS - MISCELLANEOUS METHODS

(Part 3)
TREATMENT OF HIGHLY ACTIVE LIQUID WASTES BY MINERAL ION-EXCHANGER SEPARATION

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Abstract — Résumé — Аннотация — Resumen

TREATMENT OF HIGHLY-ACTIVE LIQUID WASTES BY MINERAL ION-EXCHANGER SEPARATION. The method studied at the BELCHIM-CEN Laboratories at Mol is based on a partial deacidification of the highly acid effluent and the complete separation of the Sr90 and Cs137 isotopes by selective adsorption on mineral ion exchangers. After storage and simple chemical treatment, the mother liquor may then be discharged.

Preparation methods, structure and exchange properties in different media were studied in respect of two mineral ion exchangers - zirconium phosphate and ferrocyanide molybdate complex. The results of Cs137 and Sr90 separation by means of these exchangers are given. The decontamination factors obtained with synthetic solutions (Purex) were at least 106 in respect of Cs137 and Sr90.

By selecting appropriate elution conditions it was possible to recover, in 5 vol. of eluent beds, 99.9% of Cs137, adsorbed on zirconium phosphate.

TRAITEMENT D’EFFLUENTS LIQUIDES FORTEMENT ACTIFS, FONDÉ SUR UNE SÉPARATION DES ÉCHANGEURS D’IONS MINÉRAUX. Le principe de la méthode étudiée aux laboratoires de BELCHIM-CEN à Mol repose sur la désacidulation partielle de l’effluent fortement acide et la séparation complète des radioéléments Sr90 et Cs137 par adsorption sélective sur des échangeurs d’ions minéraux. La solution mère peut alors être évacuée après stockage et traitement chimique élémentaire.

Pour deux échangeurs d’ions minéraux, le phosphate de zirconium et le complexe ferrocyanure-molybdate, on a étudié les méthodes de fabrication, la structure et les propriétés d’échange dans différents milieux. On donne des résultats de la séparation de 137Cs et 90Sr au moyen de ces échangeurs. Les facteurs de décontamination obtenus pour des solutions synthétiques (Purex) étaient d’au moins 106 pour le 137Cs et le 90Sr.

En choisissant des conditions d’éluion appropriées, il a été possible de récupérer, en cinq volumes de lit d’éluant, 99,9% du 137Cs, adsorbé par le phosphate de zirconium.

ОБРАБОТКА ЖИДКИХ РАДИОАКТИВНЫХ ОТХОДОВ ВЫСОКОЙ АКТИВНОСТИ НА НЕОРГАНИЧЕСКИХ ИONOОБМЕННИКАХ. Метод, исследуемый в лабораториях Центра ядерных исследований в Моле, основывается на частичном уменьшении кислотности сильно кислых эфлюентов и полном выделении изотопов Sr90 и Cs137 путем селективной адсорбции на минеральных ионообменниках. После хранения и простой химической обработки оставшийся раствор может быть сброшен.

Два неорганических ионообменника - фосфат циркония и ферроцианид-молибдатный комплекс - были изучены с точки зрения методов излучения, структуры и ионообменных свойств в различной среде. Приводятся результаты отделения Cs137 и Sr90 с помощью этих обменников. Коэффициенты очистки, полученные для искусственных растворов (имитирующих отходы “Пурекс-процесса”), были по крайней мере порядка 106 для Cs137 и Sr90.

TRATAMIENTO DE EFLUENTES LÍQUIDOS DE ALTA ACTIVIDAD, BASADO EN UNA SEPARACIÓN MEDIANTE INTERCAMBIADORES DE IONES MINERALES. El método estudiado en los laboratorios de BELCHIM-C.E.N., en Mol, se basa en la desacidulación parcial de los efluentes muy radiactivos y en la separación completa de los radioelementos Sr90 y Cs137 por adsorción selectiva mediante intercambiadores de iones minerales. Después de esa operación es posible evacuar la solución madre, luego de almacenarlá y someterla a un tratamiento químico elemental.

Se han estudiado los métodos de fabricación, la estructura y las propiedades de intercambio en diferentes medios, de dos intercambiadores de iones minerales, a saber, el fosfato de circonio y el complejo ferrocianuro-molibdato. Se exponen los resultados de la separación del 137Cs y del 90Sr por medio de dichos intercambiadores. Los factores de descontaminación obtenidos con soluciones sintéticas (Purex) alcanzan por lo menos a 106 para el 137Cs y el 90Sr.
Eligiendo condiciones de elución apropiadas, se pudo recuperar, en cinco volúmenes de lechos de eluyente, el 99,9% del $^{137}\text{Cs}$ adsorbido por el fosfato de circonio.

I. INTRODUCTION

The separation of caesium and strontium from the highly active fission-product solutions was proposed by GLUECKAUF [1] as a possible way of avoiding long-term storage of large volumes of highly corrosive liquids. However, it is quite clear that the success of this procedure depends upon its operational simplicity and the degree of separation achieved.

RODGER and FINEMAN [2] drew attention to the quantitative aspects of the separation and calculated that decontamination factors as high as $10^7$ were necessary before the required storage period could be reduced from over 300 yr to 10 or 20 yr.

Precipitation methods were studied but the decontamination factor was usually of the order of $10^2$. The Ni-, Co-, or Zn-ferrous cyanide methods [3] or tungstate methods [4] were studied for separation of $^{137}\text{Cs}$ and alkaline phosphate or sulphate flocculation for the removal of $^{90}\text{Sr}$ [5].

The tungstate method [4] is the only one which removes caesium almost quantitatively (decontamination factor - DF $\approx 10^4$) from acid medium whereas, for $^{90}\text{Sr}$, according to present knowledge, either in the acid or in the alkaline medium, no precipitation method was developed which gives a decontamination factor higher than $10^2$ in a single step.

Separation of caesium and strontium by ion exchange was considered, but recovery and decontamination factors for strontium in the 0.1 to 0.5-M acidity range were mostly low.

Synthetic zeolites and clay minerals require partial deacidification followed by the neutralization of the solution up to a pH-value, where precipitation of rare earths and iron occurs.

This colloidal slurry of hydroxides is troublesome from an operational standpoint, as it is very difficult to handle, and adsors a non-negligible amount of strontium. The latter phenomenon reduces the over-all efficiency of the system because a part of the dangerous radioelement still remains with the bulk of inactive or short-lived material.

The aim of this report is to present the basic elements of a treatment scheme in which caesium and strontium are quantitatively separated from an acid fission-product solution by adsorption on artificial mineral ion exchangers.

II. CHARACTERISTICS OF THE REPROCESSING WASTE SOLUTIONS

At the present stage of the study only these reprocessing methods can be considered which lead to a waste solution with a relatively low salt content.

As is shown in Table I, the Purex and Butex processes are by far the most advantageous [7, 8, 9].

It is important to note that, beyond the macro-components, the fission products do not occur as tracer elements but in concentrations of almost g/l. Furthermore the cooling period after discharge from the reactor influences primarily the radiochemical composition of the fission-product
TABLE I
SALT CONTENT OF NON-EVAPORATED WASTES FROM DIFFERENT REPROCESSING SYSTEMS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Purex</th>
<th>Butex</th>
<th>TBP-25</th>
<th>Zirflex</th>
<th>Thorex</th>
<th>Hexone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.004</td>
<td>0.0092</td>
<td>1.2</td>
<td>0.75</td>
<td>0.05</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01</td>
<td>0.0097</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0004</td>
<td>0.0002</td>
<td>-</td>
<td>&lt;1 g/l</td>
<td>-</td>
<td>&lt;1 g/l</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0002</td>
<td>0.0002</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>-</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>2.36</td>
<td>3.00</td>
<td>0.4</td>
<td>1.0</td>
<td>3.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2.40</td>
<td>3.00</td>
<td>4.0</td>
<td>2.3</td>
<td>3.02</td>
<td>6.0</td>
</tr>
<tr>
<td>F⁻</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.4</td>
<td>-</td>
</tr>
</tbody>
</table>

solution but not so much the content of decayed nuclides (Table II). The reprocessing solutions cooled during 2 to 3 yr contain approximately 250 ppm of Cs¹³⁷, 115 ppm of Sr⁹⁰ + Y⁹⁰; 96 ppm of Pm¹⁴⁷, 250 ppm of Ce¹⁴⁴ (+ Ce¹⁴⁰) and about 22 ppm (Rh + Ru + Pd). During this cooling period the total power of fission product decreases to 1.5 to 2% of its original value.

III. SEPARATION OF Sr⁹⁰ AND Cs¹³⁷ FROM ACID REPROCESSING SOLUTIONS

As indicated before, the purpose of this work is to try the separation of Sr⁹⁰ and Cs¹³⁷ by adsorption on mineral ion exchangers, without previous neutralization of the fission-product solution. This study involves the elaboration of suitable new ion exchangers.

The requirements of a new mineral ion exchanger may be summarized as follows:

- Insolubility in common mineral acids such as HCl and HNO₃;
- Stability against radiation;
- Selectivity or high affinity towards the desired nuclides;
- Easy regeneration and good column characteristics.

Preliminary studies on zirconyl phosphates were done by KRAUS et al. [10, 11] and AMPHLETT et al. [12, 13]. Another mineral ion exchanger, ammonium phosphomolybdate(AMP) was studied by Van R. SMIT et al. [14, 15].

1. Separation and recovery of caesium

In an earlier paper BAETSLE and PELSMAEKERS [16] showed the possibility to produce a well-defined type of zirconyl phosphate, mentioned
TABLE II

FISSION-PRODUCTS CONTENT OF WASTE SOLUTIONS AFTER SEVERAL PERIODS OF COOLING*

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Activity in µc/ml and in % of total present</th>
<th>Amount in ppm (active + inactive)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>after 90 d</td>
<td>after 1.25 yr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(µc/ml) (%)</td>
<td>(µc/ml) (%)</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>33 yr</td>
<td>2.0 $10^4$ 1.64</td>
<td>1.95 $10^4$ 4.5</td>
</tr>
<tr>
<td>Sr$^{90}$</td>
<td>28 yr</td>
<td>2.3 $10^4$ 1.88</td>
<td>2.24 $10^4$ 5.16</td>
</tr>
<tr>
<td>Pm$^{147}$</td>
<td>2.5 yr</td>
<td>9.0 $10^4$ 7.36</td>
<td>6.8 $10^4$ 15.7</td>
</tr>
<tr>
<td>Ce$^{144}$</td>
<td>285 d</td>
<td>6.9 $10^5$ 56.5</td>
<td>2.8 $10^5$ 65.2</td>
</tr>
<tr>
<td>Pr$^{144}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr$^{95}$ - Nb$^{99}$</td>
<td>65 d</td>
<td>2.7 $10^5$ 22.1</td>
<td>5.5 $10^3$ 1.27</td>
</tr>
<tr>
<td>Ba$^{140}$ - La$^{140}$</td>
<td>12.8 d</td>
<td>5.2 $10^3$ 0.41</td>
<td>-</td>
</tr>
<tr>
<td>Ru$^{103}$ - Rh$^{103}$</td>
<td>40 d</td>
<td>3.5 $10^4$ 2.87</td>
<td>63.7 0.14</td>
</tr>
<tr>
<td>Ru$^{106}$ - Rh$^{106}$</td>
<td>1 yr</td>
<td>7.2 $10^4$ 5.9</td>
<td>3.6 $10^4$ 8.3</td>
</tr>
<tr>
<td>Sr$^{96}$</td>
<td>50 d</td>
<td>1.6 $10^4$ 0.16</td>
<td>1.0 $10^3$ 0.23</td>
</tr>
</tbody>
</table>

* The fission products from 1 ton of irradiated U (2500 MWd/t at 5 MW/t) are contained in 378 l of solution (basic data taken from R. E. TOMLINSON) [6].
further as ZrP, with reproducible chemical and physical properties. For its structure the following formula was suggested.

\[
\begin{array}{c}
\text{Zr} & \text{O} & \text{Zr} & \text{O} & \text{Zr} \\
\text{OH} & \text{H}_2\text{O} & \text{OH} & \text{OH} & \text{OH}
\end{array}
\]

The theoretical total capacity amounts to 4.56 meq/g at pH 7. The stability of ZrP is confined to the acid medium (pH 0 to 7) as, above pH 7, the phosphate groups are hydrolised off and replaced by OH groups.

In subsequent papers BAETSLE et al. [17, 18] reported the radiochemical and thermodynamic properties of ZrP. From these studies it is evident that caesium can be fixed selectively on ZrP in the presence of relatively large concentrations of inactive salts.

The distribution coefficients of caesium, strontium and europium in trace concentrations are shown in Fig. 1. However, as mentioned above, the con-
centrations of most radioisotopes in reprocessing solutions are not negligible. Fig. 2 illustrates the dependence of the distribution coefficient of caesium upon the carrier concentration.

1.1. Decontamination factor

Special attention was given to the maximum attainable decontamination factor (DF) in the separation of caesium from aged MFP solutions.

1.1.1. Experimental: A mixed fission-product solution, resulting from a PUREX reprocessing cycle and diluted with 0.2 N HNO₃ (5 ml first aqueous waste + 900 ml 0.2 N HNO₃) was passed through a column packed with 5 g of ZrP. The percolate was sampled and examined by $\gamma$-spectrometry. Thereafter, the column was washed with 0.2 N HNO₃ until absence of elutable activity in the wash solution. Finally, the retained Cs was eluted with 6 M HNO₃. The results are summarized in Table III.

1.1.2. Results and discussion: The presence of Ru¹⁰⁶ − Rh¹⁰⁶ and Ce¹⁴⁴ − Pr¹⁴⁴ interfered with the exact determination of Cs¹³⁷ by direct measurement. Therefore, the percolate of the column was scavenged with an oxalic acid solution after addition of lanthanum chloride. The percolate, free of interfering radiation, did not show any detectable amount of Cs¹³⁷. That indicates a minimum DF of $5 \times 10^6$. 

![Fig. 2](image_url)

Distribution coefficients of Cs on ZrP as a function of the Cs carrier content (0.5 N HNO₃)
TABLE III
EXPERIMENTAL RESULTS OF Cs SEPARATION FROM PUREX WASTE SOLUTIONS.

<table>
<thead>
<tr>
<th></th>
<th>Cs$^{137}$ (µC/ml)</th>
<th>Rh$^{194}$ - Rh$^{196}$ (µC/ml)</th>
<th>Ce$^{144}$ - Pr$^{144}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed solution</td>
<td>1.1</td>
<td>0.13</td>
<td>100††</td>
</tr>
<tr>
<td>Percolated feed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 ml</td>
<td>non-detectable</td>
<td>1.0 x 10^{-2}</td>
<td>13</td>
</tr>
<tr>
<td>300 ml</td>
<td>*</td>
<td>1.5 x 10^{-2}</td>
<td>82</td>
</tr>
<tr>
<td>600 ml</td>
<td></td>
<td>1.6 x 10^{-2}</td>
<td>120</td>
</tr>
<tr>
<td>900 ml</td>
<td></td>
<td>1.7 x 10^{-2}</td>
<td>120</td>
</tr>
<tr>
<td>0.2 N HNO$_3$ wash</td>
<td>non-detectable</td>
<td>-</td>
<td>tracer</td>
</tr>
<tr>
<td>solution (200 ml)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 M HNO$_3$</td>
<td>4.5</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* The presence of other nuclides interferes with the $\gamma$-spectrometric determination background equivalent to 2 x 10^{-4} µC Cs/ml.
** Ce$^{144}$ - Pr$^{144}$ activity is expressed in arbitrary units.

1.2. Recovery of the fixed caesium

The elution of the adsorbed caesium remained difficult, even with 6 M HNO$_3$ and the volume of elutant was too high for practical purposes.

However, a study of the temperature effect in exchange reactions with ZrP [18] demonstrated the possibility of eluting by one bed volume of 0.2 N HNO$_3$ up to 90% of the caesium, when the column was heated to 80-90°C; with 6 M HNO$_3$ at temperature of 90°C, more than 99% of the adsorbed caesium is recovered after passage of less than 5 bed-volumes of eluant.

The temperature dependence of the selectivity coefficients for the system Cs-H and for a few other exchange reactions, is shown in Fig. 3.

The Cs-containing solution can then be evaporated and used for the production of $\gamma$-ray sources or fixed into a disposable form.

1.3. Operational scheme

The aqueous fission-product solution (Purex or Butex) is first de-acidulated to a suitable concentration of HNO$_3$. The formaldehyde process, as studied by HEALY and DAVIES [19] and EVANS [20], seems to be mostly indicated although it leads to HNO$_3$ concentrations of approximately 0.5 M HNO$_3$. Further de-acidulation, needed for an economic use of a ZrP column is obtained by electrodialysis through mineral membranes. The latter process has the advantage that the final concentration of HNO$_3$ can be adjusted to the desired value (0.2 to 0.1 M).
The solution is then percolated through a ZrP column in the H⁺ form. The percolation is stopped as soon as a detectable amount of caesium breaks through. The saturated column is washed in counter-current with 1 vol. of 0.2 M HNO₃ and thereafter warmed up to 80-90°C. A 2 M HNO₃ elutant solution, preheated to the same temperature, removes all of the fixed caesium in 3 to 5 bed volumes. Thereafter, a new cycle of saturation and elution can be started. The flow-sheet outlined above is shown in Fig. 6a.

2. Separation and recovery of strontium

As mentioned above, the separation of strontium in acid medium is a difficult problem and is not as well advanced as the separation of caesium. The particular place of caesium (monovalent, heavy cation) in the table of Mendeljev gives to this element selective physico-chemical properties which facilitate the separation processes.
Strontium has not such selective properties and is therefore more difficult to separate from acid reprocessing solutions.

However, two new types of mineral ion exchangers were recently prepared: ferrous cyanide molybdate and ferrous cyanide tungstate [21]; they have both a very high affinity in acid medium for strontium and rare earths.

2.1. Ferrous cyanide molybdate (FeMo) as ion-exchange material

In the search for new ion exchanging mineral substances, it was found that, on mixing acid solutions of K₄Fe(CN)₆ and (NH₄)₆Mo₇O₂₄, a brown precipitate was formed, more or less stable in acid solution (HCl or dilute HNO₃).

The existence of such a precipitate was mentioned in earlier literature [22, 23, 24] but no ion-exchange characteristics were ascribed to it. The formula of that product is generally represented as follows: (MoO₂)₂Fe(CN)₆.

Further investigation on this substance showed many possible formulations. It was also pointed out that the polymerization of the molybdyl ions in solution and the cationic form of ferrocyanide, are the main controlling factors for the formation of the exchanger.

The factors which determine the polymerization of molybdyl ions in solution are the nature of the molybdyl salt, the concentration of the molybdate and the acidity of the solution. Many studies were reported on this subject although without much consistency in the conclusions.

Details of the investigation about formation, structure and properties of FeMo will be published separately [21]; only the main features are summarized below.

<table>
<thead>
<tr>
<th>Mo/Fe in the starting mixture</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/Mo in starting mixture</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>2</td>
<td>2.06</td>
<td>2.0</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>2.06</td>
<td>1.90</td>
<td>3.8</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>2.06</td>
<td>1.95</td>
<td>3.7</td>
<td>2.75</td>
</tr>
<tr>
<td>6</td>
<td>2.06</td>
<td>1.95</td>
<td>3.5</td>
<td>2.70</td>
</tr>
<tr>
<td>8</td>
<td>2.06</td>
<td>2.0</td>
<td>3.4</td>
<td>2.90</td>
</tr>
<tr>
<td>Mean value of Mo/Fe in product</td>
<td>1.96</td>
<td>2.75</td>
<td>2.74</td>
<td>2.80</td>
</tr>
</tbody>
</table>
2.1.1. Structure of FeMo: The chemicals used during this investigation were dilute solutions of Na$_2$MoO$_4$ and K$_4$Fe(CN)$_6$, both dissolved in 0.5 M HCl. Both solutions were mixed in (Mo/Fe) ratios of 1/1 to 8/1. In all cases the MoO$_4$ content of the mixture was equivalent to 0.1 M/l.

After precipitation, the slurry was washed with 0.2 M HCl, dried at 50°C, and then washed with 1 M HCl solution and dried at 100°C till constant weight.

The unwashed precipitate (A) and the refined product (B) were analysed and the Mo/Fe ratios deduced. They are reported in Table IV.

From these results it appears that the simple formulation (MoO$_2$)$_2$Fe(CN)$_6$ does not apply as soon as the starting mixture has a molybdate/ferrous cyanide ratio higher than 2. For the higher relative concentrations of molybdate in the mixture, the Mo/Fe ratio in the final product fluctuates around 2.75. That indicates the existence of a polymerized molybdyl ion which precipitates with the ferrous cyanide. X-ray investigation shows that the material may not be considered as amorphous.

Taking into account the very rapid changes which occur in the distribution of the molybdenum species during the formation of an insoluble compound [22, 23, 24], the following structures of the molybdyl species in FeMo (Mo/Fe = 2.7 to 2.8) are to be expected:

\[
[\text{MoO}_2]^{++}; [\text{MoO}_3\text{H}]^{+} \text{ and their polymers } [\text{MoO}_2(\text{MoO}_3)_x]^{++} \]
\[
[\text{MoO}_2\text{H}(\text{MoO}_3)_x]^+ \]

with \(x = 1, 2, 3\).

Structure is studied further by combination of X-ray analysis and infra-red spectrophotometry including chemical analysis and density determinations [21].

2.1.2. Radiochemical properties: The exchange properties of the new material for caesium, strontium and rare earths in acid medium are fairly high as compared with those of ZrP. The distribution coefficients of those nuclides on FeMo are shown in Fig. 4. The slopes of the logarithmic curves (-1 for caesium, -2 for strontium and -3 for europium) indicate an ion-exchange phenomenon between the H$^+$ on the exchanger and the tracer in solution. It is also worth noting that the distribution coefficients of strontium on FeMo are of the same order of magnitude as those of caesium on ZrP (see Fig. 1).

The influence of the concentration of strontium in solution on the distribution coefficient is shown in Fig. 5. For higher concentrations of strontium, the distribution coefficient of strontium on FeMo decreases less than what is observed for higher concentrations of caesium in the presence of ZrP. That indicates a much higher exchange rate for FeMo.

The same may be concluded from observation of the contact time, necessary to reach equilibrium, which was about 30 min in all tests with FeMo and 8 to 24 hr in the tests with ZrP.

It must be emphasized that the distribution coefficients of the rare earths are higher than those of strontium. It means that those interfere with the selective adsorption of strontium. Therefore, the main effort is now directed towards the previous separation or sequestration of the rare earths.
Tracer ion-exchange equilibria on FeMo

Fig. 4

Distribution coefficients of Sr on FeMo as a function of the Sr carrier content (0.2 N HNO₃).

Fig. 5
before strontium fixation. The macro-components Na and Fe do not interfere severely with the separation of strontium.

2.2. Preparation and properties of the exchanger ferrous cyanide tungstate (FeMo)

The major disadvantages of FeMo are the complexity of the structure, the difficulty in obtaining a reproducible quality and the lack of complete stability in dilute HNO₃ medium.

The exchanger formed by mixing solutions of ferrocyanide and tungstate does not show these disadvantages although it has similar ion-exchange properties.

However, as this exchanger is in a very early stage of investigation, it will not be discussed here into any more detail.

2.3. Operational scheme for the removal of strontium by FeMo.

As follows from the previous results, the recovery of Sr⁹₀ from dilute acid fission-product solution can be carried out when Cs is first separated by adsorption on ZrP and the rare earths separated or transformed into an anionic complex. The elution of strontium from FeMo is easy to perform with 2 N HCl which regenerates the column and, simultaneously, increases the stability of the ion-exchanging material.

A preliminary flow-sheet is shown in Fig. 6b.

3. CONCLUSION AND COMMENTS

As was indicated in the introduction, this work can lead to a purification and separation method for long-lived fission products and also to a simplification of the highly active waste-treatment methods.

As a way for separation of radioisotopes, the method is successful for the separation of caesium and it is hoped that equivalent results will be obtained for Sr⁹₀.

As a step in waste treatment, the success of the method will depend upon the interference and previous separation of the rare earths and from this standpoint, comments can seem hazardous at the present time.

Nevertheless, the following may be anticipated:

(a) The mineral ion-exchange procedures will permit complete separation between the bulk solution and the long-lived fission products;

(b) Caesium can be fixed with high efficiency and selectivity;

(c) Caesium, if not yet separated, strontium and rare earths may be adsorbed with high efficiency on ferrous cyanide molybdate and thus separated from the bulk of the inactive constituents of the solution;

(d) The latest results show the possibility for a partial removal or sequestration of the rare earths. This will increase the capacity of the exchanger for strontium.

Recently, Euratom agreed on a two years' programme on separation of Sr⁹₀ and Cs¹³⁷ by adsorption on mineral ion exchangers. It is planned
Flow-sheet of Cs recovery from first aqueous waste solutions to extend the present tracer laboratory studies to a 10 to 100-c unit using small volumes of true Purex effluent.

ACKNOWLEDGEMENTS

The authors wish to thank particularly Messrs. D. Huys and K. Peeters for their highly appreciated contribution to the present work.

REFERENCES

L. BAETSLE and P. DEJONGHE


DISCUSSION

F. DUHAMEL (Chairman): What maximum specific activity do you think you will be able to reach, in strontium and caesium, after your treatment?

L. BAETSLE: It depends on the initial specific activity of the saturating solution and on the carrier concentration. It is difficult to give a quantitative reply without having the figures at hand.

E. GLUECKAUF: The separation factor for strontium in your Fig. 5 relates to a 0.2 N solution in nitric acid. Are any data available for the uptake at higher acid concentrations or in the presence of Fe+++ and Al+++?

L. BAETSLE: We did some research on the influence of Fe+++, and up to 0.05 M concentration we did not find any adverse effects on the fixation of Sr on FeMo. We have not yet studied aluminium, as we hope to do our research on Purex waste solutions. For ferrocyanide there is a difference between the molybdate and the tungstate: if we work with molybdate, we can go to 1 or 1.5 M HNO3 without any effect on the physical stability of the exchanger. With tungstate the chemical stability is better and we can go higher but, as you know, the -2/1 slope of the curve decreases the distribution coefficient quite fast at higher concentrations.

J. M. BLUM: You said that for zirconium phosphate it was necessary to reprocess the mineral ion-exchange resins. How do you propose doing this?

L. BAETSLE: When we work with molybdate or tungstate ferrocyanides we are dealing with an ion exchanger which is quite cheap and which can
therefore probably be replaced by new resin after saturation. Reprocessing is, therefore, not strictly necessary, though attempts are being made to discover a reprocessing method which will be effective without impairing the exchanger itself. Zirconium, on the other hand, is much more expensive of course and for the zirconium phosphates it was absolutely essential to consider how the column could be used several times: we studied the effect of temperature and found that it was possible to elute practically all the caesium by raising the temperature to 80 - 90°C and using approximately 2 M acid. We were able to remove 99.9% - that is easy to calculate with the distribution coefficient. Since the zirconium phosphate fixes only caesium and to a much lesser extent rubidium we thus get a pure solution.

P. DEJONGHE: I should like to point out that the study on mineral ion exchangers was done for a dual purpose: one aim was to separate isotopes, the other was to try to find a method of treating high-activity effluent. Zirconium phosphate is more suitable in connection with isotope separation and isotope purification whereas the ferro-cyanide process, which fixes caesium and strontium as well, is of interest in connection with waste treatment.

N. BREZHNEVA: What overall decontamination factor is obtained with dynamic tests in columns filled with the sorbents you suggested?

L. BAETSLE: The overall decontamination factor obtained by passage over a mineral ion-exchanger column depends on the degree of loading of the column. If you use the full capacity of the column you get an effluent concentration of 50% of your initial value, whereas, if you use the capacity of the column up to the first break-through, you make less use of your ion exchanger but get a very high decontamination factor.

In the case of zirconyl phosphate the maximum loading of a column amounts to about 15-20% because the kinetics of the ion-exchange reaction are not very favourable. If this loading is exceeded, caesium breaks through.

In the case of ferro-cyanide molybdate, the kinetics are much more favourable and a far greater part of the available capacity may be used.

Consequently, 'up to a fixed point of saturation the overall decontamination factor will be higher for ferro-cyanide molybdate than for zirconyl phosphate, but the absolute value of the decontamination factor depends on the degree of loading.
ИЗУЧЕНИЕ СОРБЦИИ И МИГРАЦИИ РАДИОЭЛЕМЕНТОВ В ГРУНТАХ

В. Спицин, В.Д. Балукова и Т.А. Ермакова
СССР

Abstract — Résumé — Аннотация — Resumen

STUDIES OF SORPTION AND MIGRATION OF RADIOACTIVE ELEMENTS IN SOILS. The paper presents the results of investigations into the sorption and migration of radioelements during radioactive filtering flow through the soil. For this purpose the author used the types of sand, of average coarseness and effective porosity, which are to be found widely disseminated throughout the central belt of the Soviet Union. It is shown that the sorption of strontium and caesium take place separately and that the capture of caesium by soils is an irreversible process. It is also shown that sorption processes inhibit the filter-diffusion process at low diffusion rates and that the strontium movement is 40-60 times slower than the filtering and the caesium movement 100 times slower.

Trials were made with a method of calculating the basic kinetic parameters of sorption, thus making it possible to characterize the movement of radioactive strontium and describe the migration of radioactive caesium.

SORPTION ET MIGRATION DES RADIOÉLÉMENTS DANS LES SOLS. Les auteurs exposent les résultats d'une étude sur la sorption et le déplacement des radioéléments dans les sols lorsqu'ils sont entraînés par des courants intenses à travers des couches filtrantes. A cet effet, ils ont utilisé des sables de granulation moyenne, à forte porosité, qui sont très répandus dans la zone centrale de l'Union soviétique. Ils montrent que la sorption du strontium et celle du césium se produisent séparément et que la fixation du césium par le sol est irréversible. Ils constatent en outre que, lorsque la diffusion est lente, les processus de sorption tendent à éliminer les processus de diffusion par filtrage et que le mouvement du strontium est de 40 à 60 fois plus lent et celui du césium, 100 fois plus lent que la vitesse de la filtration.

Les auteurs ont éprouvé par voie expérimentale une méthode de calcul des principaux paramètres cinétiques de la sorption, méthode qui a permis à la fin de caractériser le déplacement du radiostrontium et de décrire la migration du radiocésium.

ИЗУЧЕНИЕ СОРБЦИИ И МИГРАЦИИ РАДИОЭЛЕМЕНТОВ В ГРУНТАХ. Излагаются результаты изучения сорбции и продвижения радиоэлементов в условиях движения активного фильтрационного потока через грунты. В работе использовалось широко распространённые в средней полосе Советского Союза пески среднего зерна с активной пористостью. Показано, что сорбция стронция и цезия происходит раздельно и что захват цезия грунтами происходит необратимо. Показано также, что сорбционные процессы подавляют процессы фильтрационной диффузии при низких скоростях диффузии, а также по сравнению с фильтрационным движение стронция проходит в 40-60 раз медленнее, а цезия — в 100 раз.

Был экспериментально опробован метод расчета основных кинетических параметров сорбции, которым позволил характеризовать движение радиостронция и описать миграцию радиоцезия.

ESTUDIO DE LA SORCIÓN Y MIGRACIÓN DE LOS RADIOELEMENTOS EN LOS SUELOS. Los autores exponen los resultados de un estudio de la sorción y el desplazamiento de los radioelementos en los suelos cuando son arrastrados por corrientes de gran intensidad a través de las capas filtrantes. Utilizaron arenas de grano medio y elevada porosidad, que se encuentran en gran abundancia en la zona central de la Unión Soviética. Se comprobó que la sorción del estroncio y el cesio se producen separadamente y que la fijación del cesio por los suelos es irreversible. Asimismo, se observó que los procesos de sorción ejercen un efecto inhibidor sobre los efectos de difusión por filtración cuando la velocidad de difusión es reducida y también que la velocidad de desplazamiento del estroncio es de 40 a 60 veces menor, y la del cesio 100 veces menor que la de la corriente filtrante.

Se verificó experimentalmente un método de cálculo de los principales parámetros cinéticos de la sorción que permite caracterizar el desplazamiento del radioestroncio y describir la migración del radiocezio.
При сбросе жидких радиоактивных отходов в грунтовые формации необходимо предвидеть возможность миграции радиоактивных загрязнений из зоны захоронения. Поэтому, наряду с тщательными гидрогеологическими изысканиями, непременным является исследование сорбции радиоэлементов, прочности их закрепления на грунтах, а также возможности их выноса с фильтрационными потоками.

Данное сообщение относится к изучению сорбции и продвижению радиоэлементов в условиях движения активного фильтрационного потока через грунты. Было поставлено две задачи:

1. Определение отставания активного фронта от границы перемещения фильтрующегося раствора.

2. Установление предельных концентраций очистки растворов от радиоактивных загрязнений данными грунтами.

В работе использовались широко распространенные в средней полосе Советского Союза пески среднего зерна с активной пористостью примерно 30%. Средняя характеристика изучаемых песков приводится ниже.

Химический состав:

<table>
<thead>
<tr>
<th>Компонент</th>
<th>Содержание</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57,0 - 81,1%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10 + 20%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1 + 5%</td>
</tr>
<tr>
<td>MnO</td>
<td>0,03 - 0,1%</td>
</tr>
<tr>
<td>CaO</td>
<td>0,4 + 2%</td>
</tr>
<tr>
<td>MgO</td>
<td>0,8 + 2,3%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0,03 - 0,5%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0,5 + 2%</td>
</tr>
<tr>
<td>S0₃</td>
<td>0,2%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0,5 + 2,3%</td>
</tr>
<tr>
<td>гумус</td>
<td>0,3 + 0,8%</td>
</tr>
</tbody>
</table>

Физико-химические свойства:

Обменная емкость м-экв %/100 г (3,35 - 10,00) (обменные катионы представлены кальцием и магнием); содержание водорастворимых солей (вес %) 0,3 - 0,4; pH водной вытяжки 6,6 - 6,8; удельный вес 2,60 - 2,74 г/см³; объемный вес 1,64 - 1,75 г/см³.

Исследования проводились с наиболее опасными с радиологической точки зрения радиоэлементами - стронцием и цезием из растворов высокой ионной силы, сильно засоленных азотнокислым натрием (200 и 400 г/л). Опыты ставились в статических и динамических условиях. Статические опыты ставились с целью получения максимальных сорбционных емкостей по указанным радиоэлементам при условии практически равновесного распределения как микро- так и микро-компонентов между твердой и жидкой фазами. Динамические исследования проводились на колонках различной длины, при различных скоростях фильтрации в присутствии и отсутствии таких добавок как кальций и магний.

Полученный экспериментальный материал позволил сделать некоторые выводы, в частности:

1. Сорбция стронция и цезия грунтами из нитратных растворов проходит раздельно. Выходные кривые представляют собой две независимые, хорошо выраженные волны.

2. Изменение содержания азотнокислого натрия в растворе 200 - 400 г/л не вносит практических отклонений в сорбционные характеристики. При прочих равных условиях выходные кривые по обоим растворам совпадают.
Таблица 1
СРЕДНИЙ ГРАНУЛОМЕТРИЧЕСКИЙ И МИКРОАГРЕГАТНЫЙ СОСТАВ

<table>
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<th>№ образца</th>
<th>Размер частиц, мм</th>
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</thead>
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<tr>
<td></td>
<td>0,05</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1,32</td>
</tr>
</tbody>
</table>

СОРБЦИЯ И МИГРАЦИЯ РАДИОЭЛЕМЕНТОВ В ГРУНТАХ
3. Как для стронция, так и для цезия наблюдается пропорциональное длине колонны запаздывание начала проскока и полного выхода.

4. Десорбция проходит очень медленно, особенно грунтовой водой. Наличие в десорбционном растворе добавок кальция заметнее оказывается на десорбции осевым раствором и значительно слабее на десорбции грунтовой водой, так как содержание кальция в грунтовых водах средней полосы Советского Союза достаточно высокое и небольшие добавки его не вносят существенных изменений.

5. Скорость просачивания растворов определяет практическую динамическую сорбционную емкость грунтов (естественно в неравновесных условиях) по отношению стронция и цезия, а также скорость достижения равновесного распределения микрокомпонентов между твердой и жидкой фазами, которая в свою очередь определяет время достижения максимальных сорбционных емкостей.

6. При скоростях фильтрации менее 2 см/ч динамические емкости быстро приближаются к статическим равновесным значениям.

7. Установлено, что предельное удаление радиостронция из растворов азотнокислого натрия песчаными грунтами возможно, как правило, лишь до содержания $10^{-8}$ кюри/л. В отдельных случаях, когда пески в мелкодисперсной фракции сильно обогащены минералами, показывающими высокие коэффициенты очистки по стронции, например монтмориллонитом, предельно достигается удаление радиостронция до содержания $2 \cdot 3 \cdot 10^{-10}$ кюри/л.

В дальнейшем основным направлением исследований являлось определение распространения радиоэлементов в фильтрационном потоке.

Для того, чтобы подойти к системе уравнений, описывающих процесс распространения раствора и радиоактивных загрязнений в грунтовом потоке, необходимо было получить или принять определенные зависимости кинетики сорбции, связывающие скорость сорбции с параметрами сорбционного процесса (величинами концентрации и сорбции раствора)*.

Виду того, что сорбция радиоэлементов на грунтах изучалась, как правило, для тех или иных практических целей, вопросам кинетики данных процессов уделялось малое внимание, особенно для сильносольных сред.

Имеющиеся литературные данные позволяют считать основным видом сорбции на грунтах ионный обмен. Это не исключает возможности хемосорбции и физической сорбции, но вероятность образования ионообменных процессов в достаточной степени подтверждена экспериментально. Поэтому в общие исходные положения были приняты общие положения теории сорбции на зернистых материалах.

Из закономерностей этих процессов наиболее целесообразным оказалось использование уравнения обратимой реакции второго по-

* Обработка результатов проводилась при консультации В.М. Шестакова.
СОРБЦИЯ И МИГРАЦИЯ РАДИОЭЛЕМЕНТОВ В ГРУНТАХ

рядка, широко применяемого в практике работы с зернистыми материями:

\[ \frac{dN}{dt} = \alpha \left[ C \left( 1 - \frac{N}{N_0} \right) - \frac{N}{N_0} \left( C_0 - C \right) \right], \]  

где

- \( \alpha \) - коэффициент скорости сорбции;
- \( N \) - количество сорбированного вещества;
- \( C \) - концентрация раствора в порах грунта;
- \( \bar{F} \) - параметр равновесия, причем \( \bar{F} = \frac{1}{K} \),

где \( K \) - константа обмена.

При малых концентрациях \( \bar{F} \approx 1 \), тогда уравнение (1) может быть преобразовано в уравнение линейной кинетики

\[ \frac{dN}{dt} = \alpha (C - \beta N), \]  

где

- \( \beta = \frac{C_0}{N_0} \);
- \( C \) - концентрация текущая;
- \( \alpha \) - параметр скорости сорбции;
- \( \beta \) - параметр сорбционного равновесия;
- \( C_0 \) - максимальная концентрация.

Для линейной кинетики сорбции Тодесом и Рачинским были даны основы метода обработки результатов для случая, когда явлением гидравлической дисперсии можно пренебречь, т.е. при низких скоростях фильтрации.

Совместное решение уравнения линейной кинетики и фильтрационного балансового уравнения приводит к уравнению, описывающему распределение концентраций \( C \) раствора в переходной зоне, выраженное через \( \xi \). Переходной зоной называется область, начиная от появления следов активных загрязнений до полного их выхода.

Так как содержания активных загрязнений в растворах невелики, можно принять следующее положение:

- \( C/C_0 = 0,05 \) - появление заметных загрязнений;
- \( C/C_0 = 0,5 \) - прохождение центра сорбционной волны.

Согласно уравнения Тодеса и Рачинского, в основной части выходной кривой должна сохраняться прямолинейная зависимость между величиной \( \frac{\phi}{\xi} \) и временем \( t \), причем \( \phi = \frac{C}{C_0} \), где \( \phi (\xi) = (1 - 2) C/C_0 \), (3)

где \( \phi (\xi) \) - интеграл вероятности или функция Гаусса-Крампа, определяемая по специальным таблицам.

Таким образом, зная исходную концентрацию радиоэлементов и его концентрацию для различных точек выходной кривой, всегда можно найти по уравнению (3) значения \( \phi (\xi) \), а по таблицам - значения
самой функции $\xi$. Затем, построив график зависимости $\xi v_t$ от времени, можно получить значения времени прохождения середины волны - $t_0$. Зная $t_0$, по формуле $\beta = \frac{\eta 1}{v t_0 - \eta 1}$ находим параметр равновесия, где $\eta$ - пористость грунта, $1$ - длина колонны $v$ - скорость фильтрации.

По тангенсу угла наклона $\theta$ к оси $t$ определяется параметр скорости сорбции по формуле:

$$\alpha = 4 \frac{1 + \beta}{\beta} \tan^2 \theta.$$

Пример полученных таким расчетом результатов можно видеть в табл.2.

Таблица 2

<table>
<thead>
<tr>
<th>Раствор</th>
<th>№ колонок</th>
<th>$\text{Sr}$</th>
<th>$\text{Cs}$</th>
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</thead>
<tbody>
<tr>
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<td>2631,4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0,0754</td>
<td>1834,4</td>
</tr>
<tr>
<td>400 г/л $\text{NaNO}_3$</td>
<td>3</td>
<td>0,0828</td>
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<td>4</td>
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</tbody>
</table>

Как видно из табл.2, в данном случае разбросы в значениях параметров для каждого элемента по двум растворам вполне допустимы для того, чтобы считать приемлемым примененный способ обработки. Примечания значения параметров свидетельствуют о раздельной сорбции стронция и цезия. Вместе с тем следует отметить, если для стронция данный метод всегда дает значения параметров с существенными разбросами, то для цезия это не всегда справедливо. Ряд экспериментов с цезием совершенно очевидно показывает, что его захват грунтами проходит в отдельных случаях необратимо и использование закономерностей ионного обмена не всегда правомочно. Однако ориентировочную оценку в большинстве случаев таким путем можно получить.

Значения параметров $\alpha$ и $\beta$ в дальнейшем использовались для расчетов переходной зоны. Как известно, переходная зона или зона размазывания образуется за счет двух явлений: фильтрационной диффузии и кинетики сорбции. В результате математического анализа этих процессов, проделанного В.М. Шестаковым [6], оказалось
возможным считать справедливым, что сорбционные процессы подавляют процессы фильтрационной диффузии при низких скоростях фильтрации. Причем устанавливаются закономерности развития переходной зоны, которые свойственны только сорбционным процессам, хотя параметры этих закономерностей зависят также и от гидравлических факторов.

Основным показателем справедливости такого вывода являлись экспериментальные работы, поставленные с целью установления, насколько хорошо распределение концентраций в колонне подчиняется принятым закономерностям кинетики сорбции.

Как уже указывалось выше поведение радиостронция, одного из основных радиоэлементов в наших исследованиях, вполне соответствует принятым положениям.

Расчет переходной зоны проводился следующим путем:
Принимались основные граничные условия:

\[ \frac{C}{C_0} = 0,05\% \] - появление заметных загрязнений;
\[ \frac{C}{C_0} = 0,5 \] - прохождение центра сорбционной волны;
\[ C_0 \] - исходная концентрация;

\[ \Delta t = \sqrt{\frac{t}{a(1+b)}} \]
где
\[ \Delta t \] - время от появления заметных загрязнений до середины фронта сорбционной волны;
\[ t \] - время движения потока.

Результаты для четырех колонн с параметрами а и β, показанными в табл.2, представлены в табл.3.

Данные табл.3 показывают, что зона размазывания даже при длительном движении потока весьма невелика. Иными словами ско-

<table>
<thead>
<tr>
<th>№ колонн</th>
<th>Время, сутки</th>
<th>Sr</th>
<th>Cs</th>
</tr>
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<td></td>
<td>t</td>
<td>10</td>
<td>100</td>
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<tr>
<td>1</td>
<td>(\Delta t)</td>
<td>0,24</td>
<td>0,75</td>
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<td>2</td>
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<td>4</td>
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Таблица 3

РЕЗУЛЬТАТЫ ДЛЯ ЧЕТЫРЕХ КОЛОНН С ПАРАМЕТРАМИ \(a\) И \(β\)
рост сорбционного захвата стронция и цезия настолько значительна, что общий фронт грязного потока следует на очень небольшом удалении от начала появления заметных загрязнений.

Следующей задачей являлось определение скорости и времени просачивания растворов и микрокомпонентов, т.е. как далеко может отставать фронт микрокомпонентов от фронта фильтрующегося раствора.

В результате экспериментов мы располагали значениями коэффициентов распределения микрокомпонентов между твердой и жидкой фазами \( N_{rp/C_0} \), т.е. обратной величиной параметров равновесия \( \beta \). Совершенно очевидно, что не вся пористость или поверхность грунтов работает на сорбцию. Имеется лишь какая-то эффективная величина пористости, пропорциональная коэффициенту распределения:

\[
\eta = n_0 \left(1 + \frac{N_{rp}}{C_0}\right), \tag{4}
\]

причем

\[
N_0 = \frac{N_{rp}}{V},
\]

где \( V = \frac{n_0}{\gamma_{gr}} \)

\( V \) - поровый объем,

\( \gamma_{gr} \) - объемный вес.

Внеся соответствующие значения \( N_0 \) и \( V \) в формулу (4), можно получить условную величину \( \eta \) - эффективную пористость:

\[
\eta = (n_0 + \gamma_{gr}) \frac{N_{rp}}{C_0}.
\]

Затем по эффективной пористости можно рассчитать скорость просачивания \( V_3 = W \eta \), где \( W \) - скорость фильтрации, и время просачивания \( t = S/V_3 \), где \( S \) - длина пути фильтрации.

Проделав такие расчеты для экспериментов с определенной серий грунтов, мы установили, что движение радиостронция по сравнению с фильтрацией раствора проходит в 40 - 60 раз медленнее, а цезия примерно в 100 раз.

Таким образом, в результате настоящей работы был экспериментально опробован метод расчета основных кинетических параметров сорбции, который позволил удовлетворительно характеризовать движение радиостронция в грунтовом потоке и менее точно, но вполне приемлемо описать миграцию радиоцезия.

Литература

DISCUSSION

L. BAETSLE: I understand you used second-order kinetics for calculation of the break-through curve. Did you find a correspondence with theory in the case of caesium? We found no logical explanation for the behaviour of that element in soils.

N. BREZHNEVA (on behalf of V.I. SPITSYN et al): The calculation was done for both strontium and caesium, but it has been fully confirmed only for strontium. It is not completely valid for caesium as the sorption of caesium by soils is not irreversible.
LA LYOPHILISATION DANS LE TRAITEMENT DES EFFLUENTS RADIOACTIFS

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Abstract — Résumé — Аннотация — Resumen

LYOPHILIC PROCESSING OF MEDIUM-ACTIVITY LIQUID EFFLUENTS. One of the disadvantages associated with the method of reducing the volume of liquid effluents by evaporation is that volatile radioactive elements such as ruthenium are dispersed.

On the other hand, destillation at low temperature under vacuum makes it possible to restrict the radioactivity to the dry residue.

Although the process is already known, it has not yet been applied to the various radioactive effluents encountered at atomic centres. The laboratory tests carried out show that the decontamination factor obtainable is higher than that achieved with the conventional methods of chemical treatment or evaporation.

The experiments which we have carried out and which are described in the paper have given us decontamination factors in the neighbourhood of $10^6$.

LA LYOPHILISATION DANS LE TRAITEMENT DES EFFLUENTS RADIOACTIFS. La réduction de volume des effluents liquides radioactifs par évaporation présente, entre autre inconvénient, celui de disperser des radioéléments volatils comme le ruthénium.

Le procédé de désiccaton sous vide à basse température permet, au contraire, de confiner la radioactivité dans le résidu sec.

Bien que le procédé soit connu, il n'avait pas été appliqué jusqu'ici aux effluents radioactifs de toute nature qui se rencontrent dans les centres nucléaires. Les essais de laboratoire entrepris ont démontré que le facteur de décontamination accessible était supérieur à celui obtenu par les procédés classiques de traitement chimique ou d'évaporation.

Les expériences auxquelles les auteurs ont procédé et qui font l'objet du mémoire leur ont permis d'obtenir des facteurs de décontamination voisins de $10^6$.

ПЕРЕРАБОТКА РАДИОАКТИВНЫХ ЭФЛЮЕНТОВ МЕТОДОМ ДЕОФИЛИЗАЦИИ. Концентрирование жидких радиоактивных эфлюентов методом испарения имеет недостатки, связанные с потерей летучих радиоэлементов, таких, как рутений.

В отличие от этого процесс сушки в вакууме при низкой температуре позволяет сконцентрировать всю радиоактивность в сухом кубовом остатке.

Хотя этот метод известен, но до настоящего времени он не применялся к различным радиоактивным эфлюентам, которые встречаются в атомных центрах. Проведенные лабораторные опыты показали, что коэффициент возможной очистки был более значительным, чем коэффициент, полученный при помощи классических процессов химической переработки или испарения.

Эксперименты, к которым мы приступили и которые являются предметом настоящего сообщения, позволили нам получить коэффициент очистки порядка $10^6$.

TRATAMIENTO POR LIOFILIZACIÓN DE LOS EFLUENTES LÍQUIDOS DE MEDIANA ACTIVIDAD. La reducción de volumen de los efluentes líquidos radiactivos por evaporación presenta, entre otros inconvenientes, el de dispersar radioelementos volátiles tales como el rutenio.

El procedimiento de desecación en vacío a baja temperatura permite, en cambio, confinar la radioactividad en el residuo seco.

Aunque este procedimiento era ya conocido, no se había aplicado aún a los efluentes radiactivos de diversa naturaleza que se encuentran en los centros atómicos. Los ensayos de laboratorio emprendidos han demostrado que el factor de descontaminación que puede alcanzarse es superior al obtenido por los procedimientos clásicos de tratamiento químico o de evaporación.

Los experimentos descritos en esta memoria han permitido alcanzar factores de descontaminación próximos a $10^6$.
Les différentes techniques utilisées pour le traitement des effluents peu radioactifs dans les Centres atomiques mondiaux sont essentiellement axées sur les procédés de coprécipitation, d'échanges d'ions par résines et d'évaporation. Les effluents concentrés font l'objet d'études et, dans certains centres, sont traités par des méthodes visant à en faire des solides, soit par vitrification, soit par fixation sur des matériaux divers.

Le C.E. A. n'a pas fait appel, jusqu'ici, à d'autres techniques, qu'il s'agisse d'exploiter des installations existant pour les liquides faiblement actifs ou d'études semi-industrielles sur les effluents concentrés. Il restait cependant une catégorie de liquides qu'aucune de nos installations ne pouvait traiter. Il s'agit d'effluents dont l'activité se trouve comprise entre 100 mc et 5 c/m³. Si même nos installations pouvaient absorber ces liquides, le facteur de décontamination est tel qu'il n'est pas possible d'en envisager le rejet après traitement, tant sont rigoureuses les limites qui nous sont imposées.

Une voie nouvelle nous est actuellement ouverte, celle de la lyophilisation.

Le principe de la lyophilisation, déjà appliqué en biologie, consiste à congeler un produit, puis à sublimer la glace sous une pression réduite et à basse température pour obtenir un extrait sec.

L'intérêt de cette technique porte essentiellement sur les points suivants:
- Alors que le traitement chimique des effluents assure un facteur de décontamination de 100 environ, la lyophilisation permet d'atteindre facilement 10⁶. Ce facteur résulte d'essais de laboratoire réalisés dans des conditions défavorables et permet d'envisager une amélioration.
- Le volume de l'extrait sec contenant les ions radioactifs est plus faible que celui résultant du traitement chimique qui nécessite l'adjonction d'importantes quantités de produits retrouvés dans les boues. Le traitement par évaporation donne un produit qui contient encore un pourcentage important d'eau.
- Le traitement à basse température des effluents élimine la principale source de dispersion et de contamination lors de l'obtention d'un extrait sec. Dans l'évaporation classique, par exemple, on assiste à un entraînement sous forme de vapeur de certains ions volatils.

ÉTUDES DE LABORATOIRE

Des études ont été menées en collaboration avec M. le Professeur Rey et un premier appareillage nous a permis de procéder à une série d'essais sur des solutions d'activités croissantes.

Appareillage

L'appareillage très simple (voir la figure 1) utilisé a surtout servi à démontrer la valeur du procédé sur des effluents radioactifs. Le dispositif est enfermé dans une boîte à gants mise en dépression à l'aide d'une trompe à air. La boîte à gants est équipée de filtres d'entrée et de sortie d'air. À l'intérieur se trouvent:
- un congélateur constitué par une plaque de cuivre parcourue par un serpentin dans lequel circule de l'azote liquide envoyé sous pression à partir d'une bouteille placée à l'extérieur de la boîte à gants;
- une cuve de lyophilisation surmontée d'un condenseur. La cuve est chauffée par le fond à l'aide d'une résistance électrique. Le condenseur se présente sous l'aspect d'une cheminée contenant un récipient chargé en carboglace.

L'ensemble est maintenu sous vide de $10^{-1}$ à $10^{-2}$ mm de Hg.

Par la suite nous avons refroidi le condenseur avec un réfrigérateur au fréon situé à l'extérieur de la boîte à gants.

Mode opératoire

On effectue au préalable une analyse thermique et de résistance sur le liquide non contaminé de façon à définir les conditions opératoires (température de sublimation et température finale du produit). Le liquide est contaminé avec une solution de produits de fission d'activité spécifiquement connue, puis distribué en flacons de verre du type "pénicillins". La hauteur du liquide dans les flacons atteint 10 à 12 mm. Un flacon contenant la solution non active est muni de sondes de contrôle de la résistivité et permet de suivre le déroulement de la lyophilisation.

Les flacons sont posés sur le congélateur et refroidis à -40°C. Le liquide étant congelé, les flacons sont placés dans la cuve et mis sous vide, la sublimation s'amorce et dure environ 19 heures.

En fin d'opération la cuve de lyophilisation est chauffée à une température n'excédant pas 30°C.

Le condenseur refroidi piège toute l'eau d'évaporation.

La lyophilisation étant terminée, les flacons sont retirés puis fermés, on laisse le condenseur se réchauffer et l'eau de condensation est recueillie dans un récipient mis à la place de la cuve de lyophilisation.

Les mesures d'activité spécifique sont effectuées:
- sur la solution initiale,
- sur le lyophilisat après remise en solution de ce dernier,
- sur le condensat.
Résultats

Le tableau I résume les résultats obtenus en laboratoire.

En raison de la rusticité de notre appareillage nous sommes en droit de penser que les résultats obtenus sont inférieurs à ceux qui pourraient être obtenus sur du matériel moins rudimentaire. Nous avons eu, en effet, divers incidents dus en particulier à une mauvaise régulation de la température et à une fixation cumulée de la radioactivité dans le condenseur qui, après plusieurs essais, s’est trouvée libérée dans le condensat. Nous avons également eu à enregistrer la dispersion de l’effluent dans la boîte à gants par suite de la rupture du flacon. En fait, aucune expérience parfaite n’a pu se faire, mais toutes ces imperfections jouaient dans le sens d’accroissement de la radioactivité du condensat.

Nous sommes donc en droit d’espérer que les nouvelles manipulations en cours sur un appareillage perfectionné vont nous conduire à l’obtention d’un facteur de décontamination compris entre $10^6$ et $10^7$.

PERSPECTIVES D’AVENIR

L’appareil que nous avons utilisé en laboratoire nous a permis de voir que le procédé de lyophilisation était applicable au traitement des effluents radioactifs liquides. En outre, l’extrait sec obtenu est compressible et les résultats recherchés dans une première étude ont pleinement confirmé les promesses de cette nouvelle voie.

Les facteurs de décontamination étant élevés, on peut envisager de traiter des activités spécifiques élevées, ce qui nous conduit à poursuivre nos re-
cherches. De plus, le prétraitement de l'effluent doit lui aussi faire l'objet d'études plus poussées.

Appareil d'étude

Nous allons utiliser très prochainement un nouvel appareillage qui sera enfermé dans une enceinte α β γ, c'est-à-dire entièrement étanche et protégée par une sorbonne blindée. Des télémanipulateurs permettront d'effectuer les différentes opérations sur des liquides dont l'activité spécifique pourra atteindre 3 c/l.

En outre, le bac de congélation, le tunnel de lyophilisation et le condenseur seront spécialement adaptés au traitement des solutions actives. La régulation des températures plus soignée permettra de conduire l'opération dans de meilleures conditions.

Enfin, cet appareillage permettra de définir les facteurs indispensables à l'exploitation d'une installation industrielle.

Pilote de traitement

D'ores et déjà nous avons étudié un pilote de traitement des effluents radioactifs qui nous permettrait de traiter 4 tonnes par jour de liquides d'activité spécifique limitée à 10 c/m³.

L'extrait sec à la sortie des tunnels de lyophilisation après compactage dans un conteneur étanche permet d'atteindre un facteur de réduction de volume de 100 à 200.

CONCLUSIONS

Si les avantages du traitement par lyophilisation sont, comme nous l'avons vu rapidement, très importants, il ne faut pas se dissimuler que le prix de revient au mètre cube traité est d'environ 5 fois plus élevé que celui du procédé par coprécipitation. Aussi ne faut-il s'y attacher que pour des effluents d'activité élevée, non traités actuellement et dont le coût de stockage est encore 7 fois plus fort que celui de la lyophilisation.

DISCUSSION

L. Duhamel (Chairman): This method is at present only being applied to relatively low-activity effluents compared with what we are speaking of, but I think it will certainly be capable of wider application, because calculations show that the relative cost decreases as the specific activity increases. Are there any questions?

R. Rometsch: What type of vacuum pumps were used and was any activity found in them?

P. Cerré: We did not use any special pumps in this equipment, but in the new semi-industrial pilot plant we will obviously have to employ a special technique. We did not find any activity in the pump. In obtaining a decontamination factor of less than $10^8$ we did get a little activity in the
condensate, but this was due mainly to the fact that our apparatus was rather rudimentary.

P. DEJONGHE: First of all, I think you should be encouraged in seeking new methods. Now I have a comment. At the very end of your paper you say that you obtain a concentration factor of 100 to 200. I think that that is nothing out of the ordinary, even for chemical processing, involving the addition of reagents but no concentration of the soluble salts. I think that any advantage you may have here is only small. I should also like to ask whether you have any idea as yet of the consumption of electric power by the 4 m³/d pilot plant.

P. CERRÉ: We do not get such a high concentration factor with the classical process at Saclay.

The power requirements for the pilot plant, which is fairly large and fairly complicated, are estimated at 200 kW; however, this is probably a slightly pessimistic estimate as we took into account the worst that could happen.

D.W. CLELLAND: From the figures you quote you do not seem to have made a case for this method, as an alternative to normal evaporation procedures. It is possible to get very high decontamination factors in evaporation processes if you are willing to reduce the rate of evaporation per square foot of surface area in the evaporator, and run on very low throughputs and take special precautions on disentrainment.

On the point of electricity consumption, you would presumably use the process feed liquor to condense the ice in the condensers and thereby get a saving in power.

P. CERRÉ: We have not yet got much experience of evaporation by the classical methods. The evaporators we are building at the moment will have a decontamination factor not greater than \(10^4\). By lyophilization we think we will get a much better factor. A second point is that the volatile radioactive ions can escape in the conventional evaporator, and they have to be trapped. With our method we are working at a maximum temperature of \(30^\circ\) above zero so that one can completely prevent escape, and I think this is the main point of interest with our method.

D.W. CLELLAND: I think that even on a large scale, in production processes with highly active effluents, it is possible to exceed \(10^6\) and even approach figures of \(10^5\) or \(10^6\) by evaporation. Unless your process could guarantee at least \(10^8\) or more on the full-plant scale, I do not think it would offer any advantage.

P. CERRÉ: I think we could reach \(10^7\) or \(10^8\), although we are not absolutely certain, as we have not completed the experiments. I think that within a year or eighteen months we will know whether with suitable equipment we can obtain such large decontamination factors. At present we are really in the hypothetical stage.

J.A. BUCKHAM: Could you give us an idea about the residual moisture content of the salt produced in this process? Would you intend to drive off moisture?

P. CERRÉ: We have not checked the humidity, but we have good reason to believe that the salt is sufficiently dry. It is a dry powdery substance.

W.H. HARDWICK: Would it not be technically difficult to produce dry
salts from solids of high specific activity? The self-heating might act in opposition to the freezing and the handling problems subsequently would be very difficult owing to radiolysis.

P. CERRÉ: There are, of course, certain technical problems, but I do not think they are much more difficult than those involved in calcination, which also requires substantial protective measures. The fact that our lyophilization takes place at a low temperature constitutes a considerable advantage, and if it proves industrially possible, I think we could proceed to vitrification immediately - without calcination at high temperatures.

J.A. BUCKHAM: You spoke of the product as a "powder". I assume that the pelletized material crumbles within the filter paper wrapping during the process.

P. CERRÉ: After lyophilization the dry extract retains the shape of the block of ice. It only becomes a powder after mechanical action and becomes pelletized after compacting. When we get to the industrial scale with proper equipment, we might do without the filter paper.

P. DEJONGHE: What staff is required in this 4-m³/d plant?

P. CERRÉ: The installation will work continuously, on three shifts, and I think three people per shift would be sufficient. Everything is remote-controlled.

S. LINDHE: I think that one advantage with this method is that thanks to the low temperature you would have no corrosion.

P. CERRÉ: Exactly.
Fixation of Radionuclides in Titanium Dioxide and Titanates Via Co-Precipitation

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Abstract — Résumé — Аннотация — Resumen

Fixation of Radionuclides in Titanium Dioxide and Titanates Via Co-Precipitation.
Calcination and adsorption on clay minerals are the most frequently studied ways of radionuclide fixation. A third way - fixation via co-precipitation - has not attracted much interest up to now. The characteristic for all three methods is high-temperature treatment of a pre-product containing the radioactivity, but they differ in introducing the activity into this pre-product. The disadvantages of co-precipitation are the difficult separation of the highly active sludge from solution and its bad qualification for caesium removal. Its advantages are the suitability for head-end processes, the less restricted volume capacity compared with clay mineral adsorption, and the avoidance of evaporation operations. Therefore it seemed worth while to look more closely into the chemistry of proper co-precipitation systems. The first system chosen was TiO₂ aq because of the good fixation qualities of TiO₂ and titanates.

The co-precipitation properties of TiO₂ aq were studied under different experimental conditions. For some radionuclides the distribution coefficient was found to be as good as or better than that for other oxide hydrates. High concentration of the radionuclide ion or similar ions causes decreasing distribution coefficient. This could be avoided by simultaneously precipitating carbonates or oxalates which remove the bulk of the ions. The influence of high aluminium content was studied as well. An investigation of the formation of anatase and rutile from pure TiO₂ aq precipitates and of titanates from TiO₂ aq + carbonate or oxalate precipitates during high-temperature treatment was started.
From the "Strontium-90 Power-Project" studies [1] the excellent properties of SrTiO₃ as a fixation form for radioactive strontium are well known. So it is of some interest whether titanates could also be useful for waste-fixation purposes. In this paper some considerations about this question as well as a few experimental results concerning fundamentals of such a process are presented.

1. PRINCIPAL CONSIDERATIONS

All waste-fixation processes under investigation run in two stages. A concentration treatment of the waste solution is the first stage. From the resulting product, stable chemical compounds can be formed by heating in the second stage of the process.

In the case under consideration one problem is how to produce a concentrate containing the fission products and TiO₂ with as few other materials as possible. The method which lends itself to this purpose is co-precipitation. A second problem concerns the behaviour of fission products other than strontium when they are heated with TiO₂. Finally, a third problem is to
discover which temperatures are required to form titanates or solid solutions with TiO$_2$ from the fission products. For practical applications there are many further problems, but these three shall be considered here.

The adsorption properties of TiO$_2$-aq have not been studied up to now. However, MnO$_2$-aq is known to be an excellent co-precipitant for radionuclides being present in micro-concentrations [2]. Since both these oxides MnO$_2$ and TiO$_2$ crystallize with rutile structure, TiO$_2$-aq can also be expected to be a good co-precipitant. Fission-product radionuclides in processing wastes have macro-concentrations, e.g. of an order of magnitude of 10 meq/l in a typical Purex waste. One cannot hope to remove these amounts of fission products by adsorption on TiO$_2$-aq only. It will be necessary to precipitate the bulk of fission products directly. The simultaneously precipitated TiO$_2$-aq should adsorb the remaining micro-concentrations of fission products improving the decontamination effect of the precipitation. For direct precipitation a compound must be selected which can be easily decomposed by heating to ensure reaction with TiO$_2$. Compared with evaporation or ion-exchange, co-precipitation doubtless has disadvantages from the viewpoint of chemical engineering. But certainly there are also a few advantages. For example, under favourable conditions, it should be possible - having salt-rich waste solutions - to prepare a product containing less balast than by other methods. So it seems possible to obtain a suitable starting product for the second stage of the process, the ignition stage, by co-precipitation.

During the heat treatment the formation of titanates or solid solutions with TiO$_2$ is to be expected. The titanates of the alkaline earths are well known from considerable investigations. Three-valent rare earths form compounds of perovskite structure only with Ti$_2$O$_3$ or TiO$_2$ and alkali metals. When heated in the air only the tetravalent forms of rare earths will exist. Nothing is known about the reactions between oxides of the type ReO$_3$ and TiO$_2$. The titanates of caesium are not useful for fixation purposes since they are easily soluble in water. ZrO$_2$ forms solid solutions of limited miscibility with TiO$_2$. Regarding the behaviour of ruthenium so far it should be only mentioned that RuO$_2$ crystallizes with rutile structure which have lattice constants quite close to those of TiO$_2$. Consequently the reactions between fission-product oxides other than alkaline earths and TiO$_2$, as well as their leaching properties, must be studied in detail.

The temperatures reported to be required for the formation of alkaline earth titanates are quite high. They are significantly above 1000°C. Since, for waste-fixation processes, a treatment temperature as low as possible is desired, this question must be considered. All experiments reported have been made with mixtures of TiO$_2$ and an alkaline earth compound prepared by mechanically mixing the components. We expected mixtures prepared by co-precipitation of the components to be more ready for reaction and therefore more suitable for a fixation process. At temperatures of 1000°C or below it is, of course, impossible to produce ceramic bodies from titanates or TiO$_2$. A possibility of bringing the heating product into a compact form is by incorporation into a low melting matrix, for which extreme chemical resistance would not be required.
The experiments carried out so far have dealt with the precipitation process and the alkaline earth titanate formation from different mixtures of the components.

2. CO-PRECIPITATION OF RADIONUCLIDES WITH TiO₂·aq

In order to learn something about the adsorptive properties of precipitated TiO₂·aq we studied the co-precipitation of carrier-free radionuclides from solutions of low activity.

Figure 1 shows the residual radioactivity in a mixture of Sr⁸⁹, Ce¹⁴⁴ and Zr/Nb⁹⁵ versus the amount of TiO₂ being precipitated. A precipitate concentration of 0.25 g TiO₂/l or even less appears to be optimal. The adsorption equilibrium has been reached within a few minutes.

---

![Figure 1](image_url)

Activity removal from a carrier-free mixture of some fission products by co-precipitation with TiO₂·aq versus amount of precipitate

---

Table I shows the decontamination observed with carrier-free solutions of various radionuclides. Co-precipitation with TiO₂·aq has been found to give considerably better results than with Al₂O₃·aq and Fe₂O₃·aq and equally good results with MnO₂·aq. As one would expect very poor results have been obtained only for caesium and iodine.

The pH-dependence of activity removal (Fig. 2) shows a behaviour pattern typical for adsorptive co-precipitation. With increasing pH the activity removal increases for cationic radionuclides like Sr⁸⁹ and Ce¹⁴⁴ and decreases for anionic ones like P³² in form of PO₄-ions. Three-valent Sb²²⁵ behaves like an anion, at least down to pH = 8. Beyond this value obviously its increasing cationic character becomes effective.

3. ACTIVITY REMOVAL FROM SOLUTIONS CONTAINING IONS IN MACRO-CONCENTRATIONS

In waste solutions, as already mentioned, radionuclides are not present in micro-concentrations and are free of foreign salts. Table II shows the
### Table I

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>pH of precipitation</th>
<th>Residual activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$^{89}$</td>
<td>12</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Ce$^{144}$</td>
<td>10</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Zr/Nb$^{95}$</td>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>Sb$^{125}$</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Ru$^{106}$</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>I$^{131}$</td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>Cs$^{137}$</td>
<td>11</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>MFP</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Fe$^{59}$</td>
<td>10</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>P$^{32}$ (PO$_4$$^{3-}$)</td>
<td>4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Co$^{60}$</td>
<td>10</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Fig. 2**

Removal of carrier-free radionuclides by co-precipitation with TiO$_2$·aq versus pH.

(□ Sr$^{89}$, ○ Ce$^{144}$, ○ Sb(III) - 125, X Po$^{32}$)
residual activity in a Sr\textsuperscript{89} solution containing increasing amounts of SrCl\textsubscript{2}. Up to 1 meq Sr/l it remains below 1% and then rises sharply above this value. With 10 meq Sr/l almost no activity has been removed.

For direct precipitation of the bulk of Sr-ions, simulating fission-product ions here, we tried TiCl\textsubscript{4} + Na\textsubscript{2}CO\textsubscript{3} as well as TiOK\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} as precipitants. In both cases the Sr\textsuperscript{89} removal from a solution with 10 meq Sr/l is quite satisfying. The carbonate precipitation seems to be more efficient than the oxalate precipitation. On the other hand TiOK\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} can be handled more conveniently. As expected, practically the same behaviour has been found in a solution of carrier-free Sr\textsuperscript{89} containing CaCl\textsubscript{2}.

Quite different, however, is the effect of Al(NO\textsubscript{3})\textsubscript{3}. Al-ions do not interfere at all with the strontium co-precipitation up to concentrations as high as 1 eq/l. In strong alkaline solution they are transformed into aluminate ions. Aluminate ions are not significantly adsorbed on TiO\textsubscript{2}aq at high pH-values since they are anions. It may be possible to prepare a fission-product concentrate from waste solutions containing Al-ions and leaving them in the solution.

As shown in Table III Ce\textsuperscript{144} behaves somewhat differently than Sr\textsuperscript{89}. The residual activity rises also with increasing concentration of cerium ions, but only to some extent. This is quite natural since cerium forms an insoluble
TABLE III
ACTIVITY REMOVAL FROM SOLUTIONS CONTAINING Ce\textsuperscript{144} WITH DIFFERENT CARRIER CONCENTRATIONS

<table>
<thead>
<tr>
<th>Ce(NO\textsubscript{3})\textsubscript{3} - Concentration (meq/l)</th>
<th>Precipitant</th>
<th>Residual activity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no</td>
<td>TiCl\textsubscript{4} + NaOH</td>
<td>0.1</td>
</tr>
<tr>
<td>0.01</td>
<td>TiCl\textsubscript{4} + NaOH</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>TiCl\textsubscript{4} + NaOH</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>TiCl\textsubscript{4} + NaOH</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Ti[Cr\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}] \textsuperscript{4+} + NaOH</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Ti[Cr\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}] \textsuperscript{4+} + NaOH</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Ti[Cr\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2}] \textsuperscript{4+} + NaOH</td>
<td>0.1</td>
</tr>
</tbody>
</table>

hydroxide itself whereas strontium does not. Using TiOK\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} as a precipitant in the case of Ce\textsuperscript{144}, an excellent activity removal has been obtained in solutions with macro-amounts of cerium-ions.

4. TITANATE FORMATION

In order to check our assumption that co-precipitated mixtures will react more readily than those mechanically mixed, we heated three mixtures of TiO\textsubscript{2} and CaCO\textsubscript{3} at 800\textdegree C, prepared by mixing, subsequently precipitating and co-precipitating the components. Samples taken after different time intervals were analysed by X-ray powder-diffraction. Table IV shows the relative intensities of the strongest line of TiO\textsubscript{2}, CaO and CaTiO\textsubscript{3} respectively. The results make it clear that mixtures prepared by co-precipitation react much faster than others. However, it should be mentioned that, at 800\textdegree C, even after two days heating, the reflexes of TiO\textsubscript{2} and CaO did not completely disappear. At 1150\textdegree C, after a heating period of 7 hr in a co-precipitated mixture, only the reflexes of CaTiO\textsubscript{3} are to be found. With mixed components, even at 1150\textdegree C, a period of more than a day is necessary for complete reaction.

A quite similar behaviour has been observed with mixtures of SrCO\textsubscript{3} and TiO\textsubscript{2} prepared in the same ways as that described for calcium. The only difference is that the reaction in general is much faster than with calcium compounds. Already, after one hour heating at 800\textdegree C, a co-precipitated mixture of SrCO\textsubscript{3} and TiO\textsubscript{2} has been completely transformed into SrTiO\textsubscript{3}. A mixture prepared by mixing the components after only four days has reacted almost completely.

These results confirm the assumption that co-precipitated mixtures are those most ready for solid-state reactions. Therefore, co-precipitation of the components creates optimal conditions for producing titanates at relatively low temperatures.
TABLE IV

FORMATION OF CaTiO₃ BY HEATING OF TiO₂ + CaCO₃ - MIXTURES PREPARED IN DIFFERENT WAYS; ANALYSED BY X-RAY DIFFRACTION

<table>
<thead>
<tr>
<th>Heating time (hr)</th>
<th>Substance</th>
<th>Mixing</th>
<th>Subsequent precipn.</th>
<th>Co-precipn.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Relative intensity of the strongest X-ray reflex)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>TiO₂</td>
<td>5.0</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>4.0</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CaTiO₃</td>
<td>1.0</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>TiO₂</td>
<td>3.5</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>4.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CaTiO₃</td>
<td>2.0</td>
<td>4.5</td>
<td>5.0</td>
</tr>
<tr>
<td>48</td>
<td>TiO₂</td>
<td>3.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>4.0</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CaTiO₃</td>
<td>2.0</td>
<td>4.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The experiments carried out up to now have made it quite clear that, in principle, a fixation process using TiO₂ should be possible. Some basic requirements for such a process may be said to be fulfilled. Fission-product radionuclides can be removed from solutions by combined precipitation with TiCl₄ and Na₂CO₃ or with TiOK₂(C₂O₄)₂. From co-precipitated mixtures of SrCO₃ and TiO₂ the titanate has been prepared quite easily at a relatively low temperature.

Further experiments partly in progress will deal with the co-precipitation process under simulated waste conditions as well as under head-end-process conditions, with solid-state reactions between fission-product oxides and TiO₂, and the leaching properties of the reaction products.

ACKNOWLEDGEMENTS

The author wishes to thank Mrs. I. Hohenhaus, Mr. H. Melzer and Mr. L. Seemann for their help in carrying out the experiments.

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DISCUSSION

E. GLUECKAUF: If titanium is precipitated from strong strontium solutions, what is the maximum Sr : Ti ratio that can be achieved by absorptive co-precipitation?

H.W. LEVI: The molar ratio is roughly 1 : 5 judging by our work so far.
VI

TREATMENT OF SOLID WASTES AND SHIPMENT OF GROSS QUANTITIES OF RADIONUCLIDES
TREATMENT AND PACKAGING OF SOLID WASTE IRRADIATED IN PILE. The solid waste produced in atomic centres varies greatly in nature, form and activity, ranging from weakly contaminated laboratory waste to unwieldy devices irradiated in the reactor and highly radioactive.

This paper describes methods of treatment, packaging and protection in respect of these types of waste. In particular, the paper describes a pilot unit which was operated at Saclay for eighteen months and which has led to the construction of a remote-controlled plant for treating and packaging all kinds of solid wastes, whatever their activity and shape.

STATION DE TRAITEMENT DES DÉCHETS RADIOACTIFS SOLIDES. Les déchets solides d’un centre nucléaire sont de nature, de forme et d’activité extrêmement variées, allant des déchets de laboratoire faiblement contaminés aux dispositifs encombrants irradiés en pile et fortement radioactifs.

Le mémoire a pour objet la description des techniques de traitement, de conditionnement et de protection de ces déchets. Il présente en particulier la description d’une unité pilote exploitée à Saclay pendant un an et demi, qui a permis la construction d’une usine télécommandée pouvant traiter et conditionner les déchets solides de toute nature, quelles que soient leur activité et leur forme.

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1. PRINCIPES DE BASE

L’ensemble de l’installation a été conçu pour:
- réduire le volume des déchets (cisaillement, compactage),
- les inclure dans un béton pour assurer:
  a) le confinement total de la contamination,
b) la protection contre le rayonnement,
- assurer au personnel chargé de son exploitation une protection efficace contre le rayonnement et la contamination.

2. CONDITIONNEMENT DES DÉCHETS

(rappel des principes [1, 2], voir figure 1)

- A l'intérieur d'un coffrage métallique démontable, on fixe un tube en U qui servira à l'injection du coulis de ciment et à la manutention du bloc terminé,

**CONDITIONNEMENT DES DÉCHETS**

- garnissage du fond du coffrage par un lit d'agrégats,
- dépôt, au centre du coffrage, d'un panier en métal déployé contenant les déchets radioactifs après traitement,
- garnissage total du coffrage en agrégats,
- injection du coulis par une branche de l'U. En cas de bouchage accidentel, la deuxième branche est utilisée «en secours» pour terminer le bloc.

Le coulis remonte du fond du coffrage, pénètre dans tous les intervalles, y compris ceux que peuvent former les déchets, pour constituer une sorte de monolithe.
- Collecte et contrôle de l'eau de ressuage, lissage du sommet du bloc,
- décoffrage partiel 24 heures après l'injection (sommet et corps),
- enlèvement par un palonnier avec manchons et broches 48 heures après l'injection.

Le principe très souple permet en choisissant les dimensions des paniers de faire varier l'épaisseur du béton en fonction de la protection biologique à assurer.

Pour tenir compte des autres facteurs (résistance mécanique, étanchéité), l'épaisseur du béton de protection autour des déchets n'est jamais inférieure à 17 cm.

Deux types de blocs cylindriques sont réalisés:
- le grand modèle de 1,30 m de diamètre, 1,30 m de hauteur, d'une capacité intérieure de 700 l, et d'un poids de 4 t environ;
- le petit modèle de 0,95 m de diamètre, 1,30 m de hauteur, d'une capacité intérieure de 220 l, et d'un poids de 2 t environ.

3. PLAN FONCTIONNEL DU BÂTIMENT

Le bâtiment mesure 85 m de longueur, 9 m de largeur et 8 m de hauteur sous entrait; il se divise en trois zones principales avec leurs locaux annexes (voir les figures 2 et 3):
- A une extrémité une zone semi-active destinée à recevoir les déchets à traiter, ou les châteaux de plomb à vider, avec possibilité de stockage provisoire.
- Au centre une zone active ventilée, délimitée par des murs et un plafond de béton de 30 cm d'épaisseur. Elle abrite les appareils nécessaires au traitement préalable des déchets et à leur manutention: cisaillement et compactage, manutention mécanique des déchets, introduction des déchets dans les paniers, stockage des paniers pleins, mise en place des déchets dans les coffrages.
- À l'autre extrémité une zone inactive utilisée pour la réception et le stockage des matériaux nécessaires à la confection des blocs, la préparation du coulis, la préparation des coffrages, le décoffrage et l'évacuation des blocs terminés.

3.1. Zone semi-active

Elle abrite (voir figure 4):

- a) Un stockage provisoire (déchets ou châteaux de Pb) constitué par deux grandes fosses parallèles de 10 m de longueur, 2 m de largeur et 2 m de profondeur, couvertes de dalles amovibles en béton de 30 cm d'épaisseur. Des dalles mobiles permettent de les compartimenter à volonté. Chaque
Figure 2

Station de traitement des déchets radioactifs solides
au Centre d'études nucléaires de Saclay.
Figure 3

Station de traitement des déchets radioactifs solides
au Centre d'études nucléaires de Saclay.
fosse possède un puisard de rétention. Les parois et le fond ont reçu un enduit étanche.

b) Une fosse où sont rassemblés l'ensemble de ventilation de la zone active et le groupe déprimogène utilisé pour son nettoyage périodique.

c) Un poste d'introduction qui permet le déchargement des châteaux «haute activité» du type LECI ou REA. Un coffrage est amené dans le tunnel protégé sous le poste de déchargement du château. Celui-ci est centré sur la partie supérieure d'une enceinte protégée par 7 cm de Pb sur trois faces, la quatrième étant constituée par un panneau de plexiglas.

L'ouverture des portes «à tiroirs» situées à la partie inférieure du château libère la poubelle contenant les déchets, qui descend alors par gravité à l'intérieur d'une goulotte télescopique qui la guide jusqu'au centre du coffrage (voir figure 5).

Un jeu de miroirs permet de contrôler la vidange du château et le positionnement du «container». Toutes les opérations sont effectuées à distance et le tunnel étant en dépression par rapport à la zone semi-active, il n'existe aucun risque de contamination atmosphérique.

Ce poste d'introduction permet également le passage de blocs préfabriqués pleins qui sont déposés sur une plate-forme roulante qui les conduit au poste d'injection.

d) Une face de déchargement formée par le mur de séparation des zones active et semi-active; on y trouve rassemblés:
- tous les dispositifs d'introduction des déchets en zone active,
- les commandes à distance des appareils de traitement des déchets et de manutention,
- les hublots d'observation de ces appareils.
TRAITEMENT DES DÉCHETS RADIOACTIFS

1° Alimentation de la presse à compacter

Le passage des déchets d'une zone à l'autre se fait par l'intermédiaire d'un sas. La porte du sas étant ouverte, le fût contenant les déchets compressibles est disposé sur une plaque tournante qui l'oriente dans l'axe du sas. La porte refermée, le chariot d'un monorail équipé d'une pince type «tenaille» pénètre dans le sas en poussant deux portes battantes, saisit le fût et repart en direction de la presse. Au-dessus de la presse, la pince lâche le fût qui tombe dans le caisson de compactage. L'opération entièrement automatique est observée par des hublots.

2° Introduction des paniers, vidange des châteaux «moyenne activité»

Toutes les opérations de traitement des déchets consistent à réduire le volume de ces derniers et à les placer dans des paniers. Il est donc nécessaire d'alimenter la zone active en paniers vides. Ceux-ci sont amenés à proximité d'une trappe fermée par un opercule pivotant, blindé. Un palan électrique de 125 kg monté sur une potence orientable permet par l'inter-
mediaire d'un Y basculant, de saisir le panier vide et de le descendre sur un tapis de transfert situé dans un sas. La trappe fermée, le tapis entraîne le panier qui pousse les deux portes battantes du sas, pénètre en zone active et s'arrête aux différents postes de déchargement.

Ce même poste sert au déchargement des châteaux «moyenne activité» qui s'opère comme suit: Un panier vide est déposé dans le sas et le château est centré sur un châssis mobile. Dès l'ouverture des «tiroirs» les déchets descendent par gravité dans une goulotte qui les canalise vers le panier. Le panier partiellement rempli est complété en zone active par des fûts compactés ou autres déchets arrivant par les autres voies. Enfin les paniers pleins provenant de la cellule de découpage à l'arc peuvent être introduits en zone active par ce poste.

3° Trémie blindée pour l'alimentation de la cisaille

Elle est destinée à recevoir les barreaux contenus dans les châteaux provenant des piles et les tubes ou profilés très peu actifs prélevés dans le stock de métaux contaminés. A cette trémie est lié un canal blindé dans lequel un dispositif permet l'avance régulière des barres sous les lames de la cisaille. Deux types de châteaux peuvent être vidés à ce poste:
- Château du type vertical (pour tube de 1, 50 m de longueur maximum). Le château est centré sur une console fixée au-dessus de la trémie, son axe étant placé en position verticale. Les portes à tiroir sont ouvertes, le tube descend par gravité, bascule, et vient se placer dans un canal horizontal, au bord de la trémie, de 150 X 150 mm de section, protégé par 7 cm de Pb. La partie supérieure du canal est fermée par des portes coulissantes en Pb de 5 cm d'épaisseur, isolant ainsi le canal de la trémie et limitant l'intensité d'irradiation. Un poussoir commandé par chaîne et pignon-manivelle permet d'avancer les barreaux de 150 mm par tour.

A l'extrémité du canal, 2 cales amovibles permettent de réduire la hauteur à 100 mm ou 60 mm et s'opposent au moment du cisaillement au basculement des barreaux.

Enfin une caméra de télévision orientée sur une lumière latérale permet de contrôler l'avance et le point de cisailage.
- Château du type horizontal (pour tubes de 2, 50 m de longueur maximale). Ce type de château, comme son nom l'indique, est déchargé en position horizontale. Le canal d'alimentation de la cisaille est isolé de la trémie supérieure et le château, déposé sur un châssis métallique, est centré sur une plaque d'appui située à l'extrémité du canal. La porte du canal étant ouverte, le tube à cisailer est poussé au ringard dans le canal, puis pris en charge par le poussoir automatique.

Les tubes et profilés très peu actifs sont introduits directement dans le canal et entraînés par le poussoir vers les couteaux de la cisaille.

4° Sas pour déchets de petits volumes

La section maximale est de 800 X 500 X 700 mm. Les déchets sont déposés sur une table faisant saillie dans la zone semi-active, puis ils sont poussés dans un sas isolant les deux zones. Après passage dans la zone active, une palette à commande pneumatique pousse les déchets sur un tapis
transporteur qui les conduit soit vers la presse à compacter, soit directement vers le panier. Des sécurités interdisent l’ouverture simultanée des deux portes du sas. Des grilles au sol permettent de recueillir les pous-siéres accidentelles. Elles sont aspirées par la ventilation de la zone active.

Approvisionnement
Deux grandes portes coulissantes permettent l’entrée des camions et engins de manutention.

Manutention
Toutes les manutentions intérieures se font par l’intermédiaire d’un pont roulant électrique d’une puissance de 7 t qui dessert la totalité du hall.

Accès du personnel
Les mouvements de personnel se font par l’intermédiaire d’un vestiaire type «actif».

Sécurité
Les dispositifs de commande sont asservis pour interdire toutes fausses manœuvres.

Les orifices pouvant permettre le passage des agents en zone active sont cadenassés en l’absence du chef de hall.

Les liquides accidentels sont drainés par des rigoles et dirigés vers un puisard de rétention.

Surveillance de la zone active
Trois hublots en verre au Pb de densité 6,2, mesurant 315 X 215 mm et 110 mm d’épaisseur, permettent à partir de la zone semi-active de suivre les opérations effectuées en zone active.

3.2 Zone active
Elle est formée d’une enceinte de 500 m³ environ, fermée par des murs et un plafond en béton de 30 cm d’épaisseur.

Du côté semi-actif on trouve: Deux tapis transporteurs, la presse (voir figure 6), la cisaille (voir figure 7).

Au centre: Le stockage des paniers (voir figure 8).

Du côté inactif: Un tunnel protégé avec un poste de chargement des paniers de déchets.

a) Tapis transporteurs

L’un est utilisé pour le transfert des déchets, l’autre pour la mise en place des paniers aux postes de chargement et d’évacuation.
Figure 6
Zone active. Alimentation de la presse.

Figure 7
Zone active. Remplissage des paniers.
Figure 8
Zone active. Stockage des paniers.

*Tapis de transfert des déchets*

Parmi les déchets de faible volume, les déchets incompressibles sont envoyés directement dans le panier, les déchets compressibles sont dirigés vers la presse à compacter.

Parmi les déchets provenant du cisaillage, les uns sont directement dirigés vers un panier, les autres sont envoyés dans la presse à compacter.

La différenciation entre les deux directions se fait suivant l’activité des déchets. Il est en effet parfois contre-indiqué de réduire le volume d’un déchet très actif et, dans ce cas, il n’est pas soumis au compactage.

*Tapis de transfert des paniers*

Les paniers vides déposés dans le sas de la zone semi-active sont entraînés vers deux postes de chargement situés - l’un à l’extrémité du tapis de transfert des déchets en provenance de la cisaille ou du sas de déchets de faible volume;
- l’autre sous la goulotte de sortie de la presse. Deux rampes tubulaires maintiennent les paniers centrés sur le tapis;
- les arrêts sont commandés par des cellules photoélectriques. En bout de tapis, le panier est arrêté, il est repris par un grappin fixé sous un pont télécommandé, puis déposé au stockage des paniers.

b) Presse à compacter (marque «Cosmo», type PPa60 à commande hydraulique)

**Caractéristiques**

<table>
<thead>
<tr>
<th>Caractéristique</th>
<th>Valeur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force totale déployée par les deux vérins</td>
<td>130 t</td>
</tr>
<tr>
<td>Dimensions de la caisse</td>
<td>1150 mm, 600 mm, 650 mm</td>
</tr>
<tr>
<td>Dimensions du paquet suivant</td>
<td>600 X 400 X 120 à 400 mm</td>
</tr>
<tr>
<td>Puissance du moteur électrique</td>
<td>12 CV</td>
</tr>
<tr>
<td>Dimensions hors tout</td>
<td>4200 mm, 1500 mm, 1450 mm</td>
</tr>
<tr>
<td>Poids approximatif</td>
<td>4800 kg</td>
</tr>
</tbody>
</table>

**Fonctionnement**

Toutes les commandes se font à partir d’un volant unique situé en zone semi-active et agissant sur un distributeur.

**Remplissage**

Les déchets étant déposés dans la caisse, le couvercle commandé par un vérin d’une force de 30 t tasse les déchets et se véraille par deux taquets à ressorts. Deux lames dentelées situées sur les bords supérieurs permettent de cisailier les éléments qui dépasseraient accidentellement du caisson.

**Compactage**

Les déchets sont comprimés entre une porte verrouillée située à l’extrémité de la caisse et un piston horizontal solidaire d’un vérin d’une force de 100 t travaillant à 200 kg/cm² de pression.

**Ejection du paquet**

Après compression, le piston recule et la porte se déverrouille, le piston en revenant en avant pousse le paquet qui glisse dans le panier par l’intermédiaire d’une goulotte.

Les paquets réalisés à partir de fût de 200 l (Ø 580 mm, hauteur 800 mm) ont une épaisseur variant de 120 à 400 mm suivant la nature des déchets et le niveau de remplissage. La production horaire est d’environ 25 paquets et un panier peut recevoir de cinq à neuf paquets.
c) Cisaille crocodile (marque SIRUGUE, type 200)

Caractéristiques

<table>
<thead>
<tr>
<th>Caractéristique</th>
<th>Valeur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puissance du moteur électrique</td>
<td>10 CV</td>
</tr>
<tr>
<td>Nombre de coups par minute</td>
<td>36</td>
</tr>
<tr>
<td>Longueur des lames</td>
<td>500 mm</td>
</tr>
<tr>
<td>Ouverture des lames</td>
<td>220 mm</td>
</tr>
<tr>
<td>Dimensions hors tout: longueur</td>
<td>2700 mm</td>
</tr>
<tr>
<td></td>
<td>largeur: 1300 mm</td>
</tr>
<tr>
<td></td>
<td>hauteur: 1250 mm</td>
</tr>
<tr>
<td>Poids approximatif</td>
<td>3200 kg</td>
</tr>
</tbody>
</table>

Capacité de la machine

En travaillant sur 1/3 des lames situées près de l'articulation on peut:

- cisailler un fer rond de 70 mm de diamètre ou une section correspondante en acier doux R = 40/45 kg,
- une tôle de 18 mm d'épaisseur,
- un l.P.N. de 200 mm,
- un U de 200 mm.

La cisaille est équipée de lames crantées qui évitent le glissement de la pièce à découper. Le graissage du type «monocoup» se fait à partir de la zone semi-active. Une goulotte canalise les tronçons cisaillés vers le tapis de transfert.

d) Stockage et manutention des paniers

Une plate-forme bétonnée permet de recevoir 15 paniers au sol. Par gerbage, on peut porter le stockage à 35 paniers.

La manutention des paniers s'effectue au moyen d'un pont roulant électrocommandé d'une puissance de 3 t permettant:

- l'évacuation des paniers pleins se trouvant en bout du tapis de chargement,
- le stockage des paniers pleins,
- la reprise et la mise en place dans les coffrages par un grappin suspendu au pont roulant et composé de quatre doigts rétractables, commandés par électro-aimant.

La commande du pont, du grappin et l'évacuation du coffrage plein se font à partir d'un pupitre de commande placé dans une cabine située en zone inactive. Une dalle de 1000 X 800 mm, en verre au Pb, permet de surveiller les opérations.

e) Ventilation de la zone active

L'installation comprend:

- un réseau d'aspiration,
- un groupe de filtration,
- un groupe de ventilation rejetant l'air filtré à l'extérieur par l'intermédiaire d'une cheminée.
Réseau d’aspiration

Il est prévu pour véhiculer 10 000 m$^3$/h (soit 20 renouvellements horaires) d’air pris au voisinage des plans de travail. Le débit à chaque prise est réglable entre un débit maximal et une valeur nulle. Le réglage s’effectue au moyen de volants de commande à distance. Le tableau ci-après indique la position des diverses prises d’aspiration et le débit maximal de chacune d’elles.

<table>
<thead>
<tr>
<th>Lieu d’aspiration</th>
<th>Débit maximal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presse:</td>
<td>6 000 m$^3$/h.</td>
</tr>
<tr>
<td>Cisaille:</td>
<td>6 000 m$^3$/h.</td>
</tr>
<tr>
<td>Grilles (zone semi-active):</td>
<td>10 000 m$^3$/h.</td>
</tr>
<tr>
<td>Jupe de centrage:</td>
<td>2 000 m$^3$/h.</td>
</tr>
<tr>
<td>Stockage des paniers, deux prises de:</td>
<td>800 m$^3$/h.</td>
</tr>
<tr>
<td>Sas déchets petits volumes:</td>
<td>2 000 m$^3$/h.</td>
</tr>
<tr>
<td>Goulotte tapis à déchets:</td>
<td>2 000 m$^3$/h.</td>
</tr>
</tbody>
</table>

Groupe de filtration et ventilation

Le groupe de filtration comprend deux étages:
- un dégrossisseur composé de deux cyclones à haut rendement,
- un finisseur qui comporte deux étages de filtration sur laine de verre. La laine de verre utilisée est de la qualité hyperfine rose de St. Gobain.

Le premier étage comporte un dispositif de battage des dièdres qui permet d’obtenir un certain décolmatage et de prolonger la vie des filtres.

L’installation comprend deux ventilateurs de tirage type Rotoline. Un seul des ventilateurs suffit à assurer le fonctionnement normal de l’installation, l’autre est en secours.

L’ensemble de l’installation est muni de clapets de non retour et de registres d’isolement permettant d’assurer des démontages partiels.

Un groupe déprimogène permet le dépoussiérage périodique de la zone active.

L’agent décontamineur branche le flexible de son «pot décanteur» utilisé comme préfiltre à la bouche située à proximité de la zone à nettoyer. L’installation comprend:
- un réseau d’aspiration formé de tuyauteries en chlorure de polyvinyle muni de 5 bouches d’aspiration terminées par des raccords symétriques avec bouchon;
- un groupe déprimogène constitué par une trompe à air comprimé raccordée au réseau de la station et un caisson filtre contenant quatre bougies de 25,5 cm de diamètre et de 1 m de hauteur, garnies de filtres roses Schneider-Poëlman. L’air est rejeté dans la cheminée de la ventilation.

3.3 Zone inactive

Elle abrite:
- un ensemble de réception, stockage et dosage des matériaux,
- un ensemble de préparation et injection du coulis,
- les voies de circulation des coffrages.
a) Réception, stockage et dosage des matériaux

Le sable et les agrégats livrés par camions pénètrent dans le bâtiment par une grande porte coulissante; ils sont déchargés dans une trémie et repris par deux tapis élévateurs pour être stockés dans des silos (voir figure 9).

Figure 9
Zone inactive. Vue générale.

Sable. Un premier tapis le déverse directement dans un silo d'une capacité de 18 m³.

Le système d'alimentation-pesage (voir figure 10) se compose:
- d'un alimentateur horizontal à courroie, servant à reprendre le sable sous le silo,
- d'un élévateur vertical, à godets, assurant une hauteur d'élévation suffisante et muni à son extrémité d'une trémie tampon avec casque d'ouverture à commande électro-pneumatique,
- d'une bascule à sable équipée à sa partie inférieure d'un distributeur à courroie assurant sa vidange régulière dans la goulotte des malaxeurs.
Agrégats. Ils sont entraînés par le premier tapis, repris par un second tapis orientable qui les déverse dans un silo de 20 m³. Ce silo alimente deux postes, savoir le poste de garnissage total en agrégats et le poste de garnissage des fonds de coffrage.

Ciment. Il est livré, en vrac, dans des «containers» amenés par camion et transvasé par air comprimé dans un silo de 20 m³. Le contrôle du niveau de remplissage est assuré par deux sondes électriques à variations de capacité. L'ensemble d'extraction-pesage comprend:
- une vis horizontale extractrice,
- une vis verticale élévatrice,
- une bascule équipée à sa partie inférieure d'une vis extractrice permettant sa vidange régulière dans la goulotte des malaxeurs.

Eau. L'alimentation des malaxeurs est assurée par une électro-vanne et un compteur volumétrique réglable de 0 à 100 l.

Adjuvants pulvérulents. Le produit choisi est stocké dans un «container» de 1000 l. L'ensemble d'extraction-pesage comprend:
- une vis d'extraction,
- une bascule automatique équipée à sa partie inférieure d'une vis extratrice permettant sa vidange régulière dans la goulotte des malaxeurs.

**Plastifiant liquide.** Il est stocké dans un réservoir de 250 l. Le dosage volumétrique s'effectue par un vérin pneumatique à double effet, avec clapets de non retour. Le réglage se fait par vernier.

Les opérations d'approvisionnement et de dosage se font à partir d'un bouton unique placé sur un coffret de commande. Un voyant vert signale la fin des opérations. Le bouton de vidange commande des relais temporisés permettant l'alimentation des malaxeurs, dans un ordre établi, en matériaux constituant le coulis de ciment. Les matériaux tombent par gravité dans une goulotte à deux voies, qui alimente alternativement deux malaxeurs à haute turbulence.

**b) Préparation et injection du coulis**

**Malaxeur à haute turbulence.** Il se compose d'une cuve cylindrique de 130 l de capacité utile. Le malaxage et le laminage de la pâte s'effectuent entre deux rouleaux verticaux tournant en sens inverse. Deux malaxeurs sont utilisés alternativement pour alimenter un malaxeur de reprise (voir figures 11 et 12).

![Bascules doseuses Ciment - Sable](image1)

![Malaxeurs haute-turbulence](image2)

![Malaxeur de reprise](image3)

**Figure 11**

Zone inactive. Préparation du coulis.
Malaxeur de reprise. Il est utilisé «en tampon» entre les malaxeurs à haute turbulence et la pompe d'injection. L'agitation du coulis en attente est assurée par deux palettes montées sur un arbre vertical à l'intérieur d'une cuve de 150 l.

Pompe d'injection (marque BACHY, type PI2"-100). Les caractéristiques de la pompe d'injection sont les suivantes:

- Moteur à air comprimé,
- Pompe à pistons plongeurs,
- Débit 4700 l/h à 60 coups/min,
- Pression de refoulement 0 à 100 kg (avec de l'air à 3 kg/cm² de pression),
- Dimensions hors-tout: longueur: 2,65 m, largeur : 0,50 m, hauteur : 0,80 m,
- Poids approximatif: 800-kg.

Le coulis est refoulé dans les coffrages, à la pression de 2 kg/cm² environ, par l'intermédiaire de flexibles de 25 mm de diamètre raccordés aux cannes d'injection.
c) Circulation des coffrages

Les coffrages métalliques, composés d'un fond, d'un corps et d'un chapeau, sont montés sur une plate-forme roulante à boggies.

Les déplacements s'effectuent
- à la main dans le hall inactif,
- avec le carrousel mécanique dans le tunnel protégé de la zone active.

L'entraînement est assuré par une chaîne à taquets et un pivot escamotable fixé sous le chariot. Les portes des sas s'ouvrent sous la poussée de butoirs arrondis fixés à l'extrémité de la plate-forme. Dès que le fond du coffrage est garni d'agréagats, le chariot est entraîné par une chaîne et passe successivement aux différents postes de chargement. Dès qu'il a franchi le seuil du sas de sortie, il se libère automatiquement de la chaîne. Après collecte des eaux de ressuage et lissage du sommet, il est décoffré en partie, 24 h après l'injection, poussé sur des voies extérieures et enlevé au bout de 48 h pour stockage provisoire.

Le chariot et le fond du coffrage sont introduits de nouveau dans le circuit pour nettoyage, montage et remplissage.

4. LOCAUX ANNEXES

4.1 Vestiaires du personnel

Ils sont contigus à la zone semi-active et se composent:

a) d'un vestiaire inactif avec entrée extérieure, prévu pour sept à quinze personnes, avec un lavabo et une douche; il communique avec

b) un vestiaire actif prévu pour dix personnes, comprennent deux lavabos, deux douches, un WC, avec porte d'entrée en zone semi-active.

La ventilation est assurée par un groupe composé d'un ventilateur, d'une cellule de filtration et de quatre bouches d'aspiration au plafond, rejet par une cheminée extérieure; débit 470 m³/h (soit dix renouvellements horaires).

Eau chaude par chauffe-eau électrique à accumulation de 200 l. Appareils de contrôle du personnel (CFA III - I. P. A. B.).

4.2 Bureau sur passerelle

Situé au premier étage de la zone inactive avec vestiaires et sanitaires comprenant un lavabo, une douche, un WC. Eau chaude par chauffe-eau électrique à accumulation de 80 l.

5. FLUIDES, ÉCLAIRAGE, CHAUFFAGE, SOLS, INTERPHONE

5.1 Fluides

Électricité. Toute la distribution se fait à partir d'un tableau général d'une puissance de 200 kVA alimenté en courant triphasé 380 V.

Air comprimé. La pompe d'injection et les vérins de manœuvre sont alimentés par une centrale composée
a) d'un groupe marque SPIROS, type W2 A27

**Caractéristiques**

- Trois cylindres en W,
- Type à simple effet, compression bi-étagée,
- Deux cylindres BP - 1 cylindre HP,
- Refroidissement par air,
- Vitesse 725 tours/min,
- Volume horaire engendré 326 m³,
- Pression de refoulement 7 kg/cm²,
- Débit réel en air libre 4500 l/min,
- Régulation automatique,
- Moteur électrique de 40 CV;

b) d'un groupe de secours marque SPIROS, type V3 A13

**Caractéristiques**

- Deux cylindres en V,
- Simple effet - un étage de compression,
- Refroidissement par air,
- Vitesse 1000 t/min,
- Volume horaire engendré 448 m³,
- Pression de refoulement 3 kg/cm²,
- Régulation automatique,
- Moteur électrique de 34 CV.

L'air est aspiré au travers de filtres situés à l'extérieur du bâtiment. Il est refoulé par l'intermédiaire d'épurateurs-déshuileurs dans deux bouteilles de 1000 l timbrées à 8 kg/cm² de pression. L'ensemble des canalisations est pourvu de manomètres de contrôle, soupapes de sûreté et robinets de purge.

Eau. Alimentation en tube de 26 x 34 mm partant d'un robinet d'arrêt général.

Collecte des eaux douteuses. Les eaux provenant des vestiaires, des fosses de décantation et des puisards sont collectées et stockées dans deux cuves de 6 m³ utilisées alternativement.

On préleve un échantillon et on l'analyse; si les eaux sont inactives, elles sont rejetées à l'égout, si elles sont actives, elles sont reprises par camion par la Station de traitement des effluents radioactifs.

5.2 Eclairage

Il est assuré dans les halls par des lanternes étanches à ballons fluorescents, dans les annexes par des hublots étanches à lampes à incandescence, dans le bureau par des tubes fluorescents.

5.3 Chauffage

Le chauffage du bureau, des vestiaires et groupes sanitaires est assuré par circulation d'eau chaude. Celui des halls, des zones inactive et semi-active par deux groupes mobiles à air pulsé de 80 000 cal/h.
5.4 Sols

Les sols et les murs sont recouverts de deux couches de peinture «chloratex» qualité «routier» facilitant le nettoyage et la décontamination et permettant d'effectuer tous les raccords inévitables.

5.5 Interphone

Un ensemble de haut-parleurs pour appel général et de micro-réponses assure les liaisons indispensables à l'exploitation.

6. EXPLOITATION

La station est en mesure de traiter 10 à 12 m³ de déchets par jour avec un effectif d'une dizaine de personnes. Le prix moyen d'un m³ de déchets en vrac revient, après traitement, à 600 NF environ.

La zone inactive, à l'abri du gel, lui permet de travailler même par grand froid.

Il est possible, grâce à la souplesse d'exploitation de la zone active de retourner rapidement les châteaux de Pb aux utilisateurs et de recevoir et traiter des déchets de nature et d'activité diverses.

Elle est complétée par une enceinte de découpage à l'arc utilisée pour le tronçonnage des pièces de grandes dimensions (gaines de ventilation, échangeurs, cuves etc.).

7. CONCLUSION

Dans le cadre de ce rapport nous avons pu exposer les réalisations actuelles en matière de conditionnement des déchets solides et si nous pouvons arriver à une solution satisfaisante, il reste encore un programme important à réaliser.

En particulier nous disposerons d'une presse de 400 t destinée à la reprise des 12 000 fûts de 200 l et nous avons un projet rapidement réalisable concernant un incinérateur pour les déchets combustibles.

La réalisation d'une cellule chaude de tronçonnage des bouchons de pile et de découpage des éléments encombrants très actifs fait également partie de ce programme.

L'ensemble de ces moyens de traitement et de conditionnement permettra alors de faire face à tous les problèmes de déchets solides en attente d'une solution à leur évacuation définitive.

RÉFÉRENCES


J.M. HOLMES: You mention the storage of high-level wastes using a lead carrier inside the concrete. How many curies can you get into one of these containers before the fission-product heating causes the lead to melt or the concrete to spall?

E. MESTRE (on behalf of P. CERRÉ et al.): So far we have not had any problems of this nature at Saclay, though we have only used the method on solid wastes whose activity was of the order of 500 to 1,000 c gamma. We have, however, considered the problem, but have observed no heating over 40° at the surface of contact with the concrete, so we think we will be able to deal with the problem all right.

G. CALLERI: I should like to know what method you use to check whether the concrete injection is satisfactory.

E. MESTRE: We have several methods. First of all, we can see what is happening inside the tunnel with a system of television cameras and carefully placed mirrors. Secondly, for more than a year and a half before constructing this plant we produced blocks on a pilot plant and some of them were cut in two in order to show what was happening inside; we found that for operations lasting 20 to 30 min at pressures not exceeding 2 kg/cm², there were no interstitial spaces within these concrete blocks. Lastly, we subjected the blocks to drop tests, because the transport regulations require that packages containing radioactive substances can be dropped from a height of 1 meter without breaking. We dropped them from a height of 2 m and there were no cracks. We increased the drop height, and dropping from 2.6 m produced a crack in the base of the block on the side where the injection tube is located.

F. DUHAMEL: Could you tell us of the experiment you performed with an electric heating resistance?

E. MESTRE: We were asked by another department at Saclay to investigate the problem of processing and storing damaged irradiated fuel elements coming from reactors. In our experiment we used a fuel element heated by a 200-W electric resistance. Measurements were carried out with the aid of thermocouples carefully sited in the material surrounding the element, and they showed that when the latter was placed directly in contact with the concrete block there was damage to the material. However, when the element was placed in a sufficiently thick lead container before going into the concrete block, the temperatures at the contact surface between the lead and the concrete did not exceed about 40°C, although there was fusion of the lead around the element. This is very gratifying because the concrete deteriorates at about 80°C and it would therefore seem possible to deal with waste of very high activity, e.g. irradiated fuel direct from a reactor, by processing it in this way.

B. KOLYCHEV: These 500 or 1,000 c of activity you mentioned - are they distributed throughout the whole volume of the block or is it the activity per unit volume?

E. MESTRE: The total activity is contained in a small volume at the centre of the block, so that it is surrounded by concrete which is completely free from contamination.
P. DEJONGHE (Chairman): How do you prevent contamination of the external surface of the concrete block?

E. MESTRE: Before building the installation now in operation, we worked for 18 months on a pilot plant, and during this period we noted that contamination was carried away to the surface and to the walls of the concrete blocks. For this reason we altered the shape of our internal baskets, which are now closed at the bottom and have a 15-cm rim. This arrangement forces the colloidal cement filling to circulate at the edges of the basket and to penetrate into it; the cement is thus prevented from carrying contamination towards the surfaces in contact with the external atmosphere. Contamination checks carried out on the block surfaces concerned show no migration of radioactive ions from the inside to the outside.

W.G. BELTER: What are your plans for the final storage or disposal of these concrete blocks?

E. MESTRE: At present they are stored at Saclay, where we have two or three thousand blocks in storage. Various other sites have been considered, but a final choice has not yet been made.

F. DUHAMEL: I would like to reply a little more fully to the question asked by Mr. Belter. These blocks contain activities that can be termed low as compared with those we have been dealing with at this Symposium, and we consider that they can be stored without elaborate safety measures. However, for psychological reasons we are looking for sites which will give increased safety and which are also economically acceptable.
SHIPMENT OF GROSS QUANTITIES OF RADIOSTRONTIUM

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Abstract — Résumé — Аннотация — Resumen

SHIPMENT OF GROSS QUANTITIES OF RADIOSTRONTIUM. Future applications of radionuclides as heat or radiation sources are promising. The current and anticipated needs involve megacurie quantities of such nuclides as Sr90, Cs137, Ce144, and Pm147. Because of the remote locations of the sources of supply of these fission products, it is necessary to package and ship bulk lots of these nuclides. There is little precedent for shipment of isolated specific radionuclides in quantities of the region of a hundred thousand curies in concentrated form involving a few kilograms as a bulk product. In addition to the usual radiation shielding and heat-transfer requirements, shipments of this type are subject to several types of potential accidents which could release some of the contents to the atmosphere or to a fresh-water system.

Cask-design criteria were developed for shipments from Hanford to provide containment of contents under all normal shipping conditions and under accident conditions defined as impact with an unyielding surface at 44 ft/sec followed by either loss of heat dissipation for 48 hr or immersion in a fire at 2500°F for 2 hr. In addition to containment, the early cask designs provided for loading and unloading by handling solutions, and remote operation of process fittings and closures.

Shipments of fission products to date have been made either as a filter cake which is dried and stabilized in the cask or as a cation absorbed on an inorganic, ion-exchange material. Hanford-designed casks, which have been used for shipping strontium-90 in both product forms, are described and a comparison of the differences in basic design requirements is made.

While these casks were designed to withstand the defined accident conditions, it was recognized that a severe accident could release some of the contents. Evaluation of the consequences of such postulated releases indicated that releases which could become airborne were more severe than releases to fresh-water systems; thus, the physical and chemical properties of the shipment medium are of great importance. Extensive decontamination of property and evacuation of the populace would be required if these long-lived radionuclides were dispersed in populated areas.

In view of the serious consequences of an accidental release, even though the probability of such an accident is small, it was deemed appropriate to impose administrative controls which were planned to reduce the probability of a severe accident and, in the event of such an accident, to minimize the damages.

The damage evaluations have defined certain areas as requiring further development to obtain improved shipping conditions. Work is progressing in development of shipping forms which maintain current customer utility and which offer improved stability under accident conditions. Impact testing of current cask designs is in progress and the results of these tests are being evaluated to define the optimum combination of cask rigidity and use of impact absorbers which is required to obtain the required structural integrity.

TRANSPORT DE GRANDES QUANTITES DE RADIOSTRONTIUM. Les applications futures des radio-éléments comme sources de chaleur ou de rayonnements sont prometteuses. À en juger par les besoins actuels et prévus, on aura besoin de mégacuries de Sr90, Cs137, Ce144 et Pm147. Ehel donné que ces produits de fission ne peuvent être fournis que par des installations éloignées des centres de consommation, il faut prendre des mesures spéciales pour leur emballage et leur transport. Il existe peu de précédents pour le transport de quelques kilogrammes d'un radionucléide représentant une activité de l'ordre de 100 000 c. Outre les prescriptions habituelles concernant l'isolement et le transfert de chaleur, il faut observer des règles particulières du fait que ces envois peuvent subir divers accidents qui pourraient libérer une partie de leur contenu dans l'atmosphère ou dans les eaux.

On a établi des normes pour la fabrication des récipients utilisés pour les envois de Hanford, le critère de base étant d'assurer le confinement du contenu dans toutes les conditions normales de transport et en cas d'accident (impact avec une surface immobile à 50 km/h, suivi d'une interruption de 48 h de la dissipation de chaleur ou de l'exposition à un feu de 1570°C pendant deux heures). À l'origine, les récipients étaient
pourvus de dispositifs qui permettaient leur chargement et leur déchargement à la main et la commande à distance des ajustages et fermetures.

Jusqu'à présent, on transportait les produits de fission sous forme de tourteaux séchés et stabilisés dans le récipient ou sous forme de cations adsorbés par une substance inorganique échangeuse d'ions. Les auteurs décrivent les récipients construits à Hanford pour le transport de $^{90}$Sr sous ces deux formes et comportent leurs spécifications essentielles.

Bien que ces récipients aient été prévus pour supporter les accidents définis plus haut, on a reconnu qu'un accident grave pouvait provoquer la libération d'une partie de leur contenu. L'évaluation des conséquences possibles d'une telle libération a montré que la dispersion dans l'atmosphère serait plus grave que la dispersion dans l'eau douce; c'est pourquoi les propriétés physiques et chimiques du moyen de transport ont une grande importance. Si ces radioéléments à longue période se dispersions dans des zones d'habitation, il faudrait procéder à l'évacuation de la population et à une décontamination générale.

Bien que la probabilité d'une libération accidentelle soit très faible, on a jugé nécessaire, en raison des conséquences graves qu'elle pourrait avoir, d'imposer des contrôles administratifs visant à diminuer la possibilité d'un accident grave et à minimiser les dommages qui pouvaient être ainsi causés.

L'évaluation des dommages possibles a permis de définir les améliorations à apporter pour parfaire les conditions de transport. On met au point à l'heure actuelle des récipients qui garderont longtemps leur intégrité et qui résisteront mieux aux accidents. On poursuit les essais de résistance aux chocs des récipients de type courant et on analyse les résultats pour déterminer la combinaison optimale des qualités de rigidité et d'amortissement qui assurera l'intégrité structurelle requise.

La TRANSPORTATION DES COUCHES RADIOACTIVES. L'utilisation de radioisotopes comme source de chaleur ou de rayonnement nucléaire est envisagée pour le futur. Les exigences actuelles et futures en termes de radioisotopes, tels que $^{90}$Sr, $^{137}$Cs, $^{144}$Ce et $^{147}$Pm, pourraient être satisfaites par des récipients hermétiques pouvant être transportés dans des conditions normales de transport et résistant à des accidents, comme un choc avec une force de 44 lb/ft² de choc avec une force de 44 lb/ft² et 48 heures de dissipation de chaleur ou une exposition à 2 500°F pendant 2 heures. Les premiers récipients comprenaient des dispositifs de chargement et de déchargement, ainsi que des commandes à distance pour le couvercle lors de la manipulation. Les produits de fission étaient transportés sous forme de briques stabilisées dans le récipient ou sous forme de cations adsorbés par une substance inorganique échangeuse d'ions. Les récipients fabriqués à Hanford pour le transport de $^{90}$Sr sont comparés en termes de spécifications essentielles.

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INTRODUCTION

The United States Atomic Energy Commission's Hanford Plant operated by the General Electric Company's Hanford Atomic Products Operation, represents a strategic source of large quantities of fission products needed for certain Commission-sponsored isotope development programmes. Among the more important fission products at the present time is strontium-90, a heat-producing, beta-emitting nuclide of 28-yr half-life. This paper discusses the approaches taken for shipment of strontium-90 from Hanford and covers the development, design, and appraisal of the shipping systems which have been or are being used for this purpose.

To date, 1\frac{1}{2} megacuries of strontium-90 have been shipped by railway from Hanford in one of three basic systems, designated as: the HAPO-IA, the HAPO-IB, and the HAPO-II. Table I lists the individual shipments made in each system. The HAPO-IA system is no longer in operation. In this
system, an inorganic alumino-silicate ion-exchange resin was used to adsorb the strontium cation and retain it during shipment within a demineralized water medium. Volume and heat-transfer considerations limited the maximum shipping capability of the HAPO-IA system to about 80,000 curies of purified strontium-90. Actually, the shipments of strontium-90 in the HAPO-IA cask did not reach this figure, as is evident from Table I, since heavy loadings were not needed to meet the shipping commitments.

The HAPO-IB and HAPO-II shipping systems are basically identical, the primary difference being one of size. Both systems were designed to ship strontium-90 as the carbonate salt; collected, dried, and stabilized in place within the cask. Thus, HAPO-IB and HAPO-II are characteristically "dry" shipping systems as distinct from the "wet" HAPO-IA system. Shipping capabilities of the HAPO-IB and the HAPO-II systems are about 500,000 curies and 170,000 curies of strontium-90, respectively.

Both the adsorbed cation and carbonate salt forms of radiostrontium employed in Hanford shipments to date were chosen as convenient and reasonably stable intermediates in the over-all processing sequence. The Hanford-recovered strontium, in fact, has been converted elsewhere to

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### Table I

<table>
<thead>
<tr>
<th>Shipment</th>
<th>Date</th>
<th>Destination</th>
<th>Shipment: quantity curies of Sr(^{90})</th>
<th>Cask used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>April 1961</td>
<td>Oak Ridge National Laboratory</td>
<td>16,000</td>
<td>HAPO-IA</td>
</tr>
<tr>
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<td>22,000</td>
<td>HAPO-IA</td>
</tr>
<tr>
<td>3</td>
<td>July 1961</td>
<td>Oak Ridge National Laboratory</td>
<td>15,000</td>
<td>HAPO-IA</td>
</tr>
<tr>
<td>4</td>
<td>July 1961</td>
<td>Oak Ridge National Laboratory</td>
<td>118,000</td>
<td>HAPO-II</td>
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<tr>
<td>5</td>
<td>March 1962</td>
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<td>126,000</td>
<td>HAPO-II</td>
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<tr>
<td>6</td>
<td>March 1962</td>
<td>Oak Ridge National Laboratory</td>
<td>143,000</td>
<td>HAPO-II</td>
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<tr>
<td>7</td>
<td>July 1962</td>
<td>Martin-Marietta Co.</td>
<td>130,000</td>
<td>HAPO-II</td>
</tr>
<tr>
<td>8</td>
<td>August 1962</td>
<td>Martin-Marietta Co.</td>
<td>170,000</td>
<td>HAPO-II</td>
</tr>
<tr>
<td>9</td>
<td>September 1962</td>
<td>Oak Ridge National Laboratory</td>
<td>500,000</td>
<td>HAPO-IB</td>
</tr>
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</table>
the titanate form for use in SNAP-VII thermoelectric generators and the United States Weather Bureau prototype thermoelectric generator now in service in the Arctic. However, all radiochemical refinement of the strontium in meeting the specifications of the final heat source was accomplished at Hanford by chemical treatment. The only radioactive impurity of significance in the strontium-90 shipments is strontium-89, a 50-d half-life fission product, easily controlled by aging before chemical treatment.

RADIOLOGICAL CONSIDERATIONS

At the time the design of the first cask was begun, there were no regulations applicable to shipment of multi-kilocurie quantities of radioactive materials and no established criteria covering the design of casks for shipping large quantities of highly radioactive materials. Although it was recognized that the cask should provide adequate protection during normal shipping, the degree of protection required for abnormal conditions was not specified. Therefore, a major consideration in cask design was the establishment of suitable criteria covering emergency conditions. Container features could be provided which would retain the radioactive contents in most accidents. However, accident conditions can be postulated which would result in loss of containment for almost any container design. Consequences of accidental releases of strontium were estimated to provide guidance for the container integrity requirements and other means of minimizing the probability and severity of an accident. Releases to both the atmosphere and fresh-water streams were considered.

Strontium carbonate, the medium of the HAPO-IB and HAPO-II systems, is a finely divided precipitate. The particle size was found to range from 4 to 12 μ, easily fractured to particles in the range of 1 to 4 μ. Adsorbed strontium, as was the case with the HAPO-IA shipments, was in the form of much larger particles (1 to 3 mm). However, aerosol-size particles containing strontium could be created, e.g., by volatilization or attrition of the resin.

Atmospheric release

Strontium released to the atmosphere would be distributed down-wind in accordance with the prevailing meteorological conditions. The exposure of persons in the affected area would be primarily by inhalation of strontium during the passage of the cloud. Prompt action taken to prevent consumption of contaminated crops and occupancy of highly contaminated areas would reduce exposure through ingestion of strontium. The dispersal of strontium and the estimated exposure of people are illustrated in Fig. 1. The curves assume: a constant wind-speed of 1 m/sec in a stable atmosphere; a particle-deposition velocity of $2.2 \times 10^{-4}$ m/sec; and a ground-level release. It was further assumed that the dispersion of the aerosol is adequately described by a modified form of Sutton's equation.

The lower curve shows the first-year dose resulting from inhalation within a contaminated area as a function of the quantity of radiostrontium
Estimated bone dose - in first year following release of 1 kc of Sr\(^{89}\) and 2.5 kc of Sr\(^{90}\).

released. This dose results from the deposition of radiostrontium inhaled during passage of the cloud. Evacuation of personnel from areas in the path of the cloud probably would not be accomplished in time to avoid exposure from inhalation.

The upper curve shows the first-year dose resulting from ingestion of foodstuffs produced within the contaminated area as a function of the quantity of radiostrontium released. The corresponding levels of ground contamination are shown also. The dose from ingestion assumes that inhabitants continue to occupy the area and derive their foodstuffs from locally-grown produce which was exposed during the postulated accident. For those persons present in the area at the time of the incident, the estimated dose from inhalation should be added to the dose from ingestion. In actual practice, much of the potential exposure from ingestion of contaminated foodstuffs could be avoided by appropriate actions, such as evacuation or confiscation of crops.

The estimated dose to the critical organ, bone, during the first year after exposure includes the effect of both Sr\(^{89}\) and Sr\(^{90}\). The estimated dose
is the mean skeletal dose. The dose in newly formed mineral bone tissue would be substantially greater. The estimates are based on the standard man parameters as defined by the ICRP [1]. The British Medical Research Council [2] has recommended criteria for emergency exposure of the general public. Application of their recommendations to this particular mixture of Sr\textsuperscript{89} and Sr\textsuperscript{90} implies that the mean skeletal dose should be limited to a first-year dose of about 0.5 rem, assuming that the ingestion of radiostrontium is extended over a growing season. This level is indicated in Fig. 1 and corresponds to a contamination level of about 0.6 \mu c/m\textsuperscript{2} of combined Sr\textsuperscript{89} and Sr\textsuperscript{90}.

As an example of the use of Fig. 1, the release of 1 kc of Sr\textsuperscript{90} and 2.5 kc of Sr\textsuperscript{89} is postulated. Persons within a down-wind area of about 70 square miles would receive a first-year dose of more than 0.5 rem from inhalation during cloud passage. Foodstuffs produced within a down-wind area of about 2500 square miles would be contaminated to the extent that their continued consumption would result in a first-year dose of more than 0.5 rem. Application of the afore-mentioned criteria for emergency exposure of the general public indicates that some remedial action may be required in an area of the order of several thousand square miles. The corrective measures would probably vary from temporary confiscation of crops to removal of soil from production, evacuation of personnel and destructive types of decontamination, depending largely on the degree of contamination found.

The severity of a postulated accident of this magnitude depends on the location of the incident. Other variables such as prevailing meteorological conditions would influence the situation. The conditions chosen for developing Fig. 1 are generally unfavourable but not the extreme conditions which could be encountered. More complete treatment of these variables has been reported previously [3].

Water release

Other postulated accidents could involve the release of strontium to a fresh-water stream, either in the form of carbonate particles or as the cation. Strontium carbonate is only slightly soluble; however, the particles are of a size that is normally transported by rivers as suspended solids. The elution rate of strontium from the inorganic ion-exchange medium would depend upon a number of variables (e.g., the mineral content of the river), but studies have shown that the strontium would be eluted almost completely in about one day.

In either case, gross contamination of a river for a short period of time would be expected. The paths of exposure depend on the uses of the river for drinking water, industrial supply, food fisheries and irrigation of crops. Although the exposure of people and contamination of property could be severe, the consequences were estimated to be less severe than those for an atmospheric release, partly because river contamination is more amenable to prompt, effective control measures.

These hazards analyses were then used as a basis for developing criteria for vessel integrity and other control measures appropriate for shipping gross quantities of radiostrontium.
The main conclusion of this review of the consequences of radiostrontium release was that containment of the product under severe emergency conditions is paramount to the design of the shipping system. For this reason, the design criteria adopted for the strontium shipping systems were impact upon an unyielding surface at a velocity of 44 ft/sec followed by either total loss of heat dissipation for 48 hr or immersion in a gasoline fire with direct flame impingement for a period of 2 hr. Under these conditions, no loss of shielding or of product containment would be anticipated.

**SHIPPING SYSTEMS**

As mentioned earlier, three different casks of two basic types have been used for the shipment of strontium. All of the shipping systems consist of three main parts: a product container, a cask and cover, and a cask container.

**Product container**

The product container provides for the collection and containment of the strontium in the required geometry for heat dissipation. The cask and cover surround the product container and contain the process connections for loading and unloading the product. Also, the cask and cover provide radiation shielding and a means of conducting the heat to the outer surface for dissipation to the air by natural convection. The cask container completely surrounds the cask and has openings to permit the air flow required for heat dissipation. The cask container includes cushioning elements which provide a known stopping distance for the cask and correspondingly known forces at the cask surface upon impact with an unyielding surface. HAPO-II will be described in some detail as representative of all Hanford-designed strontium shipping systems.

Fig. 2 shows the HAPO-II product container which contains the fission products as a powder in a thin layer. The annular container reduces the temperature drop through the powder and also provides additional surface for heat transfer. The annular space is $\frac{1}{2}$ in thick; the inside diameter is 9$\frac{1}{2}$ in; it is about 18 in high and contains about 350 in$^3$. The radiostrontium is collected on a wire-cloth filter screen which is supported by lands formed by a series of horizontal and vertical grooves. The horizontal grooves increase the open area behind the filter screen and the vertical grooves provide a path for the filtrate to flow out of the filter.

To load the container, an aqueous slurry is brought in and distributed around the annulus. The filtrate then passes through the screen and out of the cask leaving the strontium in the annular space. When the container is loaded, the strontium is dried and stabilized by applying additional heat with an electric heat or high-pressure steam. Helium is used to purge the container during this stabilization step. After the cake is dried, the cask is sealed to maintain the helium atmosphere during shipping to improve the heat conduction within the container.
At the receiving site the strontium is removed from the container by dissolution. To assure adequate distribution of the solvent there are a number of small distributor channels on the back side of the filter. The solvent comes into the container, around the bottom ring, and then into the distributor channels from which it enters the product annulus. The product-bearing solution is removed through the slurry inlet.

The product container for HAPO-II and its attachment to the cask cover are designed to withstand a force equivalent to an acceleration of 50 g without failure. Also the product container is designed for 200 psig at 1000°F to withstand the pressures generated as a result of high temperatures or the radiolytic decomposition of the product.
Figure 3 shows the assembled shipping cask with the product container and the cask cover in place. The cask cover supports the product container and embodies the process connections for loading and unloading the product container. The process connections are equipped with three containment barriers in series.

The cover is lead-filled and of stepped construction to prevent radiation shine through the top of the cask. It is welded to the cask to minimize the possibility of exposing the unshielded product container and to provide a seal for retaining the primary coolant. This weld is protected against horizontal motion of the cover by a shear step in the steel plate. Also, the cover is stiffened by large fins on the top of the cover, which provide a bearing surface for the cask container.

The cask is an externally-finned, lead-filled cylinder with the lead confined by a 1-in thick outer shell and a ½-in thick inner shell. The assembled cask is about 3⅛ ft in diam., about 4⅜ ft high, and weighs about 18 000 lb.

The inner shell forms a well which encloses the product container, coils for removing the decay heat during loading and unloading, and an
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electric heater for the additional heat required during the drying and stabilization. The well is filled with a low-melting eutectic alloy for the thermal bond among the various components.

The external fins serve a threefold purpose: (1) they assist heat dissipation by spacing the cask within the cask container and by providing additional surface area; (2) they stiffen the outer shell; and (3) they assure load distribution from the container to the cask in the event of impact. The cask container is designed to distribute forces over about one quadrant of the cask surface. With this force distribution and the stiffening afforded by the fins, the cask will withstand a force normal to the cask surface resulting from a deceleration in excess of 50 g.

The action of the lead shielding on impact may rupture the pipes which pass through the shield. However, if these pipes should be ruptured, they are sealed on the outside of the cask to prevent the escape of product or loss of the molten alloy.

The decay heat from the strontium is transferred from the product container to the inside of the cask by a combination of conduction through and convection of the low-melting alloy. The product container is suspended from the cask cover and, thus, permits complete circulation of the molten alloy. The heat is then conducted through the walls of the cask to the outer finned surface where it is dissipated by natural convection to the air and radiation to the inner shell of the cask container. The heat radiated to the inner shell is then given up by natural convection, since radial heat transfer in the container is negligible. The resistance to heat conduction through the walls of the cask has been minimized by a metallurgical bond between the lead and the stainless-steel shells.

Cask container

Figure 4 shows the cask container with the cask in place. The cask container was designed to reduce the decelerating forces imposed on the cask, to distribute forces over the cask surface, and to permit the air flow required for dissipation of the decay heat. The cask container consists of four concentric, steel shells which extend above the cask top and below the cask bottom and which are separated by short, rubber columns. At the top and bottom of the container, heavy steel spiders are solidly attached to the outer container's shell thereby strengthening it against end, side, or edge impacts. The HAPO-II cask container is about 8 ft in diam., 12 ft high, and weighs about 23 000 lb without the cask in place.

As stated earlier, heat dissipation is by natural convection of the air at the cask surface and by radiation to the inner shell of the cask container. For normal cooling, the air flow is in through the bottom spider, and then up through the space between the cask and the cask container and out the top of the cask container.

The combined depth of the rubber columns provides about 16-in for the cask to decelerate. If the deceleration was uniform through this distance, it would be about 20 g. However, the force is proportional to the deflection of the rubber, and the maximum deceleration is, therefore, about 50 g. Falling on an edge has been considered as a combination of end and side
Fig. 4

HAPO-II cask container

Fig. 5

HAPO-II assembly on shipping car
impacts transmitted to the cask through an outer shell and end spiders. The end spiders have been designed to withstand a force equal to the end component of the force generated if the cask container lands on an edge.

Figure 5 shows the cask container in place on the rail truck. The outer cylinder of the cask container is rigidly attached to the rail truck by tie rods which extend from the top of the container to the end of the truck to offset over-turning moments due to switching impacts. The tie-down is safe for forces considerably greater than those encountered in normal railway transport, but it is not intended to secure the container to the car under extreme conditions. It is intended that the cask container would break away from the truck in the event of a train accident.

OTHER CONSIDERATIONS

The criteria for the design of these casks were selected to permit the shipment of radiostrontium without unnecessarily endangering the public and without the imposition of impractical or unduly restrictive shipping procedures. While many of the design features of the cask, such as the use of the external cask container to absorb the impact energy, are certainly conservative, it was concluded that the elimination of these features and the use of alternate concepts, such as the absorption of the impact energy through deformation of the cask, would result in too many uncertainties and that the use of these alternate concepts could not be justified when the potential hazard of the material was considered. Much of the conservatism initially was based on lack of knowledge of the reaction of materials and of various container shapes to impact loads. Information which was lacking at the time is now being developed through impact-testing programmes which are being conducted within the Commission. For example, the impact-energy absorbing capabilities of the HAPO-designed cask containers have now been verified. With the information developed from these programmes, a more rigorous analysis of the behaviour of containers and of the impact loads which they will withstand has become possible.

Recognizing the possibilities for failure of the cask and the extensive damage which would result from the spread of the cask contents, the Atomic Energy Commission has applied certain administrative controls to reduce the probability and the consequences of accidental releases. These controls include establishment of train routings to avoid large storage areas for inflammable or explosive liquids and chemicals and to avoid large population centres. The placement of the cask truck in the train is controlled to reduce the possibility of the cask truck being involved in a head-on or rear-end collision and in the event of derailment to reduce the possibility of the cask truck coming in contact with a truck containing hazardous liquids or chemicals. In addition, a courier, trained in emergency protective measures, accompanies each shipment.

REFERENCES

DISCUSSION

F. DUHAMEL: We believe that whenever possible it would be preferable to transport products of very high activity in liquid form. The liquid can be cooled by a water jacket round the container. This is what we have done for transporting large quantities of fission products (of the order of 500,000 c) with an average energy of 1 MeV.

R. TOMLINSON (on behalf of L. L. ZAHN et al): We do not think the transportation of very large quantities of highly active materials is practical in liquid solutions. We feel that the quantity that can be safely moved as a solution is so small that many more shipments would be required and therefore the likelihood of accidents increased. We feel also that it is much more difficult to ensure the containment of liquid systems under emergency conditions.

F. DUHAMEL: I do not think one should ever ship more than half a million to a million curies at a time. I suppose you have not exceeded that level of activity. Secondly, I believe that the confinement of liquid systems is better from the point of view of atmospheric dispersion, and I think it is atmospheric dispersion which constitutes the main hazard.

R. TOMLINSON: If, say, we were to transfer 500,000 c of strontium in solution, we would experience a rather rapid rise of the pressure within the system as a result of radiolytic decay. This means that the container would be required to withstand high internal pressures.

F. DUHAMEL: Our system is vented through a filter in order to avoid this difficulty and I do not think this increases the risk of contamination.

R. TOMLINSON: How do you ensure that liquid will not be lost through this vent pipe in the event of abnormal conditions?

F. DUHAMEL: We have developed various types of container, the smallest of which have a capacity of about 10 l and are intended for wastes up to 1000 c/l. These containers are fitted with a large number of safety devices: in particular they are vented in order to avoid pressure build-up and the risk of explosion. Experience has shown that we have been extremely cautious in this respect, since we have so far never observed any important changes in pressure or any severe gas release. On the other hand, it is clear that with high-activity solutions there will be a considerable release of gas. The system we employ for transporting large quantities of high-activity substances also incorporates a vent, which is automatically closed by a valve; this could of course become blocked in special circumstances, which are difficult to imagine - it could only happen in the case of an overturn accident. In connection with overturning we have carried out experiments in which we filled small containers with fluorocine, and threw them from a lorry travelling at a speed of 50 km/hr; I should apologize for this unscientific method, but we wanted to simulate actual conditions - we could detect no loss whatsoever. It might be that with some other accident there could be
a loss, but to that I would reply that I prefer a loss of liquid on the ground rather than dispersion into the air.

L. BAETSLE: Is there any technical reason why you prefer SrCO₃ to SrSO₄, which is much less soluble than SrCO₃ and cannot be eluted in nature.

R. TOMLINSON: Our studies indicated that very little difference in hazard potential exists between the carbonate and the sulphate salt. Carbo­

nate was chosen for process reasons.

W. G. BELTER: In view of Mr. Duhamel's opinion that it is better to transport high-level wastes as liquids rather than as solids, we would be interesting in the comments of participants from the United Kingdom and the Soviet Union in this connection.

D. W. CLELLAND: In reply to Mr. Belter's question, I would like to say that in the United Kingdom we have not so far had the need to trans­
port very large sources throughout the country and we are not really in a position, at this Symposium, to make any detailed statement on the matter. We could, however, send information to Mr. Belter at a later date.

B. KOLYCHEV: I cannot see any need for the long-distance transport of highly-active wastes in liquid form. We intend, in the future, to process such highly-active waste at the place where it is produced - in or close to the plant itself. The transport of low-activity wastes is unavoidable because such waste has to be collected from various scientific institutes, hospitals, etc., but in this case the transport is not particularly difficult.

S. LINDHE: I would like to dwell upon the general problems of transport of radioactive materials. In its Safety Series No. 6 and No. 7, the IAEA has issued regulations on the safe transport of radioactive materials, but the interpretation of these regulations is not easy. What, for example, is a maximum credible accident? Is it a drop from 15 or 30 ft on to a concrete path, or is it immersion in blazing oil for 3 or 6 hr? There are many questions to be answered. I found in my work at home that it is very difficult to translate the recommendations into practice; I think there is a need for standardi­

zation of procedures for the construction, testing and approval of transport vessels and containers, and it would therefore be useful if a conference could be organized on transport problems.

F. DUHAMEL: In my view, the concept of "maximum credible accident" is a useful one but should be regarded with some distrust. There is a tend­

cy to abandon it as far as reactor safety is concerned. Efforts should, of course, be made to limit the consequences of the most serious accidents, but it would be wrong to attach too much importance to accidents the probability of which is very low. We were interested, for instance, in the hypothetical case of buildings being struck by falling aircraft, and we decided not to take into account accidents the probability of which was less than 1 in every 10 000 yr. This does not mean, however, that one should not take the necessary precautions to limit the consequences of such an accident, in case it should actually happen. One should distinguish between risk and danger.

W. G. BELTER: During the discussion this morning mention was made of the possibility of shipping 500 000 c of fission products or even more. I am wondering if Dr. Duhamel has any other information on the shipment of such large quantities of liquid waste.
F. DUHAMEL: In addition to the small containers I have already described we have a second type of container, of large dimensions, though at present we have only one of this type. It can contain up to 500 l of highly-active liquid. Calculations show that it can be used to transport 500 000 c if the equivalent energy does not exceed 1 MeV, and it might be possible to go up to 1 million curies in certain circumstances. The protection is so efficient that we have never been able to measure radioactivity outside the container. It has been used to transport liquids whose average specific activity was greater than 2 c/l, but we have had no case of contamination. The container weighs about 45 t.

W.G. BELTER: Was the material transported on-site or off-site?

F. DUHAMEL: We have used this large container to transport fission products by road from Fontenay-aux-Roses to Saclay, and we are at present using the small containers for transport from Marcoule to Saclay.

D.W. PEARCE (Chairman): I think this question of the transportation of radioactive materials, both radioisotopes and radioactive wastes, is very important. The Agency has given some attention to it in the past and will no doubt return to it again.

ADDITIONAL STATEMENTS BY MR. DUHAMEL AND MR. DEJONGHE

F. DUHAMEL. I should like to add some general information on the French programme for storing and treating high-level waste, and will start by mentioning a few historical facts.

In 1949 the first French reactor became critical and in 1954 the first plutonium extraction plant, a pilot plant, went into service. It was in this plant that the first high-level waste arose, consisting of fission products with an activity of 1 to 5 c/l. The G-1 reactor, which now has a power of 40 MW, became critical in 1956, and in 1959 came the G-2 and G-3 reactors, each with 220 MW. A programme for providing nuclear electric power is now under way with the reactors EDF-1, EDF-2, EDF-3 and EDF-4 and the differences between the waste arising from the first reactors and that arising from the EDF reactors have given rise to various studies (these differences are due to the different compositions of the alloys and of the fuel, which in the first case is natural uranium and in the second case natural uranium alloyed with molybdenum). By 1970 installed nuclear capacity will be between 15 000 and 20 000 MW. The quantity of fission products arising, as you know, is given by more or less conventional figures, and by way of example an irradiation lasting 100 d gives 1 Mc/MW after one day of decay. Thus, by 1970 France will be faced with a quantity of wastes of the order of $10^6$ Mc. (Precise figures are given in a paper submitted by Lavie and Guirlet in Monaco in 1959.) As regards our present stocks and their specific activities, the waste from the plutonium pilot plant has an average activity of about 2 c/l and is at present stored at Saclay, where there is about 1 m$^3$ of it, whilst the higher-activity wastes of up to 1000 c/l - of which there are already several cubic metres - are stored at Marcoule.

Preliminary research on waste of very high activity was carried out at Saclay in 1958 on completion of a detailed study (started in 1956) of work done in Canada, the United States of America and Great Britain. I should like to take this opportunity of stressing the importance of the fruitful collaboration we have had with those countries, which alone enabled us to achieve such useful results as we have done, despite shortage of funds and a tiny staff (8 persons in all). The studies covered such subjects as heat generation, incorporation in synthetic crystals, vitrification by impregnation of glass sponges, etc., and led to our final choice of vitrification. In addition, problems of transport were studied, and two new types of container designed, one for transporting several thousand curies in a volume of approximately 10 l, the other for transporting up to a million curies in a volume of 500 l.

I will now refer briefly to the studies being carried out at present and already referred to here in the papers presented by J. Lefèvre(2), C. Sombret(3) and R. Bonniaud(4):

Concentration (evaporation and liquid storage in the case of the U-Mo alloy) - we now regard this study as nearly terminated;

Vitrification, involving, firstly, a study of the most stable glasses and those least prone to leaching - we regard this study as almost terminated; secondly, continuous operation production of these glasses - a plant has been constructed incorporating a lead shield 5 cm thick, which will give some idea of the activity levels we intend to deal with in this plant; pot vitrification for natural uranium - a 1 m-high unit is being designed and a 2-m high unit (with 5-cm lead shielding) has been built, and studies are to be extended to uranium-molybdenum alloys; finally, gelation - a hot cell is being assembled and 10-Mc blocks are to be prepared in the near future, but Mr. Sombret gave a detailed description of this work.

Separation - the information given by Mr. Lefèvre leads one to believe that it will be possible to extract from radioactive waste many obnoxious substances that can still be used in various ways.

The organization of research at the French Atomic Energy Commission (CEA) has undergone a few changes, I think of a similar nature to those that have taken place in other countries. Waste management itself is the responsibility of the Production Department (Direction des productions), while responsibility for research rests with whatever other department or section is directly concerned in the particular aspect of the problem to be investigated (chemical, transport, safety, etc.). Naturally these aspects are closely interrelated, and co-ordination of the work of the various departments and sections is essential; co-ordination has so far been ensured by the Reactor Safety Committee (Commission de Sûreté des Installations Atomiques), under the chairmanship of the High Commissioner. The Reactor Safety Committee has also studied the possibility of extending methods of dealing with medium-

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(2) RAGGENBASS, A. et LÉFÈVRE, J., «La séparation du césium-137 et du strontium-90 pour un traitement définitif des solutions concentrées des produits de fission», These proceedings.

(3) BONNIAUD, R. et al. «Vitrification des solutions concentrées des produits de fission: études et caractéristiques des verres», These proceedings.

(4) BONNIAUD, R. et al. «Vitrification des solutions concentrées de produits de fission: études technologiques», These proceedings.
activity wastes to wastes of very high activity, and such methods are referred to in the paper by P. Cerré and E. Mestre.\(^5\)

Indeed, in our opinion considerations of safety must be paramount. I would like to compare this high-level waste to an equation of a fairly high order and to point out that in solving such an equation one usually tries to reduce the order. This is more or less what one does in the vitrification of solutions, since the problem of high-activity waste is reduced to one of containing the medium- or low-activity vitrified residue. Although the separation of useful radio-elements from waste may, on the contrary, appear to be equivalent to raising the order, here the whole problem is changed and the additional safety measures that will be required may be worth while, in view of the usefulness of such recovered radio-elements. In any event the rate of increase of high-activity waste produced will for some years be such that changes can be made in the procedures as judged appropriate in the light of experience.

P. DEJONGHE: I just wanted to make a few comments regarding the Belgian research programme. Until two years ago the research programme at Mol, now directed by a Belgian private company, was concerned only with the treatment of low-level radioactive waste and with the study of site safety. Since then we have also studied the insolubilization of low-level waste concentrates by dispersion in molten asphalt. Quite recently we have tried incorporating solutions of much higher activity - such as the decanning waste arising from reprocessing operations - in asphalt, and I should like to mention here that we are negotiating with EUROCHEMIC to establish a much more comprehensive programme in this area. As far as this incorporation in asphalt is concerned we are still in the pilot stage as judged by American or all-European standards, but for Belgium it is already the final industrial stage since we are already insolubilizing all the concentrates we produce; experience has shown us that this method is extremely easy to carry out. We are not suggesting, of course, that bitumen or asphalt should be used for the insolubilization of very highly-active effluents, for which a medium with a low melting-point should be used. We have, however, found that this system, at present employed for processing 500 l/d, presents no real practical problems, and we are looking forward to continuing various studies utilizing this same principle but employing sulphur or other substances having a relatively low melting-point.

Finally, I would like to add a comment regarding the paper presented by Mr. Baetslé and myself,\(^6\) and that is that when we speak of relatively specific mineral ion exchangers, giving very high decontamination factors in acid media, we are thinking in particular in terms of the incorporation of this mass in some other, inert, mass with a very low melting-point.

\(^5\) CERRÉ, P. et MESTRE, E., "La lypholisation dans le traitement des effluents radioactifs: études de laboratoire et perspective d'avenir", These proceedings.

\(^6\) BAETSÉ, L. and DEJONGHE, P., "Treatment of highly-active liquid wastes by mineral ion exchanger separation", These proceedings.
VII

CLOSING DISCUSSION
D. W. PEARCE (Chairman): In starting this discussion I should like to ask each of our Session Chairmen to sum up that part of the proceedings during which he took the Chair. I shall then ask for comments from the other Chairmen and then for comments and questions from the floor, and then go on to the next Session Chairman. In this way we start off with Dr. Glueckauf.

E. GLUECKAUFL: We are at the end of an interesting conference and I shall try to sum up the first part of it, dealing with the concentration and storage of waste solutions. For several reasons this is a most important aspect.

Firstly, all countries that have progressed along the road to atomic power now have considerable practical experience, which they are capable of communicating to countries only just setting out along this road so that the latter countries will be able to save on development costs. Secondly, in the course of atomic power development, the quantities and activities of primary process solutions will attain formidable figures and the cost of storage in terms of manpower and materials will be very high unless concentration can lead to economical storage. Thirdly, the public has many apprehensions regarding these high-level liquid fission products, and there is a fear that the world may become cluttered up with dangerous fission-product storage dumps; it is therefore important to give some reassurance that this fear is unjustified. Lastly, the concentration of liquid waste to the minimum volume is a starting-point for all subsequent operations, whether they lead to separation of useful fission products or conversion to solid form, and in all cases economic operation is obtained by reducing the volume of the starting solutions to a minimum. It is also important to emphasize that the concentration and storage of liquids is now done on the largest scale, while solidification is at best in the pilot-plant stage, and sometimes only at the laboratory stage.

One consequence of this advanced technology in the field of concentration and storage is that the authors of papers are faced with a difficult task in presenting useful and detailed information on large-scale operations. I congratulate all those who spoke during that part of the Symposium over which I presided for having overcome this difficulty so successfully.

Now, what can be learned from these communications? Let us consider the primary concentration process starting with reduction of the column waste to minimum liquid volume. There are essentially two main steps to minimum liquid volume, and I want to go through these in detail because I believe it most unlikely that any future processing plant will deviate greatly from this pattern. The United Kingdom and French processes both start with maximum removal of nitric acid and then go on to storage of the highly concentrated solution in stainless-steel tanks, 40 l of solution per ton of uranium processed. The difference in size of the tanks finally used is not significant because, as was shown in Mr. Clelland's paper, the optimum economic tank-size is a function merely of annual production, and at present the British power programme happens to be larger than the French one. The
methods of nitric acid removal are somewhat different. In the United Kingdom, vacuum distillation followed by vacuum steam distillation at 60°C is used to give a final 3N concentration, and the nitric acid is fully recovered, reconcentrated and re-used in the dissolution of the uranium. In France, the nitric acid is destroyed by boiling at about 90°C, as formaldehyde, until the 3N concentration is obtained; the nitric acid so destroyed is not re-used at present, but is neutralized, treated and disposed of. In the British case the re-use of the nitric acid and the smaller boiler corrosion at 60°C lead to considerable economic advantages, quite apart from the fact that one gets no low-activity waste stream from the distillate. In the United States many liquid wastes arise, and I will confine my comparison to the Purex process, in which the concentration is started by distilling the nitric acid. The waste is then neutralized and stored in a large mild-steel tank, where further self-evaporation takes place. The fact that mild steel is much easier to produce than the stainless steel used in Europe more or less cancels out the disadvantage of the larger volumes per ton of uranium which arise in the United States, as a result of neutralization. It appears indeed that the cost of the procedures in the United States and in the United Kingdom does not differ significantly.

For caesium production the three countries which have announced their techniques intend to use inorganic ion-exchangers - heteropoly acids in the United Kingdom and France and special zeolites in the United States. In the case of strontium, two countries, the United States and France, are using solvent extraction techniques, while the United Kingdom intends to use precipitation with concentrated nitric acid - a method made practicable and economic by the familiarity of the United Kingdom Atomic Energy Authority with the processes for recovering nitric acid. It may be interesting to mention the annual production of these long-lived fission products, and from what I could glean from the printed papers it seems to be about 1 Mc in France, 10 Mc in the United States and 10 Mc in the United Kingdom, while the unknown figure for the Soviet Union may very well be much larger. In addition to this, EURATOM may well be providing another 5 Mc in the not too distant future. These quantities are far in excess of any foreseeable needs, so that the complete removal of caesium and strontium to facilitate the disposal problem is not at the moment an economic proposition, although it may be at some later stage. I have not said much in this summary about the various new methods of storage discussed in several of the United States papers, because these were summarized at the beginning of the Symposium by Mr. W.G. Belter, but the interest that was shown in the discussion on these papers clearly indicates the potential importance of these new and very interesting technologies.

F. DUHAMEL: Dr. Glueckauf suggested that it is better to wait until some process is perfected before going on to the industrial level, and also suggested it would be desirable to cover all fission products. I should like to make a comment which, perhaps, applies particularly in the case of France: as I have already remarked, during the next few years the production of fission products will develop more or less exponentially. In other words, the total amount of fission products hitherto produced will be of the same order of magnitude as the amount to be expected in the next year or two. So, if we build installations for treating the fission products already produced,
then, provided their amortization period is sufficiently short, they could be used industrially without prejudice to the future choice of processes. It may even be desirable to proceed to the industrial stage as quickly as possible because of the experience which we still have to gain in this area.

D. W. PEARCE (Chairman): Thank you. Now we shall hear from Mr. Hatch, our Chairman on the solidification and fixation of liquids by calcination.

L. P. HATCH: It was very gratifying, during this meeting, to note the considerable interest in the subject of fixation in solids. This was not always the case, and it was not too many years ago that the subject of storage in tanks was predominant. The Session over which I presided were on the subject of calcination, and seven papers were presented. I would simply like to make a few brief remarks regarding those papers. Calcination has been by implication described as an interim process if we are thinking in terms of the ultimate disposal problem, and it was conceived as an adjunct method in obtaining total, final fixation in a solid; as already indicated, the long-lived fission products, strontium and caesium, are not really fixed in the calcine material. So I think at the moment the chief function of calcination is to achieve a reduction in volume and to get the fission products into an immobilized form. In this way we could certainly look forward to the storage of liquid material with much less difficulty than otherwise. It was always recognized of course that calcination was associated with a number of difficult problems, largely due to the formation of fine particles and dust.

In the development of methods of achieving calcination, therefore, this problem of dust production always requires special attention. If, however, with regard to this whole problem of disposal of long-lived radioactive materials, we have reached a point where we are largely concerned with the differences in methods of achieving fixation in solids - by calcination, vitrification, etc. - then I think we have come a long way to recognizing that the problem has a solution which is practical, not expensive and deserving of our confidence.

Turning now to the paper by J. A. Buckham and J. A. McBride(1). I would like to discuss very briefly the fluid-bed calcination process, which has been under development for quite a number of years at the Idaho Falls National Reactor Testing Station. As Dr. McBride indicated in his oral presentation, this is the method that has been most thoroughly studied and has received the most support and it is the one we probably know most about - especially as far as the difficulties are concerned. The principle involved is quite simple: material is sprayed into a fluidized bed of seed material, where it is decomposed, forming a granular free-flowing product, which can easily be removed. This, therefore, has the necessary ingredients of a continuous process, and in view of the probable large-scale development of atomic power in the future we should think in terms of continuous processes. At the moment we are only dealing with small amounts of material, and the batch processes will probably be adequate for some years to come, but in the long run I think the continuous type of process will be preferable. Another major feature of the fluid bed is that it can be readily scaled up to a very large size; Dr. McBride indicated that a capacity in the neighbourhood of 1300 gal/hr might be feasible, which would be very large indeed.

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compared with the other units we have been talking about. The generation of fine particles and the handling of the off-gas system constitute the major problems with the fluid-bed system.

J. M. Holmes et al. discuss pot calcination at Oak Ridge.\(^2\) This is necessarily a batch operation. The major cost factor here is the need for large numbers of pots; then there are the difficulties of handling and storing them, and difficulties due to the blockage of heat-flow into the pot as the material calcines and builds up an insulating layer at the wall. These are all things that have been covered in the paper, but I think we all often tend to gloss over our difficulties and to speak mainly of the things at which we have been successful. On the whole, I think that calcination is associated with a number of difficulties which have yet to be overcome. A great advantage, of course, with pot calcination is that there are no difficult off-gas problems - one gets an almost totally condensible off-gas.

Logically, the next paper to consider would be the paper by J. A. Buckham\(^3\). I think this paper brought out the fact that very extensive consideration has been given to problems connected with the design of the mechanical equipment required in carrying out these operations (I am told by Dr. Buckham that he has a very complicated system of pipes and valves). This is certainly an important point.

The paper on molten sulphur by W. E. Winsche, et al.\(^4\) describes a new and quite different method of calcination. At first it appears to be a very simple method, but I think it has definite limitations; sulphur is a very good heat insulator, so the material calcined in it would be liable, shall I say, to melt its way to the bottom of the container. Sulphur can also be burned with oxygen. I think I have no further comments on that, except to say that personally I would regard the use of molten sulphur with some doubt.

The paper by R. T. Alleman\(^5\) deals with the most successful, if not the largest or the most completely developed, operation on calcination that has been done in the United States. At Hanford, they have actually calcined full-scale high-level wastes for the first time, and I gather this has been done without much difficulty. After calcination the material falls directly into a pot, where it is converted to a glass. The off-gas handling in the spray-calcination method has a unique feature in the use of the electrostatic device; with gas passing through a water medium the electrostatic effect is applied directly to the water medium.

The paper by W. H. Regan et al.\(^6\) deals with work at Brookhaven on what I think is perhaps the least developed of all the calcination processes. The main problems here seem to have been those involved in developing a rotary seal, but I think we have succeeded in developing a practical, dependable rotary seal device so that the chances of developing the rotary kiln method into a practical means of calcination are now much more promising.

\(^2\) HOLMES, J. M. et al., "Pot-calcination process for converting highly radioactive wastes into solids", These proceedings.
\(^3\) BUCKHAM, J. A., "Design of a hot pilot-plant facility for demonstration of the pot-calcination process", These proceedings.
\(^5\) ALLEMAN, R. T., "Radiant heat-spray calcination studies", These proceedings.
\(^6\) REGAN, W. H., et al., "Continuous calcination of high-level radioactive wastes by means of a rotary-ball kiln", These proceedings.
The paper on economics, by J. J. Perona et al.\(^{(7)}\), showed that the cost of fixation of wastes by calcination, together with the cost of interim storage in the acid form for periods of 10 to 20 yr (to reduce the heat production level) and the cost of transport, represents a minute fraction of the cost of producing atomic power; this indicates that the handling of waste raises no great economic difficulties, and we can therefore turn our major attention to the question of safety in ultimate waste disposal.

J. A. McBRIEDE: I should like to comment on one statement made by Dr. Hatch concerning the implication that fluid-bed calcination is essentially a large-volume process, and that the smaller, batch processes are satisfactory as a solution to the immediate problem. I think that what is overlooked is the fact that the fluid-bed calcination process can cover the full range of requirements. We have successfully operated calciners 6 in, 12 in, 24 in and 48 in in diam., and according to our calculations this covers the range from the present requirements to those in the foreseeable future.

L. P. HATCH: I did not intend to limit the fluid-bed system to large capacity units. I am glad you brought that up.

J. A. BUCKHAM: I would like briefly to mention some reasons for performing calcination as an initial, separate step, possibly to be followed by vitrification. There are perhaps two broad reasons for employing such a process: first, it permits interim, initial storage as a solid until the fission-product decay proceeds to a point permitting conversion to a suitable vitrified form for permanent disposal. Such a waiting period may prove necessary to prevent damage by fission-product beta-decay in the vitrified solid and is apparently now necessary pending the development of suitable vitrification processes; in any event, it should result in more economical and safer permanent storage. Second, prior calcination makes it possible to design equipment to perform calcination and vitrification in turn in a safe, economical manner, instead of having to compromise cost and probably safety in order to perform both operations simultaneously.

W. H. HARDWICK: I would like to take issue with Dr. Buckham and possibly with Dr. McBride on the comments they have made. On the question of fluidized scale-up, I do not think the scale-up of fluid beds is quite as easy as is made out here. Certainly, in England there have been considerable problems in the scale-up of fluid beds and I do not imagine that the problems are any easier in the United States. Secondly, on the question of intermediate calcination, it is assumed that a great throughput could be achieved in the fluid bed and that the ensuing vitrification process could cope at the same rate as the calcined solids are produced. I am not sure here, but I believe the high throughput in the fluidized bed was obtained with a product of high nitrate content, and it is possible that when the vitrification of this product takes place difficulties of cavitation during melt-down will be experienced, like those which have made us go fairly slow at Harwell. I noticed in another pot-calcination process, referred to in another American paper, that the pot was not filled completely but continuously, which approaches our own practice. I think that the vitrification process must be

\(^{(7)}\) PERONA, J. J. et al., "Economic evaluation of tank storage and pot calcination of power reactor fuel reprocessing wastes", These proceedings.
carried out continuously with evaporation in order to get the most economical and safest process - the hold-ups are smaller with continuous vitrification.

To go back to Dr. Buckham's comment regarding initial storage as a calcine with subsequent vitrification, it would surely be highly desirable to have glass storage when the fission-product danger is greatest, namely, during the period when the heat and radiation rating is high.

J.A. McBride: It has been stated earlier in this Symposium that there are no purely economic reasons for reducing liquid wastes to solids, and that the only reason for this is the greater safety with respect to the protection of mankind against harmful contact with fission products. At some point in the programme, however, economics must be considered as a decisive factor.

In the batch processes for reduction of wastes to solids, the age of the liquid wastes at the time of the reduction is of considerable importance, economically. The younger the waste, the smaller the container required for carrying out the process (and, incidentally, the more complex the process control problem), and since the calcination is done in the final storage container, a permanent economic disadvantage is thereby incurred in processing young high-activity waste. The alternative to this is to store the wastes in liquid form until they are old enough to permit calcination in large pots, such storage then coinciding with the period during which the liquids present the greatest hazard.

These factors should be taken into account in the overall evaluation of the various processes.

W.G. Belter: In connection with this question of why we should go through a calcination step instead of going directly to vitrification, it has been the feeling in the United States that it may not be necessary in the future to go beyond a calcined-oxide form, provided that a suitable alternative disposal site can be selected. Depending on the results of research and development work on geological formations, it may be possible - if we can overcome these technical problems of gas evolution from pots - to store a calcined-oxide material in a geological formation in a way that would be considered safe. If this is the case there may possibly be some economic advantage in not carrying the process to the vitrification stage. However, we realize that it may be possible to carry the process to the glass stage in a manner which is just as economical and we realize, too, that there may be certain process advantages in so doing; at the present time it is impossible to be sure, but this is one of the reasons why the United States has been developing calcination so extensively.

Secondly, Dr. Hatch mentioned that a lot of difficulties had been encountered in the calcination programmes. Now, I think this is a general statement that could be applied to any research and development programme, but I think it should be pointed out that there have been some notable achievements also and we feel that we are just reaching the stage of full-scale activity. In this connection, the pilot-plant results obtained in the past three weeks at the Hanford radiant-spray calcination installation have been very favourable - the results of the three or four pilot-plant or hot-cell runs which have been completed were all very satisfactory. I believe we now have a melt-pot in the cell containing 42,000 c of actual full-scale activity in solid form, and this I believe represents a significant step in the programme.
Many of the analytical results are just being obtained, but I think it is worthy of note that there have been some good achievements in this programme and we feel that within the next three years further significant strides will be made.

D. W. PEARCE (Chairman): Professor Kolychev, please, on vitrification.

B. KOLYCHEV: I think we must all acknowledge that the Symposium has been of great interest both as regards the amount of material submitted and its subject-matter. From what we have heard here, it is obvious what great efforts all the main nuclear Powers are now devoting to research on the treatment and storage of high-level radioactive wastes.

I must naturally turn my attention to the section of the Symposium over which I had the honour of presiding and which is of most concern to me, for reasons which I set out in my introductory remarks to Session IV. of these Proceedings. Whereas in Monaco vitrification was still the subject of isolated papers, here a whole section of the Symposium's work has been devoted to that theme, covering ten detailed reports. There were also numerous reports on calcination, which can be regarded as the first stage in vitrification. To sum up, I would say that the great majority of scientists in the countries represented here agree that vitrification is the most promising method of processing waste so as to ensure its safe burial for all time. The theoretical research work has been carried out in considerable detail, and has resulted in determining the optimum composition for glasses and the effect of the various components on the stability and durability of the glasses formed. What remains chiefly to be done, it seems to me, is first, to determine the optimum design for the apparatus and, secondly, to plan the process as a whole. In view of the very high concentrations of activity in the preparations we obtain, an exceptional degree of reliability is required both for the apparatus itself and for the means of operating and controlling it. That is why we should welcome the endeavour to achieve the maximum simplicity.

I shall not attempt to evaluate the various methods used and the results achieved. That can be done only after work has been carried out on a large scale, and particularly after work on active compounds has been carried out. Only when such work has been done - and it is being planned in all countries, we hear - will it become apparent in the near future which method may be regarded as the most promising and the most practical. I consider that the treatment and disposal of radioactive wastes is pre-eminently that sector of work on atomic energy in which scientists of all countries should exchange the results of their work as often as possible, in order to discover the optimum method of localizing and rendering such wastes harmless and in order to remove from all countries the temptation of dispersing wastes into the environment at the risk of inestimable harm to humanity. With that expressed desire, I should like to conclude my remarks until we meet again with new successes to proclaim in this humanitarian task of saving mankind from the possible harmful effects of radioactivity, not only on this generation but on generations still to come.

J. ROUX: I should like to make a comment regarding the treatment of waste from nuclear installations. I have been engaged on the design of various installations for processing waste at the industrial level, on behalf of the Special Construction Division (Service des Constructions Spéciales)
of the French Atomic Energy Commission (CEA). I think that one should speak of "by-products" rather than "wastes" and these by-products should be treated in such a way as to allow them to be recovered, at the appropriate time, for subsequent use. I know of several recent cases where people have had occasion to regret treating these products in such a way as to render their recovery impossible.

B. KOLYCHEV: I suppose, of course, that the use of highly active waste is feasible and that applications can be found for concentrated isotopes, especially as long-term sources of current. However, at least in the years immediately ahead, all this waste taken together will hardly represent a substantial percentage of the total waste resulting from the atomic industry. For this reason, and even though we are doing research on the subject, we have not reported on this work because it is not yet of any significant interest. In any case, this cannot be a primary method of utilizing and storing radioactive waste. I think that during the next few years the subject on which we must work is precisely that of how to bury radioactive waste safely and permanently.

W. G. BELTER: I would like to ask Professor Kolychev a question concerning the "industrial-sized burial grounds" mentioned in one or two of the Soviet papers presented here. Professor Kolychev seemed to have certain reservations regarding the storage of vitrified solids in a geological formation such as salt. I am wondering if he would care to say anything about other, preferred storage methods that may be under examination in the Soviet Union.

B. KOLYCHEV: I shall begin with the salt formations. I said that we do not consider salt formations a reliable place for storing liquid radioactive waste since, as everyone knows, salt is quite soluble and the solutions boil. As a result, the upper layers, the domes of the salt formations, will dissolve and the waste may ultimately escape into the soil, with the occurrence of seepage. As far as the possibility of storing solid products in salt formations is concerned, it can be said that they offer no important advantages whatever over any other systems, say, rock excavations. On the other hand, rock excavations have the advantage that they can be carried out close to the undertakings, whereas the proximity of salt formations is a matter of chance or luck and obviously a very rare coincidence. At present we have no burial grounds whatever for solid vitreous waste, since this process is only in the developmental stage. For the initial stage we are planning to store this waste experimentally in concrete, but further work is going on. For example, we intend to try using the heat release for melting the charges, with subsequent solidification of the vitreous charges; this would really make it possible to bury active waste forever.

D. W. CLELLAND: I would like to comment on Professor Kolychev's summary because I did not put the same interpretation on the results presented to this Symposium. It seems to me that there are still a number of basic problems to be settled before the vitrification of fission products can be carried out on a large scale, e.g. evolution of gaseous elements, de-vitrification, the long-term effect of radiation on the glass, leaching characteristics, cooling provisions, etc. Bearing this in mind, also that present liquid storage methods are safe, cheap and effective, and that there may be some demand for components of the material we now call waste, I sug-
gest that it would not be wise to engage in large-scale conversion to glass until we are certain that we have a system which will provide the high degree of containment and permanence desired.

B. KOLYCHEV: I agree with you, the more so since we still have time at our disposal. A tank is not an ideal form of storage but still it seals off the activity reliably and enables us to keep it under strict control. For this reason research on glass must be continued. As I have already said, we are not yet ready to vitrify tomorrow. We must of course work out this problem to its conclusion before proceeding to apply it on a wide practical scale. Experimental work must be carried out on an industrial scale and using active materials, without which we can never obtain a final answer to this question.

E. GLUECKAUF: I would just like to come back to a comment which Professor Kolychev made, namely that it would be desirable to have another conference of this kind in a year's time. I must say I could not disagree more with this, because progress on these matters, particularly when they are concerned with technological aspects, is often slow, and I think if we meet in another three years' time it would be quite soon enough.

F. DUHAMEL: I would like to express my opinion regarding this question of vitrification. It has been suggested that there is no advantage in treating wastes just now and that we should merely continue with research on this point. But we must know whether we should at once begin storing liquids or glasses. As I pointed out a short time ago, these quantities are going to increase more or less exponentially, and since certain techniques have now reached a satisfactory stage of development I think one could carry out treatment on a fairly large scale (as far as France is concerned, on an industrial scale). One has to choose between leaving concentrated fission products in a liquid form or treating them. The methods could be changed if they did not turn out to be entirely satisfactory.

W. G. BELTER: I would like to ask Professor Kolychev another question in line with some of our previous discussion. Perhaps the point is that in the Soviet Union there are no formations, such as salt formations, easily available. However, I was interested in your comment that you would perhaps look at other types of geological formations, such as impermeable granite-type formations, which may be located in the vicinity of your atomic energy installations. Are you carrying out any laboratory or field work regarding other types of geological formations that might serve as suitable storage places for high-level waste materials?

B. KOLYCHEV: At present we are not carrying out any additional research as regards solid materials since even those concrete burial grounds which we are now able to construct will be sufficiently reliable in that respect. I mentioned rock excavation merely by way of contrast to salt formations, simply because rock excavation is easier. What I have in mind here is that one is more likely to find suitable rock formations in the vicinity of the installations than salt formations. However, we are not now doing any work along these lines because it is premature and not necessary.

D. W. PEARCE (Chairman): Thank you. Now I call upon our next Session Chairman, Mr. Duhamel, to summarize miscellaneous methods of solidification and vitrification.

F. DUHAMEL: The papers presented under my chairmanship can be divided into two groups. The first relates to the migration of radioelements
into the environment of whatever site is used for the final disposal of high-activity fission products. Although this question perhaps does not fall entirely within the scope of the Symposium, I think it is a very important point since it is very closely related and, in the long run, we have to know what happens to radionuclides when we undertake final disposal. We have seen, for example, that even the best leaching coefficient would nevertheless permit a fairly strong specific activity if the products - especially glass - were stored in water without additional shielding. It can be taken for example, that a glass brick stored in water would release about one-tenth of a millicurie of fission products to the water each day. As storage will last a very long time, it is clear that equilibrium would rapidly (rapidly in relation to the storage period, of course) be reached between the activity in the glass and that in the water. Storage in water may, in fact, result in the problem of concentrated very high-activity effluents becoming one of widely dispersed medium-activity effluents. In the long run, the activity in glass will become an activity in, for example, a treatment sludge, and we may then be obliged to treat the water in which the glass is stored. The activity will thus have been widely dispersed. I do not claim that this is what will in fact happen to the stored glass; I am merely trying to demonstrate that the study of ion migration is very important. The manner in which it has been dealt with in the paper by V. I. Spitsyn et al.\(^8\) seems to me very interesting, because it constitutes a dynamic study much closer to reality. It would be useful if investigations of this type were carried out in various countries and future work will no doubt enable us to reach conclusions.

The second group of papers dealt with processes more suitable for wastes of low and medium activity than for those of very high activity, but it may be possible to extrapolate some of these methods to wastes of very high activity. No conclusion can be reached on the basis of this morning's papers. However, they are not altogether out of place in this Symposium, because problems of low and medium activity are closely linked with those of very high activities. It was therefore necessary to review briefly the various solutions that are being tried. It is of course impossible to examine them thoroughly, but we must be grateful to the Agency for having made available at this session some papers which, although dealing with only secondary aspects of the problem, will no doubt pave the way for other meetings where we shall learn of interesting ways of treating and storing wastes of very high activity.

D. W. PEARCE (Chairman): Thank you. And now our last Session Chairman, Mr. Dejonghe.

P. DEJONGHE: The short session of which I was Chairman was nevertheless extremely heterogeneous, because it really covered three subjects in two papers. We dealt with the preparation of materials for transportation; we also touched on methods of packing wastes and finally dealt somewhat vaguely with transportation properly speaking. The subject is varied and has not always been given the attention it deserves. I think we would all agree that it is preferable not to have to transport these substances at all, but we all know of cases where it has been necessary. The French delegation has mentioned that highly active solutions are transported regularly between

\(^8\)СПИЦЫН В.И., "Изучение сорбции и миграции радионуклидов в грунтах", These proceedings.
Marcoule and Saclay, presumably for research purposes; we have also heard of much larger volumes of somewhat less active effluents. There has been a great deal of talk during the Symposium of separating certain elements; these elements might be used for the preparation of sources; and these sources, in turn, will have to be transported, then retransported after use or possibly after being damaged. Another possibility that I can well imagine is that we may, sooner or later, wish to send certain effluents to other places, possibly better equipped to deal with them.

We have not discussed administrative problems. I am thinking, for example, of transportation outside a centre in relation to internal transport; i.e. transportation from the site of production to the site of use preceded and followed by transport within the two nuclear centres. Neither have we considered emergency measures. What we did discuss thoroughly, on the basis of a paper presented by Mr. Mestre of Saclay, was a remote-controlled packing system of which I think all familiar with the problem will be a little jealous. Mr. Mestre also showed that the French system could be applied to higher activities, but that would raise a heat problem much more difficult to solve in the somewhat crude case of embodiment in concrete.

In presenting the paper by L. L. Zahn et al., Mr. Tomlinson concentrated more on the complexity of the encasing problem - which he described extremely well - and that of transferring the materials in a casing. It appears that transportations of several thousand curies are already taking place.

Finally, there was the discussion more or less forming a bridge between this session and this afternoon's session - between Mr. Duhamel and Mr. Tomlinson - regarding the relative superiority of liquid or solid transportation.

I think we can conclude that it would obviously be preferable never to transport materials before complete insolubilization has taken place, but we also know that this is not always possible. As regards liquid versus solid transport, I think that, in the last analysis, both solutions have advantages and disadvantages and the safety measures have to be adapted to suit each individual case.

D. W. PEARCE (Chairman): I believe that brings us to the end of our programme and I would now like to say a few words myself. While the title of our Symposium is Treatment and Storage of High-Level Radioactive Wastes, I have noted with a great deal of satisfaction that we have also touched on many other aspects of radioactive waste management, and since this is my favourite topic I don't feel that I can let you go before mentioning the main aspects of this subject, aspects which all demand attention.

First I would mention the treatment of radioactive wastes; and of the various types of treatment we regard fixation as one of the most important.

Secondly there is the problem of transportation; we have touched on that during the week and I think it is well that we did do because what was said on the subject has emphasized, I am sure, the importance of very careful planning before any extensive transportation of these highly radio-

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(1) CERRÉ, P., MESTRE, E. and LEBRUN, P., "Station de traitement des déchets radioactifs solides". These proceedings.

(2) ZAHN, L. L. et al., "Shipment of gross quantities of radionuclides", These proceedings.
active materials is undertaken. In the future, much consideration will be given to national or even international burial grounds for fixed materials, so the problem of transportation demands our close attention.

Storage, of course, took up a great deal of our time. I like to look on storage as the direct opposite of disposal, and I like to distinguish very sharply between these two terms. There are really two types of disposal, I think: first, planned or routine disposal and, secondly, accidental disposal, a very important type of disposal, to which I am sure the Agency will have to give a great deal more attention than it has in the past.

One aspect of radioactive waste management to which the Symposium has paid very little attention is the monitoring of storage and disposal places, and I think we must attend more to that matter.

Finally, the question of economics was touched on; I was very glad to see this, as it is clear that, in the future, we shall have to examine the economics of the whole operation of radioactive waste management as it bears on the nuclear industry.
SYMPOSIUM ON THE TREATMENT AND STORAGE OF HIGH-LEVEL RADIOACTIVE WASTES

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