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OFF-GAS CONTROL PROJECT

by

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Pinawa, Manitoba**

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Chemical Technology Branch
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Projet de contrôle des gaz effluents

par

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Résumé

Un programme visant à développer et à évaluer des techniques pour la réduction des gaz effluents a récemment été mis sur pied à l'Etablissement de Recherches Nucléaires de Whiteshell. Le présent rapport fournit des renseignements sur les propriétés et sur le comportement prévu des gaz effluents des usines de retraitement et il donne un aperçu du programme expérimental devant être entrepris.

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ABSTRACT

A program to develop and study off-gas abatement techniques has recently been initiated at Whiteshell Nuclear Research Establishment (WNRE). This report provides information on the properties and expected behaviour of reprocessing plant off-gases, and outlines the experimental program to be undertaken.

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1. INTRODUCTION

A program to develop and study off-gas abatement techniques has recently been initiated at WNRE. In this report, we wish to identify important problems in the control of reprocessing plant off-gases and to provide a basis for the experimental program associated with the project. Primary objectives are:

1. removal of radioactive effluents from off-gases,
2. preparation of effluents for disposal,
3. control of inactive gaseous pollutants.

This report describes our initial approaches to objective 1. While the control of emissions from reprocessing plants is emphasized, similar technology may be useful for abatement of radioactive off-gases from other nuclear installations. For example, storage facilities for unprocessed nuclear fuel may require off-gas scrubbers in the event of container failure. In addition, control of off-gases from nuclear reactors is important and can benefit from advanced technology.

The growth in the literature over the past three years attests to the increasing emphasis being placed on off-gas abatement technology. For effective evaluation of this literature, we must contribute to the technology, perhaps developing alternative ideas for off-gas treatment processes. Therefore, experiments to be undertaken in our laboratory are emphasized in this report. Current technology has been summarized in recent publications and is only mentioned to bring our experiments into perspective.

Finally, the control of radioactive gaseous effluents has created the need for more advanced abatement processes as, in general,

large decontamination factors are required. Therefore, the technology being developed by the nuclear industry has the potential of making significant contributions to air pollution control in other industries.

2. REPROCESSING PLANT OFF-GAS

The reference feed to a reprocessing plant, for purposes of this study, is taken to be one-year-cooled CANDU* fuel. In this event, there are four radioactive nuclei forming highly volatile compounds which must be removed in the off-gas system, as shown in Table 1. Except for krypton, these species exist in more than one chemical form which defines a fundamental requirement regarding their control. In the following sections, we discuss the expected behaviour and properties of gases in a reprocessing plant.

2.1 IODINE-129

After one year of cooling, 80% of the total iodine in the fuel will be ^{129}I and the remainder will be stable ^{127}I . Approximately 7.8×10^{10} Bq (2.1 Ci) of ^{129}I will enter a 300 t(U)/a plant each year, assuming 650 GJ/kg Pickering fuel⁽⁷⁾. It is interesting to note that the U.S. Environmental Protection Agency has recently imposed severe restrictions on ^{129}I emissions effective in 1983⁽⁸⁾. If these standards were applied to this plant, emissions would be limited to 3.3×10^8 Bq/a (9 mCi) for 650 GJ/kg fuel, requiring a decontamination factor of 2.3×10^2 .

The nuclear fuel chemistry of iodine is somewhat complicated owing to the multiplicity of oxidation states and the corresponding

* CANada Deuterium Uranium

variety of chemical compounds. Thus, iodine material balances in re-processing plants have been deficient and non-reproducible. An Environmental Protection Agency (EPA) study at the West Valley Plant of Nuclear Fuel Services Inc., quoted in reference⁽¹⁾, found that 25% of the total iodine was emitted from the stack, 20% was found in the liquid streams, and 55% was not accounted for. Iodine forms volatile, semi-volatile, and involatile compounds which become distributed throughout reprocessing plants in gas and liquid streams as well as on surfaces.

Some idea of the chemical forms of iodine in the nuclear fuel cycle can be obtained from the analysis of effluent air from CANDU reactors (small amounts of iodine are emitted from reactors, and are collected in off-gas filters). At Pickering, a recent study showed that over 90% of the airborne iodine was organic iodides and HOI⁽⁹⁾. This is consistent with an Idaho Falls study showing that iodine evolved from BWR fuel is 4-5% I₂, 20-25% HOI, and 70-77% organic iodide⁽¹⁰⁾. The organic iodide is thought to be primarily CH₃I, the formation of which is highly favored in the presence of metal surfaces, radiation, heat, and in a reducing atmosphere⁽¹¹⁾. In addition, organic iodides readily form in HNO₃ solutions via reactions with organic impurities⁽¹²⁾. Therefore, it appears that a significant requirement for the management of iodine off-gases will be the control of CH₃I.

Voloxidation* of the fuel at 550°C releases 30%-70% of the total iodine and as much as 74% is released at 650°C^(13,14). The maximum amount of gaseous fission product release occurs between 450 and 650°C⁽¹⁴⁾.

The amount of iodine evolved from the dissolver depends on the plant design. It is generally felt that most of the iodine will be in the gaseous state in the dissolver, but that some will be returned by

* "Voloxidation" is a process whereby UO₂ is oxidized to U₃O₈ in air or O₂ using temperatures in excess of 300°C.

the HNO_3 reflux/recovery unit. In some instances, only 5% of the iodine is emitted from the dissolver⁽¹¹⁾. By contrast, the Barnwell plant of Allied-Gulf Nuclear Services is designed to release 99% of the iodine from the dissolver to the off-gas system⁽¹⁵⁾. Other studies have shown that most of the iodine can be evolved using steam stripping techniques in the presence of excess N_2O_3 ⁽¹¹⁾. It is expected that some of the I_2 in the dissolver will become oxidized to the nonvolatile IO_3^- . However, the presence of the reducing agent NO will retard this process.

Once in the process streams, a significant portion of the iodine will dissolve in the organic phase reflecting the favourable distribution coefficients for I_2 and organic iodides. One expects that this will result in the formation of other volatile organic iodides which will be emitted into the vessel off-gas flow. Washing the organic streams with NaOH will remove I_2 , but may not substantially extract the organic iodides. Thus, the organic phase may become increasingly contaminated with ^{129}I until equilibrium with the vessel off-gases is attained.

Aqueous streams will likely contain iodine principally in the forms HI, HOI, and HIO_3 . Both hydroiodic acid and hypoiodous acid are volatile and are expected to be evolved during concentration of the aqueous wastes. Thus, some of the iodine may condense out with water and end up in the low-level wastes. Iodates, on the other hand, tend to be insoluble; this is particularly true of the +4 oxidation states of Ce, Zr, Hf, and Th in HNO_3 solutions.

In conclusion, iodine will follow virtually every process stream and the off-gas treatment system must be capable of scrubbing a variety of chemical forms.

2.2 KRYPTON-85

Krypton-85 constitutes $\sim 0.8\%$ of the total volume of noble gas in spent fuel, and its behaviour in a reprocessing plant is thought to be well-understood owing to its chemical inertness. After irradiation, no Kr is found in the cladding⁽¹⁶⁾ and only 0.16% of the total Kr produced (^{85}Kr and stable Kr) is released in the puncture gases⁽¹⁸⁾. There is ~ 10 times as much stable Kr as ^{85}Kr in the fuel.

About 10% of the ^{85}Kr should be released in shearing operations^(16,17). A voloxidation step after the shear is reported to release 45% of the remaining ^{85}Kr at $\sim 550^\circ\text{C}$ ⁽⁴⁾. However, the release appears to depend on the fuel burnup and on the temperature of voloxidation. Oak Ridge work has shown that $> 98\%$ of the krypton is emitted at 800°C for a $(\text{U}, \text{Pu})\text{O}_2$ fuel irradiated to 8640 GJ/kg⁽¹⁸⁾. There has been some concern that higher temperatures lead to the formation of microcrystals in the fuel which traps the krypton and reduces its emission. However, since krypton has low solubility in aqueous solutions, all the remaining ^{85}Kr is released during dissolution.

While hazards and pathways are beyond the scope of this report, it appears that there are no significant sinks for ^{85}Kr ⁽¹⁹⁾ and that it does not substantially enter the food chain. The U.S. EPA emission limit⁽⁸⁾ for a 300 t(U)/a plant would be 3.3×10^{15} Bq (9×10^4 Ci) per year for 650 GJ/kg fuel, requiring a decontamination factor of 7.3.

2.3 CARBON-14

The question of ^{14}C emission from fuel reprocessing plants has only recently been addressed. In CANDU fuel, ^{14}C is produced via neutron reactions with ^{14}N impurities, with the natural ^{17}O component of oxygen in UO_2 , and with ^{13}C if a carbon-based lubricant is used. The largest contribution is due to (n,p) reactions with ^{14}N . The concentration of

^{14}N in fuel to be reprocessed in the Barnwell plant is about 30 ppm⁽²⁰⁾. Because ^{14}C can enter the food chain, it may constitute a greater hazard than ^{85}Kr ^(20,21,22).

In the absence of working experience, it is assumed that ^{14}C will be emitted from reprocessing plants primarily as CO_2 ⁽²³⁾. Under the dissolver solution condition, we expect most of the CO_2 to be emitted into the dissolver off-gas system. Recent measurements on emissions from boiling water (BW) reactors revealed that ^{14}C was evolved as CO_2 (95%), CO (2.5%), and the remainder as hydrocarbons⁽²⁴⁾. Similar measurements for pressurized water (PW) reactors where H_2 was employed as a cover gas, however, showed that 80% of the ^{14}C existed as CH_4 and C_2H_6 , while less than 5% was CO_2 and CO ⁽²⁴⁾. Therefore, as in the case of iodine control, some effort will be required to ensure that all possible ^{14}C compounds can be removed. The task of ^{14}C effluent control is somewhat simplified by the fact that nearly all the emission is expected at the head end.

2.4 TRITIUM

Tritium is produced in fuel as a ternary fission product. It is interesting that in CANDU reactors, more tritium is produced in the heavy water moderator via $\text{D}(n,\gamma)\text{T}$ reactions than in the fuel⁽²⁵⁾. Thus, the removal of tritium from aqueous solutions is an important consideration for reactor chemistry.

Information on the chemical forms of tritium in reprocessing plants is based on a study at West Valley⁽²⁶⁾ which found that the HTO/HT ratio in the stack gases was 3. As this was reported to represent $\sim 4\%$ of the total tritium, it follows that $\lesssim 1\%$ of the tritium was emitted as HT, all of which was expected to be emitted via the stack. However, the amount of HT in the fuel is apparently dependent on the burnup with higher burnup favoring the formation of HTO ⁽²⁷⁾.

Hydrogen isotopes form a stable hydride with zirconium which is not disturbed by fuel reprocessing procedures; thus, some fraction of the tritium produced in the fuel will remain with the hulls. This fraction appears to depend on the temperature of the fuel element during irradiation and, therefore, qualitatively increases with the power rating⁽²⁸⁾. As much as 80% of the total tritium has been found in the Zircaloy cladding⁽²⁹⁾, although most measurements fall within a range of 2%-60%^(18,28,30,31). Correlating these data with CANDU fuel conditions, \sim 5% of the tritium is expected to be bound as a hydride. Puncture gases contain only 0.001% of the total tritium⁽¹⁸⁾ which indicates that tritium is held relatively strongly in the fuel matrix.

Shearing operations release 1%-9.3% of the tritium and a further \sim 5% is released during dissolution⁽²⁵⁾. The 9.3% value from shearing was only attained by measuring the emission of tritium over a few days⁽²⁸⁾, a condition not likely to be encountered in reprocessing plants.

Voloxidation removes essentially all the tritium from UO_2 fuels when carried out at \gtrsim 450°C for 3-4 hours⁽²⁵⁾. Most of the tritium not removed at the head end follows the aqueous streams as HTO and the equilibrium amount remaining in the organic phase is only 0.2%⁽³²⁾.

As a consequence of the technological difficulty of separating HTO from H_2O , the most effective procedure for tritium control may be removal at the head end. Thus, voloxidation of UO_2 fuels is desirable.

3. OFF-GAS CONTROL AND PROPOSED EXPERIMENTS

With the background presented in Section 2, we now summarize the status of current technology and the approaches to be taken in our

laboratory. The initial emphasis will be on procedures not requiring complex technology, thus making the most efficient use of available resources.

3.1 CONTROL OF IODINE-129

Iodine recovery processes are summarized in Table 2. The classical methods for iodine removal from gas flows are caustic scrubs and adsorption on activated charcoal, but neither method is appropriate for control of iodine in reprocessing plants because each is relatively ineffective for organic iodides^(1,3). The use of impregnated charcoals (using, for example, KI or triethylenediamine) allows retention of organic iodides with reasonable efficiency^(33,34,35). However, objections can be raised regarding the use of charcoal in any form in a reprocessing plant. Most notable are the combustion and explosion potentials, especially in the presence of nitrogen oxides⁽¹⁾.

An alternative approach to iodine control is absorption in nitric acid solutions. The IODOX process⁽³⁶⁾ uses 19-22 mol/L nitric acid in a bubble cap or packed column to oxidize every form of iodine to IO_3^- . The solution is concentrated and eventually evaporated to dryness to form the pentavalent $\text{I}_2\text{O}_5 \cdot 1/3 \text{H}_2\text{O}$. Decontamination factors as high as 10^4 are reported, and the process appears to be immune to poisoning. However, the formation and handling of the 19-22 mol/L hyperazeotropic nitric acid required for the process to work is not straightforward. For example, vessels cannot be made from common materials (i.e. stainless steel) due to corrosion, and, for economic reasons, the hyperazeotropic nitric acid must be regenerated.

A related technique uses more modest HNO_3 concentrations (8-12 mol/L) with 0.2 to 0.4 mol/L $\text{Hg}(\text{NO}_3)_2$ ⁽³⁷⁾. Iodine is recovered in solution as HgIO_3 , and is eventually solidified as NaIO_3 . A minimum

decontamination factor of 10 should be attainable, but it has been found that aromatic iodides penetrate the system and that aromatic vapors poison the scrub solution.

Sorption of iodine compounds on Ag-impregnated inorganic supports is simple and effective. Perhaps the best known sorbent is AgX, a silver substituted zeolite^(38,39). Advantages include non-flammability, resistance to poisoning, and non-explosive operation in the presence of NO_x . Decontamination factors depend on such parameters as the shape and size of the adsorbent particle, humidity, and gas composition. For example, 12-14 mesh granular AgX has a DF for I_2 of 10^3 at 98 + % relative humidity while 10-20 mesh spherical AgX under the same conditions has a DF of 6.2⁽³⁸⁾. Other zeolites, for example those containing Pb and Cu, are less expensive but are ineffective at removing CH_3I . The performance of AgX in removing other organic iodides requires further study.

A notable development in iodine sorbents is AC6120 - an amorphous silicic acid impregnated with AgNO_3 ^(40,41). This material has approximately twice the iodine loading per unit Ag content as does AgX and has been observed to react with several organic iodides. More significantly, AC6120 has been tested using off-gasses from the Karlsruhe reprocessing plant and an ^{129}I decontamination factor of 10^4 was reported⁽⁴¹⁾. We anticipate that some testing of AC6120 will take place in our laboratory.

While inorganic iodine compounds probably can be handled using caustic scrubbing techniques, the organic forms are more difficult to remove. The general approach to be taken in our laboratory will be to decompose the organic iodides to inorganic species which can then be removed efficiently. If total conversion can be effected, the decontamination factor becomes independent of the iodine compounds present.

Since methyl iodide is presumably the most abundant species, the following discussion uses this as a representative organic iodide. However, it must be stressed that any procedures developed must be capable of treating all possible organic forms.

3.1.1 Thermal Decomposition and Catalytic Cracking

Since the $\text{CH}_3\text{-I}$ bond strength is only $\sim 2 \text{ eV}$ ⁽⁴²⁾, it is not surprising that thermal decomposition of methyl iodide occurs by rupture of the $\text{CH}_3\text{-I}$ bond^(43,44). Also, iodine atoms rapidly react with CH_3I to produce I_2 ⁽⁴⁵⁾, even in the presence of air. Therefore, a straightforward procedure for decomposing organic iodides may simply involve passing the flow over a heated inert surface. A typical surface which is apparently inert to methyl iodide at least in the liquid state, is silica⁽⁴⁶⁾. A shift in the Raman spectrum of methyl iodide adsorbed on porous glass indicates that there is some degree of chemisorption which may make these surfaces effective at transferring heat⁽⁴⁷⁾.

Usually, however, it is better engineering practice to use a catalytic surface because lower temperatures can be employed. Pure alumina has been used to decompose liquid methyl iodide⁽⁴⁶⁾ at 20°C , and its activity was ~ 30 times greater than a commercial cracking catalyst. The activity was attributed to the greater Lewis acidity of the Al_2O_3 surface as compared to SiO_2 . It would be interesting, therefore, to explore the use of Al_2O_3 and similar Lewis acids as cracking catalysts for organic iodides in air streams. An important problem in using a catalyst with organic iodides however is deactivation of the surface by the decomposition products. For example, dissociation of gaseous CH_3I over zinc oxide irreversibly deactivates the surface owing to the adsorption of iodine⁽⁴⁸⁾. While simple thermal dissociation avoids this problem, one possible solution is to use a platinum catalyst. Elemental iodine apparently does not react with Pt at temperatures $< 1400 \text{ K}$, and

only dissociation to iodine atoms occurs⁽⁴⁹⁾. Further discussion on catalysts is deferred to the section on ¹⁴C abatement.

3.1.2 Plasma Chemistry of Organic Iodides

The fundamental idea in our approach to CH₃I control is to couple enough energy into the air flow to bring about dissociation. Perhaps the most intriguing technique to be attempted in our laboratory for accomplishing this will be the use of a catalytic plasma. Plasmas have been extensively studied with respect to fusion research and atmospheric phenomena⁽⁵⁰⁾, and significant progress has been made in understanding some of the chemical reactions involved⁽⁵¹⁾.

Much of the experimental and theoretical work on plasmas has involved the use of the noble gases and/or low pressures. The presence of air often leads to complex electrode processes which confuse the basic interactions being studied⁽⁵²⁾. Moreover, discharges at atmospheric pressure are difficult to obtain since the breakdown voltage is a function of the pressure and electrode gap. However, it is important to note that breakdown fields in air are less sensitive to impurities than in other gases.

A discharge results from the acceleration of randomly occurring free electrons in a gas by an electric field until the electrons are able to ionize some of the gas molecules. These secondary electrons are subsequently accelerated in the field thus producing more ionization. The overall effect is a discharge in which there is equilibrium between the rate of electron formation and loss. There is a broad spectrum of electron energies, and only the most energetic electrons will produce ionization. In a high frequency discharge, the electron energy distribution is in fact Maxwell-Boltzmann⁽⁵³⁾. Therefore an electric discharge plasma, as opposed to an electron-impact ion source, contains predomi-

nantly low velocity electrons and one expects excitation and dissociation processes to predominate.

Several mechanisms can be postulated as contributing to the decomposition of organic iodides. Some possible electron reactions are



in which [1] sustains the discharge. It is known that CH_3I is an effective electron scavenger^(54,55) and that CH_3I^{-} in the gas phase decomposes to $CH_3(g)$ and $I^{-}(g)$. This appears to be an effective means of methyl iodide scrubbing because electron capture cross sections are higher for the low-energy electrons found in a discharge. We expect direct inelastic processes [3] to contribute relatively less if low-power discharges are used.

Electron collisions with abundant N_2 molecules are highly probable. Relatively long-lived vibrational states in N_2 are excited in discharges and there is evidence that these can react with organic molecules⁽⁵⁶⁾. We feel that the C-I bond can be broken, if de-excitation of vibrationally excited species occurs via Penning-type reactions with organic iodides. Reactions may also occur with nitrogen atoms and activated oxygen species. Since collision cross sections are of the order of atomic dimensions, these secondary processes may be significant if the probability of energy-transfer is high.

Several other procedures for converting iodine compounds using a discharge and suitable reagents can be envisioned. For example, ethyl

iodide reacts with hydrogen atoms to form ethane and HI⁽⁵⁷⁾. It is known that hydrogen atoms are produced in abundance in electric discharges when H₂ is present⁽⁵¹⁾. This is not practical for our purposes owing to the presence of oxygen, but other reagents may be found which react more exclusively with the iodides. Moreover, selective gas phase chemistry may have relevance to the control of reprocessing plant pollutants other than iodine-containing molecules.

Probably the simplest procedure for maintaining a discharge in gases is by use of a DC field. At higher pressures (i.e. 100 kPa), the electron mean free path is short, and sufficient energy must be attained to produce some ionization. Therefore, large fields, perhaps of the order of 10⁷ V/m, are necessary. One method of producing these fields is through the use of electrodes with a curved surface. For example, a strong radial field can be generated by a thin wire electrode coaxial with a hollow cylinder. Owing to the large field strength in the vicinity of the wire, breakdown occurs at modest voltages. The resulting corona operates at a low degree of ionization and is characterized by the formation of vibrationally excited species⁽⁵⁸⁾. For a coaxial configuration, the field, E, decreases with distance, r, from the wire according to $E = V/(r \ln(b/a))$, where V is the applied voltage and a, b are the diameters of the wire and cylinder, respectively. For an applied voltage of 4000, a cylinder diameter of 1 cm, and a wire diameter of 10⁻² cm, the field at the wire is 10⁷ V/m. Preliminary work with this configuration has shown that corona discharges can easily be attained in air streams.

The chemistry effected in the air stream by the discharge will have to be studied carefully. For example, conditions will have to be found where the production of undesirable species (such as ozone and nitrogen oxides) is minimized. One advantage of this approach is that chemical reactions take place with virtually no restriction in the flow.

Some advantages may be gained by using a microwave discharge as opposed to a DC corona, since internal electrodes may be subject to corrosion and may cause undesirable catalytic effects. In employing microwave discharges, energy is coupled into the flow via an external wave guide, thus avoiding all contact with the gas. The system would be essentially maintenance free. Further, it is known that these discharges produce concentrations of excited molecules⁽⁵²⁾.

3.2 CONTROL OF KRYPTON-85

3.2.1 Current Technology

Several methods have been proposed for separating Kr from air streams, as summarized in Table 3. Of these, the most extensively developed are low temperature distillation⁽⁵⁹⁾ and fluorocarbon absorption⁽⁶⁰⁾.

In the low temperature distillation technique, the gas flow is scrubbed by a counter flow of liquid nitrogen which removes Kr, Xe, and O₂. The bottoms from the scrubber column are transferred to a batch still where the gases are selectively removed depending on their volatility. Compounds which are solids at low temperatures must be removed because they plug the scrubber column. Moreover, it is advantageous to remove oxygen and nitrogen oxides from the flow owing to the explosion potential. The usual procedure is to remove NO_x using a caustic scrub and to decompose N₂O over a rhodium catalyst. However, O₂ must be removed by catalytic reaction with H₂ which means that large quantities of hydrogen are consumed. The efficiency for krypton removal is reported to be 31%⁽⁵⁹⁾, but the low temperature distillation part of the system has a recovery efficiency of approximately 83%. The most significant advantage is that Kr and Xe are separated.

For the past nine years, a fluorocarbon absorption pilot plant has been in operation at Oak Ridge. The process makes use of the fact that Kr (and Xe) are more soluble than N_2 and O_2 in certain halocarbons, notably Freon-12. The first step involves absorption of 99.9% of the Kr and 33% of the air in the off-gas using a counter flow of Freon at $T \sim -5^\circ C$ and $P \sim 3300$ kPa(gauge). The bottoms are transferred to a fractionator column operating at $\sim 0^\circ C$ and ~ 300 kPa(gauge) where a counter flow of gas, obtained by heating the bottom of the column, removes the absorbed air. The gas stream from the top of the fractionator must be recycled because it contains a small amount of krypton. The Freon/ Kr/Xe mixture is then transferred to a stripping column operating at $\sim 0^\circ C$ and ~ 170 kPa(gauge) where the remaining gases are removed. Decontamination factors of 10^3 are possible, although Kr and Xe are not separated. Nitrous oxide must be removed because it follows the Kr/Xe stream. Freon absorption appears to be the best choice for ^{85}Kr abatement since the process is efficient, has no explosion hazard, and is relatively unaffected by contaminants.

3.2.2 Selective Adsorption Studies

As is evident from the preceding discussion, the removal of Kr from air streams requires relatively involved technology. A potentially simpler approach is to develop a solid sorbent capable of selectively adsorbing Kr from air. It has been demonstrated that charcoal beds are the most effective adsorbents for Kr⁽⁶¹⁻⁶⁸⁾, but their use in a reprocessing plant is undesirable, as discussed previously. Molecular sieves are also capable of adsorbing Kr although the loading capacities are only 15-50% that of charcoal.

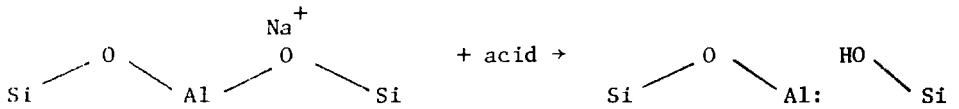
The problem that has not been solved is efficient selective adsorption of Kr in the presence of air. This is to be studied using zeolite molecular sieves to avoid explosion and combustion hazards.

Molecular sieves are composed of AlO_4/SiO_4 tetrahedra forming a pore structure containing cations which greatly affect sorption properties. Since it is essential to process large amounts of gas, chromatographic separation of air and Kr using sieves^(72,73) is perhaps of limited use in a reprocessing plant, and only bulk adsorption is viable.

One of the best commercial sieves for Kr retention is Ca^{++} -impregnated zeolite A (5A)^(61,62,63,69) and adsorption properties have been measured over a wide variety of conditions^(66,70,71). There is some evidence that the zeolite 13X may be more effective in a flowing system⁽⁶²⁾, although this conflicts with the results of reference 63. The sieve AW500 is reported to bind Kr stronger than either 13X and 5A⁽⁶¹⁾. These three zeolites, therefore, appear to be good starting materials for further studies. Indeed, Forsberg⁽⁷⁴⁾ has recently found that 5A is capable of removing Kr and CO_2 from O_2 and that decontamination factors of 10^3 should be possible. These studies were carried out at 273 K and 101 kPa. However, there is evidence that 5A will not be able to separate N_2 from Kr, especially at temperatures above 253 K.

Temperature is an important variable in the performance of molecular sieves. At 90 K, for example, O_2 is adsorbed on 5A much more effectively than N_2 . However, as the temperature is raised to 193 K, N_2 becomes preferentially adsorbed⁽⁶⁹⁾.

Molecular sieves may also be tailored for a specific process by changing the energetics of adsorption. This is accomplished by modifying the internal pore structure. Barrer et al^(75,76) have found that the pore cation population has a profound effect on the affinity for molecules having permanent electric moments. For example, decationation via reactions of the type



reduces the polarity of the pore. This decreases the heat of sorption for a molecule such as CO_2 having a quadrupole moment, but has virtually no effect on Kr. A similar effect can be achieved by removing framework aluminum ions⁽⁷⁶⁾.

Finally, the gas composition can also have an effect on sorption properties. In an O_2/N_2 mixture, unsubstituted zeolite A at -183°C adsorbs neither gas to any extent; however, pure O_2 is readily adsorbed under the same conditions⁽⁷⁷⁾.

Systematic studies of tailoring, temperature, and composition effects are important requirements for developing a molecular sieve procedure to separate Kr from air streams.

3.3 CARBON-14 CONTROL

There is currently no developed technology specifically for control of ^{14}C compounds in off-gases from a reprocessing plant. Since most of the ^{14}C will be evolved as carbon dioxide, proposed control methods have focussed on retention of CO_2 on adsorbents or the use of caustic solutions⁽⁶⁾. It is impracticable, due to the 5730 year half life, to store $^{14}\text{CO}_2$ as a gas and retention as an involatile solid is favored. An extensive review of fixation methods is contained in reference 78, but perhaps the simplest procedure is to precipitate $^{14}\text{CO}_2$ as CaCO_3 using a slaked-lime scrubbing solution^(23,79).

However, as previously stated, some ^{14}C may be evolved in the form of hydrocarbons and CO . Therefore, to obtain better decontamination factors, it would seem to be advantageous to oxidize these compounds to CO_2 prior to scrubbing. Extensive automotive emission control work has relevance to this project and it seems appropriate to study the feasibility of adapting some of this technology to the problem of ^{14}C abatement.

The performance of a catalyst is dependent on several conditions, not the least of which is the gas composition. Several catalysts may be capable of oxidizing CO and hydrocarbons to CO_2 , but important operating criteria for a reprocessing plant are:

- (1) high conversion factors; if 5% of the ^{14}C is not CO_2 , then a conversion factor of $\sim 98\%$ is required to attain an overall DF of 10^3 for ^{14}C , assuming all the CO_2 can be removed;
- (2) operation under high humidity conditions and in the presence of catalyst poisons; a considerable amount of NO_x will be present which is not only a poison for many catalysts but also will react with the water vapor to form HNO_3 ;
- (3) large throughput volumes.

Preliminary screening of catalysts, therefore, must be carried out to ascertain which have the highest activity for conversion under reprocessing plant conditions. Once the high activity catalysts have been selected, the kinetic data and equations necessary for proper reactor design will be developed.

Considerable guidance regarding the choice of appropriate catalysts can be obtained from the literature of automotive emission control⁽⁸⁰⁾. Common oxidation catalysts are the base metal oxides which are p-type semiconductors such as ZnO and NiO . A criterion for high activity appears to be partly filled d electron shells⁽⁸¹⁾, especially the configurations d^3 , d^7 , or d^9 ⁽⁸²⁾. Several of these, however, such as hopcalite (mixed Mn and Cu oxides), have low activities for some hydrocarbons⁽⁸³⁾.

Perhaps the most successful oxidation catalysts are the noble metals, especially Pt and Pd⁽⁸⁰⁾. Considerable work has been reported on oxidation using Pt⁽⁸⁴⁾, and, more recently, Al₂O₃-supported Pt^(85,86). The kinetics of oxidation over Pt are somewhat complex as the reaction is enhanced by oxygen and inhibited by CO, hydrocarbons, and NO. However, these effects are temperature dependent. For example, at temperatures greater than ~ 400°C, the reaction is not strongly inhibited by CO⁽⁸³⁾ and at ~ 200°C, NO apparently does not inhibit reactions over alumina supported Pt⁽⁸⁷⁾. One of the important consequences of the oxidation reaction being negative order with respect to CO and hydrocarbons is that the catalyst will have higher activities at lower concentrations of reactant⁽⁸⁰⁾.

All oxidation catalysts apparently have low activity for methane conversion and highest activity for unsaturated compounds⁽⁸¹⁾, indicating that dehydrogenation is an important primary step in the oxidation of hydrocarbons. However, there is some evidence that a supported rhodium catalyst has high activity for oxidation of methane⁽⁸⁸⁾. Our initial efforts, therefore, will be to study the activity of noble metal catalysts using reprocessing plant off-gas compositions.

3.4 TRITIUM CONTROL

Oxidation of UO₂ fuels to U₃O₈ releases essentially all the tritium into the off-gas stream as HTO and a small amount of HT. Procedures are well developed for oxidation of the HT to HTO and subsequent collection on solid sorbents. Decontamination factors of about 10³ should be attainable.

Tritium control in ThO₂ fuels, however, is not as straightforward since further oxidation is not possible. There are, therefore, two approaches that can be taken:

- (1) alternative head end procedures for removing tritium,
- (2) removal of tritium from the aqueous streams.

Removal of tritium from D_2O is important in CANDU reactors. Consequently, there is some effort underway to develop a hydrophobic HT/ H_2O exchange catalyst⁽⁹⁰⁾. Once this technology is fully developed, it may be adaptable to a reprocessing plant if decontamination factors are suitable⁽⁹¹⁾.

Ideally, a new head end procedure for tritium control should operate within the constraints of the existing process design. We have noted that some fraction of the tritium in UO_2 fuels dissolves in the sheath depending on the fuel's operating temperature. Therefore, a study of tritium mobility in ThO_2 as a function of temperature gradient would be interesting. By using chopped fuel, a large surface area is available which may enhance tritium emission over that experienced during reactor operation. A thermal gradient could be obtained by heating the chopped fuel (to a temperature below the melting point of zirconium, $\sim 1850^\circ C$), and then allowing the fuel to cool. During the cooling cycle, tritium may migrate from the hot core to the exposed surface and may be emitted into the off-gas system. Any tritium dissolved in the sheath can be embedded along with the hulls in polymer-impregnated concrete. Owing to resource limitations, there are no immediate plans to study the feasibility of this approach.

4. EXPERIMENTAL CONSIDERATIONS

Experiments are to be performed using the gas rack shown in Figure 1. To the extent possible, the reprocessing plant off-gas composition will be simulated by introducing gases, volatile liquids, and volatile solids into the flow.

Referring to Figure 1, the air manifold is connected to a filtered air supply or to nitrogen and oxygen air cylinders. The flow is partitioned using rotameters so that small amounts of air pass through vaporization chambers designed for introduction of volatile liquids and solids (eg. H_2O , I_2 , CH_3I) into the main stream. By changing the rotameter flows, different amounts can be introduced. Other gases are added to the stream through rotameters and the overall flow rate is measured using a thermal conductivity meter. Before the flow enters the chemical reactor, the composition can be measured by allowing a small amount of gas to pass through a micrometer valve into the mass spectrometer. Once the flow has passed through the reactor, product gases enter the exhaust manifold or are collected in sample bottles. Normally, the exhaust gases will be continuously monitored by diverting a small amount of the flow through a micrometer valve into the mass spectrometer.

The ultimate test of any given procedure for removing contaminants will be the effectiveness of the process under the simulated conditions. The following criteria are important for evaluation:

- (1) the decontamination factor ($\frac{1}{1-\text{removal efficiency}}$),
- (2) performance over a wide range of operating conditions,
- (3) performance over extended periods of time,
- (4) simplicity, ease of scaling, costing estimates.

Data are to be obtained using a quadrupole mass spectrometer interfaced to a programmable multichannel analyser. This choice was based on the experimental requirements:

- (1) analysis of a wide variety of chemical compounds,
- (2) identification of unknown products formed in the chemical reactor,
- (3) rapid, continuous monitoring of the flow.

Because a large amount of data will be generated, the programmable analyser is included to allow rapid reduction of a spectrum to the salient parameters - mass identification and concentration. In this way, the data base is reduced to manageable proportions, allowing instant decisions to be made regarding the effects of experimental variables.

5. PRESENT STATUS OF PROJECT

Current efforts are directed towards the development of a gas-phase scrubber for organic iodides using the apparatus shown in Figure 2. While further development of "electron-capture scrubbing" must be deferred until the on-line mass spectrometer is obtained, preliminary results have been encouraging. On passing air streams contaminated with CH_3I through the device, there are two important observations:

- (1) There is a substantial reduction in the discharge current when CH_3I is added to the air flow, indicating that electrons are being consumed.
- (2) A yellow-brown precipitate forms on the walls of the cylinder when negative voltage is applied to the central electrode.

Some attempt has been made to characterize the precipitated solid. A portion of the precipitate was washed with CCl_4 , forming a purple solution. The solution was observed to contain I_2 from U.V. spectroscopy analysis. The washed precipitate was pale-yellow, and a broad U.V. absorption band was observed at ~ 262 nm when the sample was dissolved in H_2O . Aqueous solutions of I^- , IO_3^- , and IO_4^- were all known to absorb in this region. Direct probe mass spectrometric analysis led to the formation of I_2^+ , I^+ , HI^+ , HOI^+ , and OI^+ ions when the precipitate was heated over a range of a few hundred degrees. At lower

temperatures, peaks characteristic of organic species were observed and these may be attributed to reaction products formed from the methyl moiety of CH_3I . At higher temperatures, there was an increase in CO_2 and I_2 being emitted from the sample. Both X-ray fluorescence and emission spectroscopy studies showed that no other elements were present in the sample.

The above observations are consistent with the formation of iodine-oxygen compounds, iodide, and I_2 in the scrubber. Iodine-oxygen compounds are effective oxidizing agents and it is known that the products of reactions with organic compounds are CO_2 and I_2 , perhaps explaining the mass spectroscopy results. Moreover, allowing the solid to remain in a closed container over a period of a few days results in the liberation of free iodine, perhaps indicative of slow oxidation of the organic impurities.

6. FUTURE REQUIREMENTS

Several different investigations using various technologies to develop the necessary off-gas abatement processes have been outlined. With the presently assigned personnel only one program at a time can be undertaken and resources must be carefully allocated. Additional personnel would mean that several projects could be run simultaneously.

In addition to abatement procedures, future work must include an experimental study of packaging technology for gases and semi-volatile species (e.g. RuO_4). This program will likely involve the use of existing technology and will be more straightforward than the development of gas scrubbing methods.

Finally, some effort is required to control the emission of non-radioactive gaseous pollutants, notably NO_x . Present technology (using aqueous or caustic scrubbers) is inefficient and more advanced procedures should be examined.

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TABLE 1

RADIOACTIVE OFF-GASES FROM PICKERING FUEL
IRRADIATED TO 650 GJ/kg

Isotope	Half-life years	Possible Chemical Forms In Off-Gas	Annual Activity Entering 300 Mg/a Reprocessing Plant	Mode of Production
^{129}I	1.6×10^7	CH ₃ I ORG-I I ₂ HOI HI	7.8×10^{10} Bq (a) (2.1 Ci)	Fission product
^{85}Kr	10.7	Kr	2.4×10^{16} Bq (a) (6.6×10^5 Ci)	Fission product
^{14}C	5730	CO ₂ CO hydrocarbon	4.53×10^{12} Bq (b) (1.22×10^2 Ci)	^{14}N (n,p) ^{17}O (n, α) ^{13}C (n, γ)
^3H	12.3	HTO HT	1.8×10^{15} Bq (a) (4.8×10^4 Ci)	Ternary Fission product

(a) CANIGEN output for UO₂ Pickering fuel.

(b) Assumes: 1) 1.09 year irradiation at an effective thermal neutron flux of $5 \times 10^{13} \text{ s}^{-1}\text{cm}^{-2}$; 2) ^{14}N impurity is 25 mg/kg by weight. The contribution from the ^{13}C content in the fuel lubricant is negligible.

TABLE 2

IODINE RECOVERY PROCESSES

<u>Process</u>	<u>Principle</u>	<u>Status</u>
Caustic scrubbing	Iodine reacts with caustic solutions to form I^- and OI^- .	Ineffective for organic iodides
Activated charcoal	Adsorption	Ineffective for organic iodides; explosion and combustion hazard, especially in the presence of nitrogen oxides.
Impregnated charcoal	Chemical reaction with impregnated species (e.g. KI, triethylenediamine)	Explosion and combustion hazard.
Silver zeolites	Reaction with silver-exchanged molecular sieves to form involatile iodides	No explosion hazard; relatively insensitive to contaminants but readily poisoned by halides.
"AC 6120"	Amorphous silicic acid impregnated with $AgNO_3$ to form involatile iodides	Approximately 2X loading factor for iodine per unit Ag compared to silver zeolites. Reacts with most iodine compounds except aromatic forms.
Mercuric nitrate Scrub	Scrubbing solution composed of 10 mol/L HNO_3 and 0.2 mol/L $Hg(NO_3)_2$.	Removes aliphatic iodides, but not aromatic forms; poisoned by aromatic vapors.
IODOX	19-22 mol/L nitric acid scrub oxidizes iodine compounds to IO_3^-	Removes all iodine forms; handling hyperazeotropic nitric acid requires special procedures.
Electric discharge scrubbing	Organic iodides scavenge electrons and decompose	Under development

TABLE 1
KRYPTON RECOVERY PROCESSES

<u>Process</u>	<u>Description</u>	<u>Comments</u>
Selective absorption in halocarbons	Kr, Xe more soluble than air in some organic solvents (e.g. CCl_4 , CCl_2F_2).	Pilot plant working for 9 years; relatively insensitive to contaminate.
Cryogenic distillation	Gases absorbed in liquid nitrogen, separated by distillation.	Explosion hazard if NO_x , oxygen present; good method to separate Kr from Xe.
Adsorption in liquid CO_2	Kr, Xe more soluble than air in liquid CO_2	Applicable to HTGR fuel reprocessing.
Room temperature adsorption	Absorption on charcoal or molecular sieves.	Large amounts of material required; contamination problem.
Low temperature adsorption	Absorption on charcoal or molecular sieves.	Combustion-explosion hazard if NO_x , O_2 present in charcoal.
Membranes	Noble gases preferentially sorbed into silicone membranes and evaporated from low vacuum side	Not yet applicable to large amounts of gas.
Thermal diffusion	Small concentration effect along a thermal gradient.	Not yet applicable to large amounts of gas.
Electromagnetic separation	Ionization and separation using a magnetic field.	Not yet applicable to large amounts of gas.
Chemical reaction	Reactions of Kr, Xe with powerful oxidizing agents.	Products are unstable; reagents probably react with other species in flow.

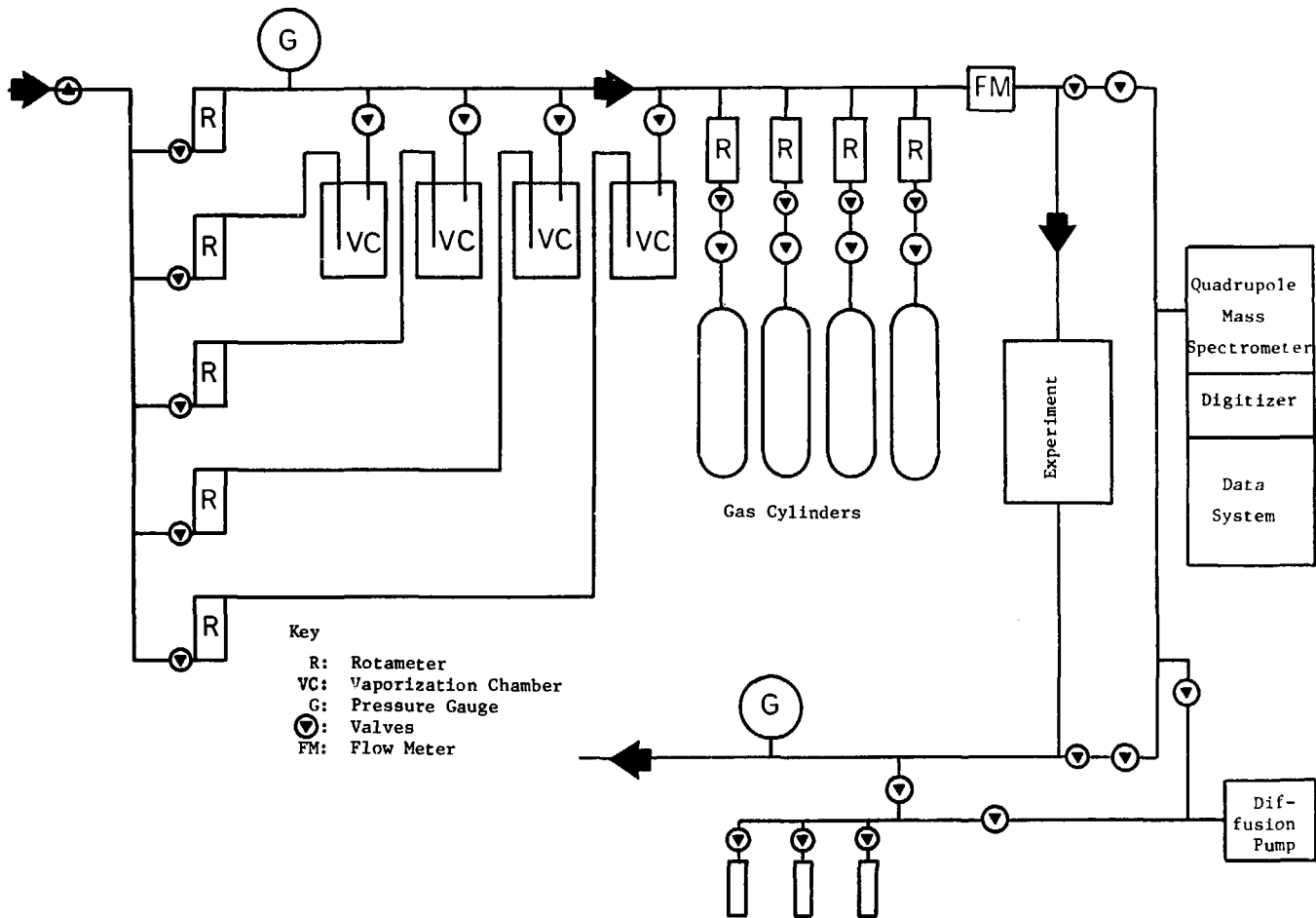


FIGURE 1: EXPERIMENTAL GAS LOOP ASSEMBLY

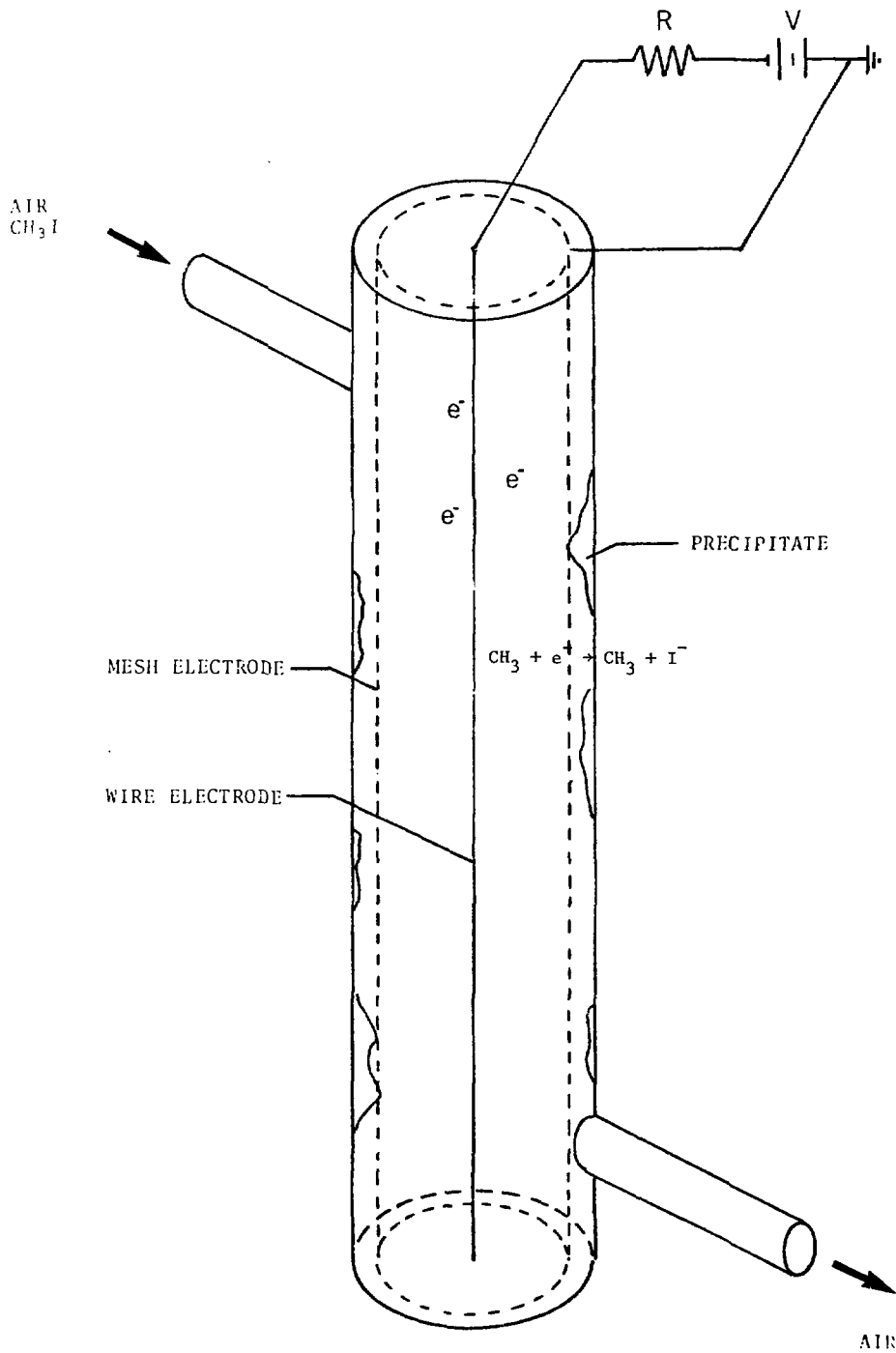


FIGURE 2: GAS PHASE "ELECTRON CAPTURE SCRUBBING" OF ORGANIC IODIDES



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