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**UNDERLYING CHEMISTRY RESEARCH FOR THE
NUCLEAR FUEL WASTE MANAGEMENT PROGRAM**

**RECHERCHE CHIMIQUE DE BASE POUR LE
PROGRAMME DE GESTION DES DECHETS DE COMBUSTIBLE NUCLEAIRE**

D. F. Torgerson, N. H. Sagert, D. W. Shoesmith, P. Taylor

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Pinawa, Manitoba R0E 1L0

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rédigé par

D.F. Torgerson, N.H. Sagert, D.W. Shoesmith et P. Taylor

RÉSUMÉ

Ce document décrit la partie recherche chimique de base du Programme canadien de gestion des déchets de combustible nucléaire, exécutée au service Chimie de recherche. Cette recherche comprend le développement et la compréhension des connaissances chimiques de base nécessaires pour les autres parties du programme. Il y a quatre domaines de recherche de base: chimie des formes de déchets, chimie des solutés et des solutions, interactions roche-eau-déchets et diminution et surveillance des radionucléides en phase gazeuse.

L'Énergie Atomique du Canada, Limitée
Établissement de recherches nucléaires de Whiteshell
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edited by

D.F. Torgerson, N.H. Sagert, D.W. Shoesmith and P. Taylor

ABSTRACT

This document reviews the underlying chemistry research part of the Canadian Nuclear Fuel Waste Management Program, carried out in the Research Chemistry Branch. This research is concerned with developing the basic chemical knowledge and understanding required in other parts of the Program. There are four areas of underlying research: Waste Form Chemistry, Solute and Solution Chemistry, Rock-Water-Waste Interactions, and Abatement and Monitoring of Gas-Phase Radionuclides.

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1. INTRODUCTION

There are several phenomena that must be understood and modelled correctly to assess the long-term performance of a waste vault constructed in plutonic rock. This can be done by carrying out integrated experiments and supporting them with information on the underlying principles affecting the observations. By elucidating these underlying principles, it is possible to develop models that extend experimental observations to geological time periods with considerable confidence. Thus, the Canadian Nuclear Fuel Waste Management Program includes a fundamental research component that aims at characterizing processes that will be important under geological disposal conditions. In this document, we review the underlying chemistry part of this research that is carried out in the Research Chemistry Branch.

Transport of radioactivity from the waste vault can only occur by the flow of groundwater. Therefore, the chemical nature of the groundwater and its interactions with various components are of paramount importance. Some of the more important chemical interactions in the waste vault are illustrated in Figure 1-1. As indicated at the bottom of Figure 1-1, groundwater will enter the vault from the surrounding geological media. The mineral surfaces may be altered by hydrothermal reactions, and these surfaces must be characterized to assess their ability to sorb radionuclides. In addition, the groundwater chemistry can be altered by the nature of the mineral surfaces.

Groundwater interactions with the buffer, container, investment material, and waste form will depend on aqueous parameters such as temperature, pH, oxidation potential, and dissolved ions. For example, corrosion of the waste form and mechanisms for the release of radioactivity may depend on the formation of surface films. The properties of these films, such as their solubility, will depend on the groundwater solution composition. Thus, the stability of the waste form may ultimately depend on the nature of these films, as well as the bulk properties.

Corrosion of the waste form may occur by leaching, or by a dissolution process involving break-up of the waste form. The various dissolved species can interact with the investment, container, and buffer materials, and with the geological media. The nature of these interactions, and therefore the transport of radioactivity, will be strongly dependent on the aqueous chemistry. Possible reactions include hydrolysis, oxidation/reduction, precipitation, and complexation with groundwater species.

Colloidal transport may also be an important phenomenon occurring in the waste vault. Besides direct break-up of the waste form, radioactive colloids could form from adsorption of fission products and actinides onto groundwater particulates. Depending on the aqueous chemistry, some species (particularly actinides) can undergo hydrolysis, polymerization, and colloidal formation.

Thermodynamic and kinetic data are required to model many of the processes outlined above. Although there are data bases available at 25°C for some species, there are few data available at the higher temperatures of interest (e.g. 100°C). Therefore, new experimental procedures are required to provide experimental data, and extrapolation techniques are needed to extend the 25°C data base to higher temperatures.

The general approach used in the underlying chemistry program is to develop predictive and experimental tools that can extend current fundamental knowledge to complex systems. The output, besides being used directly in waste management codes, also defines the key experiments for improving the data bases and for assessing our ability to predict the chemistry. Ultimately, of course, the information from this program becomes part of the overall waste management assessment process. By performing underlying research, we ensure that this assessment will have a sound scientific basis.

2. WASTE FORM CHEMISTRY

One of the principal barriers to the release of radionuclides from a waste vault is the limited ability of the waste form to dissolve. We have, therefore, directed a substantial research effort toward understanding the fundamental factors that control the dissolution of a waste-bearing matrix and the surface alteration processes which may accompany dissolution. In the case of recycled fuel wastes, we are also investigating phase relationships as they relate to the manufacture of the waste form and its subsequent performance.

Since there is, at present, no commitment to recycle nuclear fuel in Canada, irradiated UO_2 fuel bundles comprise one candidate waste form. In the event that fuel is reprocessed, then waste actinides and fission products will be incorporated into a relatively insoluble oxide matrix, such as a borosilicate or aluminosilicate glass, a glass ceramic or a crystalline ceramic. At present, processing limitations favour a borosilicate glass, although the alternative products could theoretically be more durable toward dissolution.

In this section, we describe work in four main areas: electrochemical studies of the dissolution mechanism of UO_2 , determination of phase relationships with respect to liquid immiscibility and hydrothermal crystallization of complex borosilicates, preliminary studies of the interactions between certain waste elements and investment or container materials, and phase diagram studies of systems that may provide "tailored" host phases for specific radionuclides.

2.1 UO_2 WASTE FORM CHEMISTRY

(D.W. Shoesmith, S. Sunder, M.G. Bailey and G.J. Wallace)

2.1.1 Introduction

In order to assess the option of irradiated fuel as a waste form, an understanding of the possible chemical reactions of UO_2 under vault

conditions is necessary. There are two main types of reaction whereby radionuclides can be released from irradiated UO_2 :

- (1) Matrix dissolution, where radionuclides incorporated in the UO_2 crystal lattice are released as the fuel dissolves
- (2) Dissolution of radionuclides that are insoluble in the UO_2 lattice, and exist in separate phases or are concentrated at grain boundaries.

The work of Johnson et al. [1] distinguishes the elements that behave in these two manners. The former route appears to be the principal release mechanism for most radionuclides, while substantial fractions of the inventories of cesium, iodine, tellurium and noble gases follow the latter route. Matrix dissolution will be dominated by the chemistry of UO_2 ; the dissolution of unirradiated fuel is, therefore, being studied in detail under a variety of water chemistry conditions.

Under reducing conditions the solubility of UO_2 is very low [2,3], but becomes substantial under more oxidizing conditions due to the generally higher solubility of U(VI) than U(IV). Consequently, it is reasonable to assume that exposure of UO_2 fuel to oxidizing solutions is likely to result in significant dissolution and that the rate of radionuclide release will be determined, at least in part, by the degree of oxidation of the fuel. A series of experiments is, therefore, being conducted to determine the mechanism of dissolution of unirradiated UO_2 under oxidizing conditions. Electrochemical techniques are being used to accurately control the redox conditions at the UO_2 surface. The films formed on UO_2 are being identified by X-ray photoelectron spectroscopy (XPS) [4-6], and morphological changes are being observed by scanning electron microscopy (SEM).

Various electrochemical techniques, including cyclic voltammetry, potentiostatic and galvanostatic oxidation, and cathodic stripping voltammetry using a rotating disk electrode, are providing information on:

- (1) The nature, thickness and mechanism of formation of surface films.
- (2) The effect of redox potential on the extent of film formation and dissolution.
- (3) The effects of variables such as pH, convection, pellet structure (e.g. porosity, grain boundary structure), and anion concentration.

2.1.2 Work Accomplished

2.1.2.1 Film Formation and Dissolution

Figure 2-1 shows the variation in surface composition of the UO_2 surface with time for oxidation at +300 mV (vs. SCE) in $0.5 \text{ mol.dm}^{-3} \text{ Na}_2\text{SO}_4$ in neutral solutions. The composition is expressed as the ratio of U(VI) to U(IV) in the UO_2 surface as determined by XPS, and the ratios expected from the possible uranium oxides are indicated. The surface oxidation proceeds in stages.

A combination of XPS and electrochemical experiments has shown that the mechanism of film formation and dissolution proceeds via the reaction scheme shown in Figure 2-2 [7,8]. Film formation is accompanied by dissolution as UO_2^{2+} , which is usually complexed by the anion (SO_4^{2-}, CO_3^{2-}) in solution.

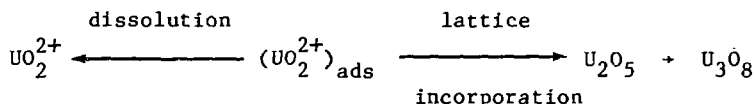
The nature and extent of film formation depends on the potential applied to the surface. In neutral solutions, for moderately oxidizing conditions ($+200 \text{ mV} \geq E \geq 0 \text{ mV}$; vs. SCE), the surface is usually covered by U_2O_5 or U_3O_8 . For higher potentials extensive dissolution leads to local supersaturation and precipitation of $UO_3 \cdot xH_2O$.

Our data indicate that for potentials $\leq -100 \text{ mV}$ (vs. SCE) the fuel pellet will undergo transitory oxidation leading to the formation of

surface films but very little dissolution. Potentials more reducing than -100 mV can be considered to represent relatively benign redox conditions for waste storage.

In acidic solutions, dissolution is more extensive and the surface films are extremely thin. In alkaline solutions (pH = 12) a passivating surface layer of amorphous UO_3 is formed [9].

The presence of complexing anions in the solution, such as carbonate, leads to more extensive dissolution of uranium oxide fuel, due to the complexation of the uranyl ion [7], and film formation is correspondingly less extensive [9]. If films such as U_2O_5 and U_3O_8 are formed by the incorporation of UO_2^{2+} species into the growing lattice, then dissolution and film formation processes can be envisaged as competition for surface UO_2^{2+} species, i.e.,



Obviously, as observed with carbonate, other complexing solutions would be expected to promote dissolution at the expense of film formation. The presence of carbonate does not appear to affect the observed redox barrier at ≈ -100 mV (vs. SCE), supporting our conclusion that, at potentials more reducing than this value, soluble uranyl ion species are not formed.

2.1.2.2 Accelerated Dissolution Tests

A series of accelerated dissolution tests have been performed [1] in an attempt to assess the fate of UO_2 after extensive dissolution. The object of these experiments was to obtain information that could be used to predict how UO_2 might behave over an extended time period.

When dissolution is occurring into a medium in which U(VI) has a low solubility (e.g., low $[CO_3^{2-}]$), $UO_3 \cdot xH_2O$ is precipitated both on the

surface, and in the solution where it appears as a fine yellow dispersion. If dissolution is occurring into a high-solubility medium (e.g., high $[\text{CO}_3^{2-}]$), then the UO_2 surface is severely attacked, leading to etching out of the individual particles in the pellet and to the erosion of UO_2 particles from the surface. Figure 2-3 shows electron micrographs of the UO_2 surface before and after 78 d of dissolution (at 10 μA) in sulphate plus carbonate ($0.01 \text{ mol}\cdot\text{dm}^{-3}$).

These results indicate that under oxidative dissolution conditions, pellet break-up and consequent accelerated release of intergranular fission products are possible.

2.1.2.3 Modelling of Radionuclide Release from Fuel

Radionuclides are not homogeneously distributed throughout the fuel and, consequently, radionuclide release will be very dependent on physical, as well as chemical, aspects of the dissolution process. For instance, if dissolution occurs preferentially at grain or particle boundaries, as suggested above, then radionuclides that have concentrated at these sites could be released more quickly than those homogeneously distributed throughout the fuel.

If such preferential dissolution processes occur, then radionuclide releases cannot simply be described by a straightforward matrix dissolution model, and the amount of radionuclide release will not be directly proportional to the amount of uranium dissolved. A more complex model, including a term for preferential dissolution due to pellet break-up, is being evaluated.

2.1.3 Future Directions

The work on UO_2 dissolution is being extended to assess the effect of other anions that may occur in groundwater (e.g. PO_4^{3-} , Cl^- , F^-), on the dissolution/film formation mechanism.

In order to use electrochemically generated data to interpret the behaviour of UO_2 in O_2 -containing solutions, it is necessary to study the behaviour of UO_2 under selected, comparable electrochemical and aqueous O_2 conditions. Data so far suggest that the behaviour is similar, but experiments are being extended to include variations in temperature and O_2 pressure for verification.

The significance of the electrochemically accelerated dissolution experiments is still being assessed. The data suggest that grain and particle boundaries will be preferentially attacked. The UO_2 microstructure (e.g. porosity, grain structure, etc.) determines how serious this effect is, and experiments will determine how these variables affect the progress of the dissolution reaction.

2.2 GLASS WASTE FORM CHEMISTRY (P. Taylor and S.D. Ashmore)

2.2.1 Introduction

The selection of an appropriate glass composition for incorporation and disposal of fuel recycle wastes requires a basic understanding of glass chemistry. Several general types of chemical change may occur to a glass, either during processing or after burial, which have a direct bearing on the release of radionuclides from that glass. Two anhydrous processes - amorphous phase separation and devitrification - are only likely to occur under processing conditions ($T > 500^\circ C$), but can substantially affect the subsequent dissolution behaviour of the glass. Dissolution of the glass in groundwater is the only credible means of release of radionuclides; this may occur congruently ("matrix dissolution") or incongruently ("leaching"), and may be accompanied by the re-precipitation of dissolved material ("hydrothermal alteration"). Several aspects of devitrification and glass dissolution are being examined by members of the Geochemistry and Applied Chemistry Branch [10]. Supporting chemical research to date has concentrated on the occurrence of amorphous phase separation and hydrothermal alteration in complex borosilicate systems.

2.2.2 Work Accomplished

2.2.2.1 Phase Separation

The occurrence of liquid immiscibility, or amorphous phase separation, is well known in many glass-forming silicate systems. It was first recognized over 50 years ago, and has been the topic of much research in the last two decades [11]. However, relatively little is known about its occurrence in systems of more than three components.

Phase separation generally produces a composite of two glass phases with widely disparate compositions and dissolution rates, and it may result in a substantial increase in the overall dissolution rate of a glass [12]. We are, therefore, trying to extend our understanding of phase separation to systems of substantial complexity, with the primary aim of confidently avoiding its occurrence during glass processing. We note, however, that the production of some more advanced waste forms, such as "stuffed glasses" and glass ceramics, may require the deliberate induction of phase separation. To date, we have examined the occurrence of phase separation in a variety of three-to-five-component borosilicate glasses containing oxides of alkali metals and/or divalent metals.

Our first project [13] was to examine the occurrence of liquid immiscibility in the quaternary system, $\text{Na}_2\text{O}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$. This system had shown some promise in the early stages of the U.S. and Canadian waste-form development programs. In addition, the occurrence of phase separation in several of the sub-systems was already fairly well understood. We found that, for $\text{SiO}_2/\text{B}_2\text{O}_3$ ratios between about 1 and 5, the miscibility gap can be described as a low dome, contiguous with that in the ternary system, $\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$. This dome expands with decreasing temperature and intersects the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ face of the phase diagram below 755°C (the consolute temperature of the "island" miscibility gap in the sodium borosilicate system). At higher $\text{SiO}_2/\text{B}_2\text{O}_3$ ratios the topography of the miscibility gap appears to become more complex, with a second feature growing from the $\text{Na}_2\text{O}-\text{SiO}_2$ edge of the phase diagram.

Further work on six additional quaternary systems ($X_2O-MO-B_2O_3-SiO_2$; $X = Na, K$; $M = Mg, Ca, Ba$) has shown that this behaviour is characteristic of systems of this type [14,15]. The extent of the miscibility gap increases with increasing polarizing power (decreasing radius) of each cation: $K < Na$ and $Ba < Ca < Mg \approx Zn$ (Figure 2-4). Since phase separation only occurs below about $625^\circ C$ in the system $K_2O-B_2O_3-SiO_2$ (cf. $755^\circ C$ in the corresponding sodium system) [16], the behaviour of the quaternary systems with $X = K$ at $650^\circ C$ resembles those with $X = Na$ at $800^\circ C$; under these conditions the miscibility gaps do not quite extend to the $X_2O-B_2O_3-SiO_2$ faces of the phase diagrams.

By normalizing* the MO component relative to the extent of the miscibility gaps in the $MO-B_2O_3-SiO_2$ ternary systems [15], we obtained "master curves" which describe the behaviour of the two sets of systems ($X = Na$ or K) at $650^\circ C$ (Figure 2-5). These master curves show some promise as a tool for predicting the behaviour of other or more complex systems; preliminary results for the five component system $Na_2O-MgO-BaO-B_2O_3-SiO_2$ are encouraging in this regard (Figure 2-6).

In parallel with our determination of the topography of miscibility gaps in these systems, we are attempting to elucidate the orientation of tie-lines within the miscibility gaps. Data thus far are limited, but in general phase-separation seems to be best described in terms of "network-former-rich" and "network-former-poor" phases, with SiO_2 and B_2O_3 showing a modest tendency to concentrate in these respective phases.

In conclusion, we have obtained a description of the behaviour of systems of this type that can be rationalized in terms of existing knowledge of simpler sub-systems.

* The normalized MO content, \underline{m}^1 , for compositions lying on the $650^\circ C$ isotherm of the critical miscibility surface, and having the general formula $\underline{n}X_2O \cdot \underline{m}MO \cdot B_2O_3 \cdot 1.07SiO_2$, (lying on the critical miscibility surface) is defined as $\underline{m}/\underline{m}_0 \times 100$, where \underline{m}_0 is the value of \underline{m} when $\underline{n} = 0$.

2.2.2.2 Hydrothermal Alteration

Since all glasses are metastable with respect to some crystalline phase assemblage, there is a thermodynamic driving force for them to crystallize ("devitrify"). The kinetics of anhydrous crystallization of glass compositions of interest in radioactive waste management are sufficiently slow to be ignored under disposal conditions, although they may be an important factor in glass processing. (Inadvertent devitrification can lead to increased leachability, whereas deliberate crystallization is a principal step in the fabrication of glass ceramics). The presence of water can greatly enhance the crystallization of a glass, by providing a medium for dissolution and re-precipitation. This could have several important consequences for radionuclide release from a waste vault:

- (1) Certain radionuclides may be retained by the alteration products.
- (2) Alteration products may provide a sink for dissolved glass-matrix species, thus enhancing glass dissolution and the release of soluble radionuclides.
- (3) A coherent layer of alteration products could confer some passivation on a glass surface, but enhanced localized corrosion could occur at cracks or pores in such a passivating layer.
- (4) The initial alteration products may themselves be metastable, and undergo further alteration at some later time.

This situation is clearly complex, with the possibility of both desirable and harmful effects on the integrity of the waste form. It is much more difficult to generalize about crystallization phenomena than about amorphous phase separation, since the diversity of possible phases is high.

As a preliminary exploration of this problem, we have examined the hydrothermal alteration of a variety of single-phase sodium zinc

borosilicate glasses [17]. Both coupons and powdered samples were allowed to react with water in titanium autoclaves at 150-200°C. Crystallization was generally apparent after a few days' reaction; it was least extensive for SiO₂-rich glasses, as expected. Two major crystalline products, both hydrated zinc silicates, were observed: hemimorphite (Zn₄Si₂O₇(OH)₂·H₂) and sauconite (approximately Zn₃Si₄O₁₀(OH)₂·nH₂O). The conditions favouring formation of each of these phases were further examined by studying the hydrothermal reaction of ZnO with SiO₂. The results indicate that hemimorphite is the stable product under all conditions below about 200°C, above that it dehydrates to willemite, Zn₂ZnO₄. Sauconite appears to be metastable, albeit very persistent once formed, under all conditions examined. Sauconite has a montmorillonite-like structure, and is likely to have more desirable ion-exchange properties than hemimorphite.

We come to the following tentative conclusions about hydrothermal alteration of a waste form consisting of a dilute solution of radionuclides in a sodium zinc borosilicate glass:

- (1) Crystallization of hydrated zinc silicates is likely to occur readily in water above about 100°C.
- (2) These products are usually loosely adherent on the surface, and do not form a coherent layer. They are, therefore, not expected to confer effective passivation on the surface, and may well promote dissolution by providing a sink for dissolved zinc and silicon in intimate contact with the glass surface.
- (3) The formation of sauconite may be more desirable from an ion-exchange viewpoint, but being metastable it is unlikely to persist indefinitely. Its stability may be enhanced by incorporation of other cations such as Al³⁺.

2.2.3 Future Directions

We plan to extend our study of phase separation to glasses containing oxides of tri- and tetravalent cations of importance either as

fission products (e.g. rare earths) or glass-making components (e.g. Al, Ti). We shall also investigate more efficient methods for the detection of phase separation. A study of the effect of phase separation on the leaching behaviour of sodium borosilicate glasses is also planned.

In view of the complexity of hydrothermal alteration reactions, detailed work must await a narrower definition of candidate waste-glass formulations. Some exploratory work on selected borosilicate systems is planned. A project to examine the solid-solution chemistry of sphene, the crystalline component of a proposed glass-ceramic waste form, will be initiated.

2.3 INTERACTIONS OF FISSION PRODUCTS WITH CONTAINER MATERIALS

(D.W. Shoesmith, S. Sunder, M.G. Bailey and G.J. Wallace)

2.3.1 Introduction

As discussed in Section 3, a fundamental knowledge of the behaviour of fission products under geological disposal conditions is essential for the thorough assessment of the behaviour of a waste vault. Two of the more important fission products in terms of quantity, half-life, mobility and toxicity are technetium (^{99}Tc) and iodine (^{129}I). Both elements are capable of forming negative ions, TcO_4^- and I^- , which are not very strongly adsorbed by many geological materials. However, it is possible that such anions could react with container materials, such as copper or lead, to form highly insoluble solids. The purpose of the work described here is to investigate the mechanism of interaction of these species with container materials.

2.3.2 Work Accomplished

2.3.2.1 Chemistry of Technetium Interactions

Some preliminary work on the interaction of TcO_4^- and copper metal indicated that a substantial reaction did occur. It appeared that the TcO_4^-

was reduced at the copper surface, probably to TcO_2 , the copper metal being oxidized to Cu_2O . However, the system proved too complex to elucidate the details of the reactions occurring, especially in the absence of good thermodynamic data and a knowledge of the basic chemistry of technetium.

With this lack of knowledge in mind, a more fundamental study of the redox chemistry of technetium has been initiated. Electrochemical experiments are being performed using platinum electrodes. Figure 2-7 shows a series of anodic stripping voltammograms of films potentiostatically deposited on platinum at -300 mV (vs. SCE) for varying times in a solution consisting of 10^{-1} mol.dm $^{-3}$ HCl and 1.2×10^{-3} mol.dm $^{-3}$ TcO_4^- . The formation of three separate phases, formed in the sequence a-b-c, is observed, suggesting the reduction of pertechnetate is a multistage process. The nature of the surface phases has not yet been determined. One possibility is that peak (a) is due to TcO_2 , peak (b) to Tc_2O_3 , and peak (c) to technetium metal. The greater part of reduced pertechnetate appears as Tc^{3+} in solution.

These experiments, coupled with those of J. Paquette (see Section 3.1) offer the possibility of understanding the basic redox chemistry of technetium. At present, a coupled electrochemical-Raman spectroscopical experiment is being designed to attempt an identification of the surface phases formed on platinum. Once a better fundamental understanding of the chemistry of technetium exists we will return to a study of technetium interactions with copper and lead.

2.3.2.2 Reaction of I^- with Copper and Lead

The thermodynamics and kinetics of iodide sorption on Cu, Cu_2O and CuO have been studied using an ion-selective electrode and a radio-active tracer to measure I^- in solution [18]. Both Cu and Cu_2O adsorb I^- rapidly from solution but CuO is a poor adsorber for I^- . The details of these interactions are still sketchy, however, and electrochemical methods coupled with XPS and Raman Spectroscopy are being applied in an effort to

obtain a better mechanistic understanding of the reactions involved. We hope to extend these studies to the lead oxide/ I^- system, in conjunction with work of the type described in Section 2.4.

2.3.2.3 Formation of Oxide Films on Container Materials

In order to predict the interaction of fission products with investment and container metals, it is important to understand the mechanism of corrosion and film formation on these metals in simple, well-defined electrochemical conditions. We have studied extensively the mechanism of film formation and passivation of copper metal [19-21] and similar investigations are planned for other metals that are candidate materials for waste management applications.

2.3.3 Future Directions

We plan to extend our studies of fission product/container materials interactions to include the effects of groundwater chemistry. For instance, both copper and lead interact strongly with anions such as SO_4^{2-} likely to be found in groundwater. Such interactions would be expected to have some impact on the reaction of the container materials with fission product anions such as I^- and TcO_4^- . Also, there is a strong possibility that the concentration of anions such as carbonate will be reduced by interaction with lead and lead oxides. As a consequence, their impact on UO_2 dissolution would be significantly lowered. We plan to study the nature and scope of these reactions in detail.

2.4 NOVEL WASTE FORMS

(P. Taylor and V.J. Lopata)

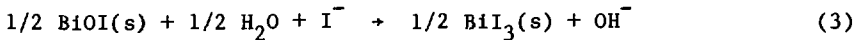
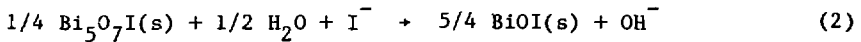
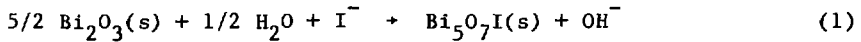
2.4.1 Introduction

As noted in the previous section, special attention must be paid to the chemistry of anion-forming radionuclides, such as ^{129}I and ^{99}Tc . We are evaluating various phases as "tailored" waste forms for such species. This work is relevant to the abatement of these species in aqueous solution

as well as to the waste form development per se, and has evolved from an investigation of heavy metal oxides as reagents for the removal of $^{14}\text{CO}_3^{2-}$ from aqueous solution.

2.4.2 Work Accomplished

Basic salts of the heavier elements in Groups IVA and VA of the Periodic Table are generally insoluble. We are examining the chemistry of some systems of this type. At present, we are determining phase relationships in the system $\text{Bi}_2\text{O}_3\text{-BiI}_3\text{-H}_2\text{O}$. The sequential conversion of Bi_2O_3 to BiI_3 can be represented by reactions (1) to (3):



When described in this way, the equilibrium constant for each reaction in dilute aqueous solution can be expressed as a quotient, $[\text{OH}^-]/[\text{I}^-]$. We are examining these reactions by determining equilibrium iodide concentrations as a function of pH, for solutions in contact with pairs of solids. The pair $\text{Bi}_2\text{O}_3/\text{Bi}_5\text{O}_7\text{I}$ behaves close to the expected linear relationship between pH and $\log [\text{I}^-]$ over the experimentally accessible range, $9.5 \leq \text{pH} \leq 13$. The equilibrium quotient, $[\text{OH}^-]/[\text{I}^-]$ is about 3000, corresponding to an equilibrium concentration of I^- near $10^{-10} \text{ mol}\cdot\text{dm}^{-3}$ at $\text{pH} = 7$. This system thus shows promise for application to iodide abatement and/or waste-form development. However, we need to thoroughly investigate interactions with anions that commonly occur in groundwater. For example, preliminary results suggest that ion-exchange between CO_3^{2-} and I^- may preclude $\text{Bi}_5\text{O}_7\text{I}$ as a waste form for ^{129}I if CO_3^{2-} containing groundwaters are allowed to contact the $\text{Bi}_5\text{O}_7\text{I}$.

The equilibrium constants for reactions (2) and (3) have not been measured accurately, but they are certainly several orders of magnitude

lower than for reaction (1), so that BiOI and BiI₃ do not merit consideration for the applications described here.

We have also briefly considered the possible utility of paraperiodate salts as ¹²⁹I waste forms. Some salts of this type, e.g., Ba₅(IO₆)₂, show surprisingly high thermal stability, but it seems unlikely that they would be sufficiently stable towards reduction or hydrolysis.

2.4.3 Future Directions

This work will be extended to investigate the occurrence and stability limits of basic iodide salts of lead, and possibly also lanthanum. Further extensions to include other important anions, such as TcO₄⁻, may be included. The kinetics of anion abatement will be examined in systems that show promise on thermodynamic grounds. Whenever possible, detailed structural analysis will be performed, to help understand the mechanism whereby anions are incorporated or exchanged in these basic salts. Recent results indicate that it may be possible to grow Bi₅O₇I crystals large enough for single-crystal X-ray crystallographic analysis.

3. SOLUTE AND SOLUTION CHEMISTRY

3.1 FISSION PRODUCT CHEMISTRY

(J. Paquette and W. Lawrence)

3.1.1 Introduction

Irradiated CANDU fuel contains more than 30 different elements produced by nuclear fission. Many of these fission products are short-lived and, therefore, are not important when considering long-term waste management. Others, because of their long half-lives and their chemical, geochemical or biological properties deserve closer examination. This is the case for the radionuclides ¹²⁹I, ⁹⁹Tc, ⁷⁹Se, and ¹⁰⁷Pd.

Although their specific activity is low and their beta radiation rather weak, these isotopes are a potential long-term hazard because of their long half-lives and the relatively large quantities involved. Technetium, iodine and selenium are capable of forming negative ions (e.g., TcO_4^- , I^- , IO_3^- , SeO_4^{2-}) that do not interact strongly with geological material. Furthermore, preliminary environmental and safety assessment studies for an underground disposal vault, found that ^{99}Tc and ^{129}I could be the major contributors to radiation doses delivered to the public [22].

The chemistry and geochemistry of technetium are poorly known and the aqueous chemistry of iodine is complex. Reliable chemical data are needed for compounds and complexes of these fission products, to better assess their behaviour in the vicinity of a deep underground disposal vault.

3.1.2 Technical Program

The long-term objective of this program is to obtain fundamental understanding of the solution chemistry of important fission products under geological disposal conditions. The program is in four parts: technetium chemistry, iodine chemistry, selenium chemistry and palladium chemistry.

In the short term, our efforts are aimed at examining the oxidation-reduction, hydrolysis, and complexation behaviour of technetium and iodine in dilute aqueous media. This information will be used in a thermodynamic analysis to calculate the species present and their solubilities under various conditions of pH, oxidation potential, temperature, and groundwater composition.

Currently, the technetium chemistry work is focussing on the determination of complexation constants of reduced technetium species with simple inorganic ions, such as phosphate and carbonate, with parallel measurements of the oxidation-reduction kinetics of technetium. Iodine chemistry experiments are focussing on measurements of the hydrolysis constant of iodine, and iodine oxidation-reduction chemistry.

The oxidation-reduction behaviour of technetium and iodine is being studied using a combination of electrochemical and spectrophotometric techniques. A combination of potentiometric and spectrophotometric techniques quantitatively determines hydrolysis and complexation constants. Computer programs are being used extensively to calculate equilibrium thermodynamics.

An analysis of the thermodynamic properties of selenium and palladium will be initiated during 1983. This analysis will define the future experimental effort required to characterize the groundwater chemistry of these species.

3.1.3 Summary of Work Accomplished

3.1.3.1 Technetium Chemistry

A review of technetium chemistry in relation to nuclear waste disposal has been published as a Technical Record [23]. This contains the best information available on the thermodynamics of the technetium/water system.

The stable form of technetium in an oxidizing aqueous medium is the pertechnetate ion, TcO_4^- . To study technetium oxidation-reduction behaviour, constant current reduction at a platinum electrode, and potentiostatic reduction at a mercury electrode have been performed on pertechnetate solutions. The solutions were examined by uv-Vis spectrophotometry during and after the reduction.

Dissolved, reduced technetium species were obtained by constant current electrolysis in a non-complexing medium with the solution pH below 4. Coulometric studies at constant potential showed that, in acid media, TcO_4^- is reduced directly to soluble Tc(III), which can be oxidized easily to Tc(IV), either by air oxidation or electrochemically. Spectrophotometric examination of the effect of pH on the reduced species indicated that both Tc(III) and Tc(IV) hydrolyze when the pH is raised, with Tc(IV)

precipitating at a pH of around 4, and Tc(III) disproportionating if the pH is above 4. Reduction at a pH above 4 leads directly to solid TcO_2 .

Constant current electrolysis and potentiostatic reduction were also performed on dilute TcO_4^- solutions in the presence of Cl^- , F^- , SO_4^{2-} , PO_4^{3-} , and CO_3^{2-} ions. Complexation was observed in all cases, for both Tc(III) and Tc(IV). Complexation appreciably stabilized reduced technetium, especially the complexes with phosphate and carbonate ions [24].

These studies show that, contrary to what has been generally assumed, the chemistry of technetium in a deep geological system should be dominated by the lower oxidation states, which are more likely to interact with geologic material than is TcO_4^- .

This has been confirmed by some more applied work done in collaboration with the Geochemistry and Applied Chemistry Branch. A mixing cell has been designed that allows the kinetics of interaction between geological materials and radionuclides to be examined. A study of the interaction between augite, an iron-rich mineral, and TcO_4^- showed that, as expected, there is no detectable interaction between augite and TcO_4^- under oxidizing conditions. On the other hand, when technetium was introduced as the Tc (IV) carbonate complex under reducing conditions, rapid sorption of technetium on augite was shown to occur. Thus, technetium transport may be strongly attenuated by iron-rich minerals if reducing conditions exist.

3.1.3.2 Iodine Chemistry

A self-consistent thermodynamic data base has been assembled for the iodine/water system [25]. Data for temperatures up to 150°C were either obtained from the literature or extrapolated from 25°C data using the computer program COTDET, which performs a modified Criss-Cobble extrapolation.

The data base was used to calculate the iodine species present in very dilute solution as a function of pH, potential, and temperature. An example is given in Figure 3-1 which is a potential-pH diagram for a total

iodine activity of 10^{-9} at 100°C . Such a diagram represents compactly the behaviour of aqueous systems under various pH and potential conditions. As expected, the iodide ion was calculated to be the dominant species under reducing conditions for the whole temperature and pH range. Under strongly oxidizing conditions, the iodate ion was calculated to be the major species. Iodine and hypiodous acid are expected to be important only under acid oxidizing conditions [25,26].

Cyclic voltammetry and potentiostatic oxidation are being used to characterize the oxidation-reduction behaviour of iodine in dilute solutions. The results were strongly dependent on the electrode material. The couples I^-/I_2 and I_2/IO_3^- were observed on platinum, pyrolytic graphite and vitreous carbon electrodes, the first couple being reversible in all cases and the second being irreversible in all cases. In addition, a couple corresponding to I^-/I^+ was observed on the pyrolytic graphite electrode and was close to being reversible.

3.1.4 Future Directions

A final assessment of the behaviour of technetium, iodine, selenium, and palladium in the waste vault will be completed by 1986/87. The work will then be extended to other fission product species identified from the waste management assessment codes as requiring further characterization.

3.2 ACTINIDE SOLUTION CHEMISTRY

(R. Lemire and G. Boyer)

3.2.1 Introduction

One option for the Canadian Nuclear Fuel Waste Management Program is disposal of irradiated fuel without reprocessing. If this is done, the primary waste form will be uranium dioxide itself. The rate of dissolution of UO_2 is then expected to control the release of many of the fission products and higher actinides. If groundwater flow in the disposal vault is slow, such release may be limited by UO_2 solubility. Transport of other

products and higher actinides. If groundwater flow in the disposal vault is slow, such release may be limited by UO_2 solubility. Transport of other actinides after their release (either from UO_2 or glass waste forms) may also be solubility limited.

Good solubility data are scarce for many sparingly soluble metal oxides at all temperatures, and this is particularly true for the actinide oxides [27]. Furthermore, the solubility of actinide oxides in groundwater may be influenced by the ability of the actinide ions to form water-soluble complexes with inorganic ions in the groundwater. While some actinide association constants are available for solutions at 25°C, such information is scarce for the higher temperatures (e.g. 80 to 100°C) expected in the waste vault [27].

3.2.2 Technical Program

The program is divided into two main parts. The first is an analysis of the equilibrium thermodynamic behaviour of solutions of uranium, neptunium, and plutonium. The effects on actinide solubilities and on the stability of UO_2 as a waste form can be calculated as a function of concentrations of ions likely to be found in deep granitic groundwaters. Complex formation with anions such as OH^- , F^- , SO_4^{2-} , PO_4^{3-} , Cl^- , and CO_3^{2-} is considered, as is the formation of actinide solids with these ions or with common alkali metal and alkaline earth cations. Existing thermodynamic data have been critically assessed for uranium, neptunium, and plutonium, and a data base for these elements is being maintained. For those species for which no experimental high-temperature thermodynamic data are available, a modified Criss-Cobble entropy extrapolation [28,2] is used to derive self-consistent analytical expressions of the partial molal Gibbs energies from 25°C to 200°C. The data base can be used to calculate actinide solubilities needed in the environmental and safety assessment studies carried out in the Environmental and Safety Assessment Branch.

The data are also analyzed to determine which species are important for a wide range of values of solution pH and oxidation potential.

This analysis identifies species that should be important for the anticipated vault conditions, but for which thermodynamic information is either lacking or inconsistent.

The second part of the program consists of experiments designed to supplement available data. Initially, we have concentrated on uranium complexation. Carbonate is one of the strongest complexing agents for the uranyl ion, and the stability of anionic uranyl carbonate complexes, e.g. $\text{UO}_2(\text{CO}_3)_3^{4-}$, can enhance the oxidation and dissolution of UO_2 even under slightly reducing conditions. Data for the formation constants for these complexes are sparse except at 25°C [27]. Potentiometric experiments to obtain data for this system at temperatures up to 100°C are underway. A study of uranyl/chloride complexation as a function of temperature is also in progress. Carbonate complexation of other actinide ions is also quite strong, and may merit study in the future.

3.2.3 Summary of Work Accomplished

Data base assessments and calculation of Gibbs energies for uranium and plutonium ions, hydrolysis species, and simple complexes and solids have been done for temperatures from 25 to 200°C. These were used together with other literature data to calculate equilibrium constants for the hydrolysis, complexation and solubility reactions over this temperature range [2].

The data have been used to construct potential-pH diagrams describing the expected thermodynamic behaviour of uranium and plutonium in water as functions of temperature, solution pH and oxidation potential [29-31]. Uranium dioxide is quite stable under reducing conditions, with a solubility of less than $0.1 \mu\text{mol}\cdot\text{dm}^{-3}$ even for solutions in which the hydroxide concentration is $10 \mu\text{mol}\cdot\text{dm}^{-3}$. For more oxidizing conditions, complex formation (especially formation of $\text{UO}_2^{2+}/\text{CO}_3^{3-}$ complexes) becomes important. High-alkali metal and alkaline earth cation concentrations in solution may result in transformation of UO_2 to less soluble uranates (Figure 3-2). Similarly, phosphate, even at concentrations near

$1 \mu\text{mol}\cdot\text{dm}^{-3}$ may stabilize uranyl phosphate solids. Materials dissolved in the UO_2 matrix may be released if the stability field of the UO_2 is decreased, even if the solution uranium concentration becomes lower.

The data for plutonium indicate that highly insoluble plutonium dioxide is the most stable plutonium solid over a wide range of conditions for temperatures between 25°C and 200°C . Only for highly reducing and acidic conditions does the equilibrium solubility of plutonium become significant in the model groundwaters considered.

A closed potentiometric titration system has been developed to determine the complexation constants for a uranyl ion with carbonate. A closed system prevents substantial loss of CO_2 during the course of an experiment. This is essential for making these measurements above 50°C . Spectrophotometric measurements on the uranyl/chloride system are also underway.

3.2.4 Future Directions

Experimental measurements on uranium complexation for the uranyl carbonate and chloride systems should be finished by the end of 1983, and some work on selected transuranic systems will be done in 1983/85. Data base work will be maintained, but at a low level, at least to 1984. Starting in 1983 some effort will be devoted to obtaining primary thermochemical data for selected actinide compounds, and to a detailed examination of salt effects on calculated solubilities.

3.3 THERMODYNAMICS OF AQUEOUS SOLUTIONS

There are several areas of the nuclear industry that require thermodynamic data for aqueous solutions at high temperature and pressure. These areas include corrosion and fission product transport in the CANDU primary coolant circuits [32], reactor safety analysis [25], and the waste management program of interest here. Such data are needed to discuss the dissolution of uranium dioxide fuel [1] or glass matrices, and to assess

the long-term behaviour of solutions of actinides and fission products. Since vault temperatures may remain as high as 100°C for long periods, data are needed at least up to this temperature.

There are essentially four approaches to obtaining such data. The Gibbs energy is the function that determines solubility, and one approach is to measure the Gibbs energy (or solubility) directly as a function of temperature. This is usually a very difficult measurement. More frequently, the Gibbs energy is measured at room temperature, along with enthalpies and heat capacities. Ideally, the heat capacities should also be measured as a function of temperature. From this information, Gibbs energies at elevated temperatures can be calculated exactly. These two procedures will be termed "experimental" and will be discussed in Section 3.3.1, below.

Measuring enthalpies and heat capacities at several temperatures for all the possible systems of interest would require a large and protracted effort [33,34]. Thus, it is desirable to extrapolate room-temperature data to higher temperatures using reliable procedures. The third approach for determining Gibbs energies at higher temperatures is, therefore, to develop reliable extrapolation procedures to use with room-temperature data. Finally, the fourth approach is to use some method such as the Monte Carlo technique to calculate Gibbs energies directly. These latter two techniques, extrapolation and direct calculation, are termed "theoretical" and will be discussed in Section 3.3.2, below.

3.3.1 Experimental Methods (P.P.S. Saluja and J. Leblanc)

3.3.1.1 Direct Solubility Measurements

The solubility of carefully characterized UO_2 , under basic reducing conditions, has been measured from 25 to 300°C using a flow apparatus and neutron activation analysis [3]. These results indicate that UO_2 solubility is even lower than previously predicted at 25°C [35] and that results at 300°C are not significantly different from those at 100°C.

These experiments provided useful results on a system of direct interest. However, they proved to be very difficult and the precision and accuracy of the solubilities obtained were disappointing. A tremendous amount of effort would be required to measure all the systems of interest. Thus, this method is not being used at present.

3.3.1.2 Heat Capacity Measurements

3.3.1.2.1 Introduction

Heat capacity data as a function of temperature can be used to extrapolate Gibbs energies, enthalpies, activity coefficients and osmotic coefficients of aqueous ions from 25°C to other temperatures, providing data are available at 25°C to evaluate the integration constants.

We are establishing a thermochemistry laboratory to provide precise thermodynamic information on fission products and actinide species in water and saline groundwater at temperatures up to 150°C. We have recently commissioned a high-temperature heat capacity flow microcalorimeter [36,37] to generate high-quality heat capacity data.

The importance of precision and accuracy of the heat capacity measurements must be stressed. An error of only $\pm 0.01\%$ in the measurements at concentrations of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ corresponds to an error of $\pm 40 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in the heat capacities derived from the data. This would lead to significant uncertainties in the Gibbs energies calculated from the data. However, our microcalorimeter can measure heat capacities to at least $\pm 0.005\%$ routinely. This precision is about a factor of 10 better than any other method. Thus, we are in a good position to obtain precise data in the temperature range 25 to 100°C for dilute solutions.

3.3.1.2.2 Technical Program

Our long-term goal is to develop a thermodynamic data base for solutions of fission products and actinide ions at elevated temperatures.

The first priority has been to check the accuracy and precision of our heat capacity flow microcalorimeter [36,37] in the 50 to 100°C range using simple electrolyte (NaCl and Na₂SO₃) solutions for which there are recent accurate data. These are two of the major electrolytes found in many natural brines and geothermal fluids.

The next priority is to obtain data for several aqueous ions of importance for assessing chemistry in the waste vault. Ions of current interest are I⁻, IO₃⁻, TcO₄⁻, SeO₄²⁻, Cs⁺, Sr²⁺, Mg²⁺, and Na⁺. However, the list will expand as information from other programs defines new requirements.

3.3.1.2.3 Summary of Work Accomplished

Two reference systems, NaCl and Na₂SO₄, for which recent data were available at ~ 50°C, were chosen for assessing the performance of the microcalorimeter. The apparent molar heat capacity results were in good agreement with the NaCl data of Smith-Magowan and Wood [34] and the Na₂SO₄ data of Rogers and Pitzer [38]. The data for Na₂SO₄ are shown in Figure 3-3.

Data have now been obtained up to 75°C for the fission product electrolytes NaI, KIO₃, SrCl₂ and for the groundwater electrolytes NaCl, Na₂SO₄, MgCl₂ and MgSO₄. Manuscripts describing this work are being written.

3.3.1.2.4 Future Directions

Eventually, we will want to carry out high-temperature heat capacity measurements on solutions of key radioactive species by re-commissioning the entire flow microcalorimeter system in an active laboratory. At this stage, it will be necessary to measure heat capacities above 100°C. We will have to assess the feasibility of using the existing C_p microcalorimeter for measurements above 100°C with or without modifications to the sample injection system and circulating thermostat bath, or, alternatively,

to design, develop, and commission a new high-temperature C_p flow microcalorimeter to permit precise heat capacity measurements in the 100 to 300°C range. This will require major modifications [34,38] to the microcalorimeter.

Finally, we would eventually hope to use the data base to formulate a theory for moderately concentrated multicomponent solutions at 25°C and then to extend it to 100°C. We would then apply this theory to simulated granitic and saline groundwaters.

3.3.2 Theoretical Methods

(F. Garisto)

3.3.2.1 Extrapolation Techniques

Thermodynamic data for many aqueous species are available at 25°C, but experiments at elevated temperatures are difficult and, as a result, high-temperature data are sparse. Therefore, it is important to develop reliable methods for extrapolating room-temperature thermodynamic data to higher temperatures.

The thermodynamic function that determines the stability of an aqueous species is the Gibbs energy, $\bar{G}^{\circ}(T)$. The partial Gibbs energy is related to the partial entropy, $\bar{S}^{\circ}(T)$, and heat capacity, $\bar{C}_p^{\circ}(T)$, by the equations [39]

$$\begin{aligned}\bar{G}^{\circ}(T) - \bar{G}^{\circ}(298) &= - \int_{298}^T \bar{S}^{\circ}(T) dT \\ &= - \bar{S}^{\circ}(298)[T-298.15] - T \int_{298}^T \frac{\bar{C}_p^{\circ}(T)}{T} dT + \int_{298}^T \bar{C}_p^{\circ}(T) dT\end{aligned}$$

If $\bar{S}^{\circ}(T)$ or $\bar{C}_p^{\circ}(T)$ are known, then $\bar{G}^{\circ}(T)$ can be calculated from the room-temperature data. The best empirical method for determining $\bar{G}^{\circ}(T)$ is to

extrapolate $\bar{C}_p^{\circ}(T)$ if values are known over a reasonable temperature range since $\bar{G}(T)$ is less sensitive to errors in $\bar{C}_p^{\circ}(T)$. Unfortunately, $\bar{C}_p^{\circ}(T)$ data are only rarely available in the required temperature range. However, the partial molal entropies of ionic species at high temperatures can be estimated using the well-known Criss-Cobble correspondence principle [28] which relates $\bar{S}^{\circ}(T)$ to $\bar{S}^{\circ}(298)$ through the equation

$$\bar{S}^{\circ}(T) = a(T) + b(T)\bar{S}^{\circ}(298)$$

The temperature-dependent parameters $a(T)$ and $b(T)$ have been determined [28] for the temperatures $T = 60^{\circ}\text{C}$, 100°C , 150°C , and 200°C . These are based on correlations of the high-temperature data for a few dozen simple ions, such as the alkali metals, alkaline earths, halides, first row transition metals and some oxyanions. There is doubt about this method's applicability to heavy elements (lanthanides and actinides) and to temperatures above 150°C .

The aim of the high-temperature solution research program is to improve the Criss-Cobble extrapolation method either by experimentally determining new values for the parameters $a(T)$ and $b(T)$ which are suitable for estimating the entropies of heavy element ions, or by developing new empirical ionic models. This will involve improving the classical Born model (spherical ion in a continuum of constant dielectric constant) by incorporating a solvation shell [40,41] with an adjustable hydration number around the ion in solution. This model may be adequate for fitting $\bar{C}_p^{\circ}(T)$ data over the temperature range 50 to 300°C , since the Born model with adjustable ion radius has been found adequate in explaining the temperature dependence of \bar{C}_p° above $\sim 130^{\circ}\text{C}$ [34,42]. The solvation shell is intended to model the solvent structure, which is more important at lower temperatures in determining the properties of the ions in solution.

In many cases, a knowledge of the activity coefficients of the aqueous species is required to determine the thermodynamic behaviour of a system. This may be particularly true in the waste vault if saline

groundwaters are present. The activity coefficient, a_i , of the i th species is defined by

$$\mu_i(T) = \bar{G}_i^0(T) + RT \ln a_i m_i$$

where $\mu_i(T)$ is the chemical potential and m_i is the molal concentration of the i th species. Activity coefficient data are available for many electrolytes at room temperature.

Theoretical methods based on simple statistical mechanical calculations [43,44] are being developed to extrapolate activity data to elevated temperatures and to calculate activity coefficients for ionic species in electrolyte mixtures. The ultimate objective is to use the derived activity coefficient data in the calculation of multicomponent equilibria for systems that simulate the conditions expected in a waste vault.

The techniques described above have been used extensively in the Research Chemistry Branch. The Criss-Cobble correspondence principle, modified to allow for the entropy contribution due to the electronic degeneracy of the ground state of uranium and plutonium ions, has been used to estimate the Gibbs energies of uranium and plutonium ionic species [2]. The theoretical approaches for the development of new extrapolation procedures are based on a semi-continuum electrostatic model for ions in solution, formulated by Goldman and Bates [45]. The theory has been used to predict the effect of changes in temperature (and hence, in the physical properties of water) on the thermodynamics of ions. The results are superior to the Criss-Cobble values for ions that do not form covalent bonds with water, including the trivalent lanthanides and actinides, in the range 150 to 250°C [40].

The extrapolation techniques purport to calculate functions representing single aquo-ions, (e.g., Na^+ , Cl^- or U^{+4}). Unfortunately, all equilibrium experiments to obtain thermodynamic data are constrained by the need to preserve electroneutrality, which requires that all the cations in solution are balanced by an equal number of equivalents of anions. The

data tables, therefore, apply only to anion-cation pairs. Methods have been devised [46] to measure or approximate single-ion values for the Gibbs energy and entropy, but these have been applied only near 25°C. Experiments were done to estimate single-ion entropies up to 100°C by measuring the thermoelectric power of the Ag-AgCl thermogalvanic cell as a function of temperature and concentration to estimate the properties of the single chloride ion [47]. The results gave a self-consistent ionic scale, $S^\circ(\text{H}^+, 25^\circ\text{C}) = -19.4 \pm 2.5 \text{ J.K}^{-1}.\text{mol}^{-1}$ and $-57 \text{ J.K}^{-1} \text{ mol}^{-1} \leq C_p^\circ(\text{H}^+, 25^\circ\text{C}) \leq 13 \text{ J.K}^{-1}.\text{mol}^{-1}$. Accurate Soret coefficient measurements at higher temperatures and theoretical treatments for the effect of ion-solvent interactions on entropies of transport would be required to refine this approach, but these are not contemplated at present.

3.3.2.2 Direct Calculation

Monte-Carlo simulation techniques have been used successfully in the Research Chemistry Branch to model water at high temperatures [48]. The isochoric heat capacities and internal energies derived from the simulation agree with experimental values to within $5 \text{ J.K}^{-1}.\text{mol}^{-1}$ and 5 kJ.mol^{-1} at unit density, respectively. However, extending these calculations to solutions of salts in water is not practical at present, since the original quantum mechanical calculations required to determine the water-ion interaction potential are presently limited to the light halide and alkali metal ions (F^- , Na^+ , K^+ , Cl^-).

3.3.2.3 Future Directions

Improvement of the Born model (which does not explicitly consider solvent molecules) will be pursued using the integral equation theories of statistical mechanics. Ion solvation energies in various model solvents will be calculated. At present, solvation of ions in dipolar fluids is being investigated. These dipolar fluids, which are not intended to model water, can provide valuable information about ion solvation processes. More complicated solvent models, which can simulate the dielectric properties of water, will be considered in the future.

Statistical mechanics can also be used to derive expressions for the activity coefficients of ions. These calculations are more difficult than those described above (the ion concentration is finite). However, simple theories and models can give analytical expressions for the ion activity coefficients. The aim is to use these expressions to fit the experimental 25°C data for single electrolytes. The suitability of the model and/or theory can then be tested by calculating the high-temperature activity coefficients or the activity coefficients for ions in binary electrolyte solutions.

4. ROCK-WATER-WASTE INTERACTIONS

Plutonic rocks including granite, gabbro, syenite and anorthosite are currently being considered as potential vault host rocks. Hence the major components of these rocks form the object of our investigation. The components include feldspars (microcline, albite, labradorite), micas (biotite and muscovite), amphibole (hornblende), quartz, and pyroxene. In order to assess the interaction of these minerals with radionuclides it is helpful to have an understanding of the chemistry of hydrothermal alteration of the minerals in the expected groundwater environment. Reactions such as dissolution, ion-exchange, and precipitation will be important in determining the mechanism of the alteration process.

Whether a radionuclide will be immobilized or transported will depend on the relative importance of a variety of possible reactions. Interaction of a radionuclide with rock-forming minerals could lead to immobilization via reactions such as sorption, ion-exchange, precipitation, redox reactions, and combinations of these processes. Alternatively colloid formation, or the interaction of a radionuclide with a preformed colloid, offers a mechanism whereby the radionuclide could avoid interaction with the geologic barrier and hence be transported back to the biosphere.

The number of different radionuclides involved and the complexity of the rock/groundwater system make an in-depth study of the whole system extremely difficult. The purpose of our work is to obtain accurate thermodynamic and kinetic data on well-defined systems. This will enable us to characterize quantitatively the basic chemical reactions involved. The information obtained can then be used to interpret more phenomenological and qualitative experiments on a large variety of more complex systems. Finally, our experiments will provide a thermodynamic and kinetic data base that can be confidently used in computer models designed to predict long-term behaviour in the waste vault.

4.1 SURFACE CHEMISTRY OF MINERALS
(R. Haines and D.G. Owen)

4.1.1 Mineral Dissolution

Research has been concerned with the kinetics and mechanisms of mineral-water reactions, initially dealing with the feldspars [49,50]. Dissolution of microcline, a potassic feldspar, KAlSi_3O_8 (Perth Feldspar Mine, Ontario), was monitored via release rates of alkali metal ion, silicon and aluminum. After an initial ion-exchange stage, the mineral was observed to dissolve incongruently over the first few days, and congruently thereafter, at ambient temperature. X-ray photoelectron spectroscopy was used to follow changes in surface composition as a function of time. However, there was no evidence for a "leached layer" [51] of alteration product. Scanning and Transmission Electron Microscopic (TEM) studies suggested the formation of localized aluminosilicate precipitates. These surface-sensitive techniques indicated that initial dissolution proceeded preferentially along crystallographic imperfections, cleavage fractures and liquid inclusions.

Experiments on dissolution rates of microcline and labradorite, a calcic feldspar, in deionized water at 80°C have recently been performed. The amount of silicon released to solution is shown in Figure 4-1, for finely ground microcline (a) prewashed and (b) ultrasonically cleaned

(> 400 mesh); and for (c) 40-60 mesh microcline, also ultrasonically cleaned. SEM photomicrographs of similarly treated microcline show the prewashed surface to be covered with fine particles of varying size, less than 10 μm . Ultrasonic cleaning followed by washing in deionized water removes the bulk of these fines, although some sub-micron particles remain. The commonly observed [52] non-linear kinetics in mineral dissolution are markedly reduced by the latter treatment. Similar behaviour for albite [53], and amphibole and pyroxene [54,55] dissolution has been observed. The non-linear kinetic phenomenon was explained by the initial rapid dissolution of fines, followed by progressive deceleration as the high-surface-energy particles are consumed.

4.1.2 Hydrothermal Mineral Alteration

Currently, experiments are underway on hydrothermal alteration of pertinent minerals under various conditions of temperature, pH, aqueous phase composition and time. Initial conditions chosen were 200°C, at room-temperature pH = 8.0 (unbuffered) in deionized water, for periods of up to two weeks. Six finely ground samples, comprising microcline, albite, labradorite, hornblende, augite and biotite were treated in preconditioned teflon-lined titanium autoclaves. Transmission infrared spectra (KBr discs) of the reactants and products were measured, and showed negligible (< 10%) alteration in the bulk material. Surface analysis of the materials is planned utilizing SEM/EDX (energy dispersive X-ray analysis), and XPS to characterize any surface alteration. Clearly, pH is a very significant factor in determining the alteration process. Labradorite, for example, shows significant changes in the infrared after only days at 230°C at a pH (ambient) of 1.0 [56], with formation of amorphous silica, kaolinite, boehmite and amorphous aluminosilicates at various acidic conditions.

4.1.3 Future Directions

The investigation of the surface chemistry in these systems is planned, utilizing such surface-sensitive techniques as XPS and SEM/EDX. Combined use of these methods should yield information concerning surface

composition and its alteration during reactions. Note that XPS has already been extremely useful in mineralogy and geochemistry [57]. Evidence for congruent and incongruent dissolution of certain minerals has been reported [58] using Al_{2p}/Si_{2p} and Mg_{2p}/Si_{2p} peak area ratios after leaching. XPS has also been used to study the surface dissolution of feldspars [59]. We intend to use laser-Raman spectroscopy to study the mineral-solution interface in situ. Such experiments would be complemented by infrared and photoacoustic infrared spectroscopy (PA-IR). PA-IR spectra may be measured without prior sample preparation, which allows repeated reaction/spectral observation on the same sample.

The products of reactions at the mineral-aqueous interface will be characterized with these techniques, and the kinetics and mechanisms of their formation elucidated, under conditions that should enable us to forecast the changes in the geosphere likely to occur in the vicinity of a waste vault.

4.2 FISSION PRODUCT/ACTINIDE INTERACTIONS WITH MINERALS (R. Haines and D.G. Owen)

4.2.1 Radionuclide Sorption by Minerals

The interaction of radionuclides with exposed mineral surfaces will play a major role in determining the mobility of dissolved species in the groundwater, should they escape from the waste vault. We have done some work on the sorption of ionic species onto minerals [50]. In studies of Cs^+ and Sr^{2+} sorption onto feldspars at high temperatures we showed that although Sr^{2+} is poorly sorbed by microcline, and readily desorbed, Cs^+ is sorbed to a significant extent, and is held quite strongly. This agrees with literature reports of formation of a secondary phase of the cesium aluminosilicate, pollucite ($CsAlSi_2O_6$) in hydrothermal solutions of feldspars and Cs^+ ion [60].

4.2.2 Future Directions

This work is qualitative in nature and will be extended to study, quantitatively, the kinetics and mechanism of the sorption process. Similar techniques to those described in Section 3.1 will be employed. We expect that PA-IR spectroscopy will be particularly useful in providing sorbed ion - surface bonding information. The usefulness of XPS in sorption studies has already been demonstrated in, for example, the sorption of metal ions onto clay minerals [61]. In the sorption of Pb^{2+} onto montmorillonite, Pb was shown to have the same bonding as in PbO_2 [62]. In the adsorption of Ni^{2+} , Ba^{2+} and La^{3+} onto hydrous MnO_2 [63], the dependence of ion-uptake on time was shown to be characteristic of the sorption process. Sorption/desorption of radionuclides will be followed kinetically, to determine reaction mechanisms, and gain insight into the phenomena from sorption isotherms.

4.3 Thermochemical Sorption Data (P.P.S. Saluja and J.C. LeBlanc)

4.3.1 Introduction

Surface microcalorimetry is a powerful and convenient tool for determining and monitoring the surface properties of solids [63] and is a complementary technique to the more commonly used surface analytical and electrochemical methods. The principle of surface microcalorimetry is that the small heat effects accompanying adsorption, desorption, dissolution or displacement of any compound (gas or solvent or solution) that interacts with a solid surface and its existing films can be detected by the instrument. Such data provide valuable information about the properties of the surface (e.g., surface area of minerals, heat of adsorption of fission products and actinides onto mineral surfaces, heat of adsorption of radionuclides onto colloid particles). Measurements of these surface interactions, which are difficult to follow by other analytical techniques, can now be performed conveniently because of the fast response, improved sensitivity of the sorption instrument and the capability for sequential experiments on the same sample.

4.3.2 Technical Program

We are presently commissioning a surface microcalorimeter system to operate in batch as well as in the flow mode in order to provide sorption thermochemical data. Once the surface microcalorimeter system is satisfactorily commissioned, the following research programs are planned:

- (1) Investigation of the effects of mineral-surface pretreatment and cleaning procedures. This will be achieved by checking the reproducibility of the chemical behaviour of the initial surface and by monitoring the variation in the heat of dissolution of selected minerals with time. The potassium feldspar, microcline, has been chosen for the initial study because of the amount of dissolution rate data already available [51].
- (2) Study of sorption thermodynamics and sorption rate data for Cs^+ and Sr^{2+} on selected mineral systems.
- (3) Determination of the surface area of microcline and other selected minerals (e.g., albite, labradorite, biotite, quartz, etc.).
- (4) Determination of sorption thermodynamics and kinetics of I^- on selected mineral and oxide surfaces.
- (5) Study of ion-exchange thermodynamics for feldspars.

4.3.3 Future Directions

Surface microcalorimetry will eventually provide thermochemical data on the adsorption-desorption behaviour of radionuclides onto colloidal particles, and on colloid-mineral interactions. We will also attempt to obtain sorption thermodynamics and kinetics data for competitive sorption of carbonate, hydroxide and iodide on Bi_2O_3 surfaces to assess possible candidate waste forms with optimum sorbent characteristics for removal of ^{14}C and ^{129}I .

4.4 COLLOIDAL TRANSPORT OF RADIONUCLIDES
(C.H. Ho and D.C. Doern)

Colloid formation by radioactive elements is of interest because of its importance in nuclear waste management. Though previous studies on waste-containing glasses and spent nuclear fuel have shown no positive evidence for the formation of colloids, their existence is generally claimed to explain behaviour that cannot be rationalized otherwise [1,64,65,]. For instance, Walton [64] found that a one-dimensional ion-exchange model was inadequate to predict the migration of ^{137}Cs released from buried glass blocks at Chalk River. Colloidal transport was suggested to explain the deviation. Further investigation by Champ [65] also suggested that fine particulates within the soil were responsible for the transport of ^{137}Cs . In a recent paper, Johnson et al. [1] reported the rate of release of fission products from irradiated fuel pellets, and concluded that a more detailed study on colloid formation was necessary to elucidate the fuel leaching mechanism.

There are two types of colloids: true colloids and pseudocolloids. True colloids are formed by hydrolytic or condensation processes, whereas pseudocolloids are formed by adsorption of dissolved ions onto particulates already present in the solution. A review by Kepak [66] has summarized the methods used to study the colloidal properties of radioactive elements in aqueous solution. Most probably, the sorption behaviour of colloids will differ from the dissolved ions. Since the migration of radioactive elements will depend very much on their physico-chemical state, the formation of colloids and their adsorption-desorption behaviour with respect to storage vault conditions are of major interest.

Work has been initiated on U(IV) hydrolysis leading to colloid formation, and these will be extended to other actinides. Furthermore, interaction of released radionuclides with mineral particulates leading to pseudocolloid formation will be studied. Finally, the dissolution mechanism of UO_2 , and how this leads to the formation of uranium colloids, will be investigated.

5. ADVANCED METHODS OF ABATEMENT AND MONITORING
OF GAS-PHASE RADIONUCLIDES

(A.C. Vikis and D.F. Torgerson)

In various steps associated with the nuclear fuel cycle, particularly in reprocessing, gaseous radionuclides (^{129}I , ^{85}Kr , ^{14}C , ^3H) will be released into the off-gas streams at concentrations of a few parts per million in air [67]. To ensure that environmental release limits are satisfied, these radionuclides must be removed from air, retained in stable forms and disposed in a safe manner. On-line, real-time monitoring techniques are also necessary for their detection [68,69].

Existing methods of abatement of gaseous radionuclides use solid or liquid sorbents [67,70-72]. However, there are various disadvantages associated with these processes. For instance, they are slow processes, the sorbents are poisoned by air impurities, they generate secondary nuclear waste and demand complex handling procedures.

Research on the removal and monitoring of gas-phase radionuclides is being conducted in the Research Chemistry Branch. The objective is to develop advanced methods for the recovery of these species from air and to develop real time monitors for their detection. The main thrust of the work to date has been in support of a gas-phase method of removal of radioactive iodines from air. Research towards the development of a method for the removal of ^{85}Kr from air and methods for the detection of radioactive iodines have been initiated recently.

5.1 RADIOIODINE

The main gaseous chemical forms of radioactive iodines present in various off-gas streams are elemental iodine (I_2), organic iodides (CH_3I , $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_5\text{I}$ etc.) and possibly hypoiodous acid (HOI). Two methods of removal of these species from air and supporting chemical research are outlined below.

5.1.1 The Corona Iodine Scrubber (CIS) Method [73,74]

In the original CIS method a high-voltage corona discharge between two electrodes - a cylindrical one, normally at ground potential, and a coaxial wire, normally at ~ -10 kV potential - is applied to the air stream containing the iodine species to be removed. The resulting electrons, ions (O^- , O_2^- , O_2^+) and possibly neutral species (O , O_3) react with the iodine species to form involatile compounds (I_4O_9 , I_2O_4 , I_2O_5), which deposit on the walls of the scrubber [75]. The detailed chemistry of the system is not known; however, the following very fast ion-molecule reactions must play a significant role in the decomposition of the organic iodide:



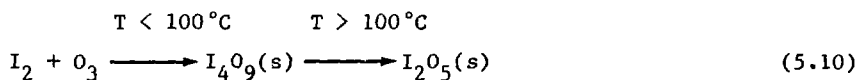
The CIS method was demonstrated at the laboratory scale with non-radioactive CH_3I and C_6H_5I in the concentration range of 10 to 100 $\mu L/L$, and air flows of $0.02 \text{ dm}^3 \cdot \text{s}^{-1}$. Decontamination factors (D.F. \equiv concentration of species before the scrubber/concentration of species after the scrubber) increased rapidly with discharge current (see Figure 5-1). At Chalk River Nuclear Laboratories, the method was demonstrated with ^{131}I -labelled CH_3I , and also on the ventilation system of the ^{99}Mo facility [76]. In the latter case, employing four corona scrubbers in series and air flows of 0.005 to $0.050 \text{ dm}^3 \cdot \text{s}^{-1}$, DF's of 10^2 to 10^4 were achieved for ^{131}I concentrations of 10^{-10} to $10^{-8} \mu L/L$. An improved larger scale unit is now being designed for engineering scale tests.

5.1.2 The Photochemical Method [77-79]

The photochemical method (Figure 5-2) employs uv light (200-300 nm) to convert the organic iodides to elemental iodine and the oxidized forms of the organic group. The principal reactions are



The iodine reacts with ozone (O_3) to form solid iodine oxides (I_4O_9 or I_2O_5),



which deposit on the walls of the scrubber and can be subsequently removed either chemically or physically.

This method was demonstrated with air as the carrier gas at a flow rate of $0.04 \text{ dm}^3 \cdot \text{s}^{-1}$, a total pressure of 100 kPa and a temperature of $\sim 125^\circ\text{C}$. Concentrations of non-radioactive CH_3I and/or I_2 , in the range of 5-50 $\mu\text{L/L}$ in air, were reduced by factors in excess of 100. The decontamination factor of the organic iodides is given approximately by Equation (5.11),

$$\ln \text{D.F.} \approx \ell f_v^{-1} \int_{\lambda} I_o(\lambda) \alpha(\lambda) d\lambda \quad (5.11)$$

where $I_o(\lambda)$ is the incident light intensity, $\alpha(\lambda)$ is the light absorption coefficient of the organic iodide, ℓ is the radiation path length, and f_v is the volume flow rate of air.

The reaction of I_2 with O_3 is a key step in the photochemical method. The rate of this reaction was studied in a flow system, at room temperature ($20 \pm 2^\circ C$) and a total pressure of 100 kPa. Nitrogen and oxygen were used as the carrier gases for I_2 and O_3 , respectively. Rate measurements were done with initial I_2 pressures of 2 to 10 Pa, and initial O_3 pressures of 20 to 100 Pa. Reaction times ranging from 32 to 120 s were used. The rate measurements consisted of measuring either the rate of consumption of I_2 or the rate of consumption of O_3 . The results obey the differential rate law,

$$-d[I_2]/dt = -d[O_3]/Rdt = k [I_2] [O_3] \quad (5.12)$$

where k is the observed rate constant and R is the O_3/I_2 reaction stoichiometry. The integrated form of the above rate law is

$$([O_3]_i t)^{-1} \ln \frac{[I_2]_i [O_3]_t}{[I_2]_t [O_3]_i} = k(1-R[I_2]_i/[O_3]_i) \quad (5.13)$$

where the subscripts i and t refer to initial and final concentrations (at time t), respectively.

The plot of the left side of Equation (5.13) vs. the ratio $[I_2]_i/[O_3]_i$ is shown in Figure 5-3. Two sets of data are shown in this figure: the solid circles are from measurements of the rate of I_2 consumption and the open circles are from measurements of the rate of O_3 consumption. The $[O_3]_t$ in the first case and the $[I_2]_t$ in the second case [cf. Equation (5.13)] were calculated from the reaction stoichiometry, i.e. from $[O_3]_i - [O_3]_t = R([I_2]_i - [I_2]_t)$. The error bars in Figure 5-3 are due to the uncertainty in R . The value of $R = 3.9 \pm 0.2$ was determined independently, from measurements of the amount of O_3 consumed per I_2 molecule reacted. The rate constant, k , determined from the intercept in Figure 5-3 was $1.5 \pm 0.1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \cdot \text{s}^{-1}$. Thus, under conditions of excess ozone, Equation (5.13) reduces to Equation (5.14):

$$\ln D.F. = K[O_3]V/f_v \quad (5.14)$$

which gives the expected D.F. as a function of O_3 concentration, volume of the scrubber and flow rate. For instance, with $[O_3] = 2.3 \times 10^{-5} \text{ mol.dm}^{-3}$ (560 ppmv), $V = 10 \text{ m}^3$ and $f_v = 0.05 \text{ m}^3 \cdot \text{s}^{-1}$; a D.F. of 1000 can be obtained at 22°C .

5.1.3 Properties of the Iodine Oxides

In both the CIS and photochemical methods, removal of iodine is effected by conversion to involatile iodine oxides (I_4O_9 , I_2O_4 , I_2O_5). The thermal stability of these oxides was studied by thermogravimetric and differential thermal analysis [75]. It was shown that the room temperature I_4O_9 and I_2O_4 products decompose above $\sim 125^\circ\text{C}$ to I_2O_5 , releasing elemental iodine. The I_2O_5 decomposes above $\sim 325^\circ\text{C}$ to elemental iodine and oxygen.

The room-temperature iodine oxide products are, therefore, sufficiently stable for the purpose of removing the radioiodines from air. Furthermore, an extra margin of stability can be achieved by running the iodine scrubber at 100 to 200°C , in which case the more stable I_2O_5 will be the end product. The I_2O_5 can be removed from the scrubbers by heating or by washing with water. In the first case elemental iodine will be released, and in the second case an aqueous iodate will be formed. In either case the concentrated iodine can be subsequently converted to more stable forms, suitable for permanent disposal.

5.1.4 Optical Methods of Iodine (I_2) Detection

The need for development of real-time monitors for the detection of gas-phase radionuclides, particularly ^{129}I has been emphasized recently [68]. For this purpose, and also in support of our present research on methods for removal of I_2 from air, we have begun to develop optical methods for I_2 detection at the parts per million level. Two such optical methods presently under study are resonance fluorescence and light absorption.

With the resonance fluorescence method, I_2 is excited to the $B^3\Pi_u$ state using the 632.8-nm radiation from a helium-neon laser. The I_2

fluorescence is observed perpendicularly to the direction of excitation, at 650 and 660 nm, using a photomultiplier preceded by narrow-band (± 10 nm) interference filters. At present, due to instrument limitations, I_2 below 50 ppm by volume in helium cannot be detected with this method.

Absorption of the 546.1-nm radiation of a mercury lamp was used to detect I_2 in air at the part per million level. We have measured the I_2 extinction coefficient [$\epsilon \equiv (\log_{10} I_0/I)/C\ell$] for this radiation in the presence of air. A value of $928 \pm 26 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ was determined. Thus with an optical path length of 50 cm, I_2 concentrations as low as $1 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ (2 ppm) can be detected. A compact double-beam spectrophotometer based on this principle was constructed, and is presently being tested for detection of I_2 in off-gas streams under various conditions.

5.2 SEPARATION OF KRYPTON-85 FROM AIR

Separation of ^{85}Kr from air is difficult due to the lack of any significant chemical reactivity of krypton. Low-temperature distillation and absorption in fluorocarbons have been under development for several years now and are at present the only available methods, despite their complexity [72]. Other methods proposed or under study are adsorption on zeolites [80,81], thermal diffusion [82] and selective permeation through membranes [83,84]. We have been studying a gas dynamic method for the separation of krypton from air. The technique has been demonstrated at low pressures for various gas mixtures. It is, at the moment, premature to predict the viability of this method in a large-scale system for the separation of ^{85}Kr from air, although it may be attractive for removing other gaseous nuclides.

5.3 FUTURE DIRECTIONS

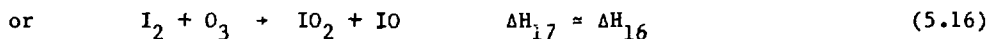
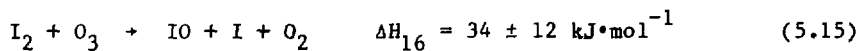
The CIS and photochemical methods of removal of gas-phase radio-nuclides are sufficiently advanced to warrant an engineering scale demonstration. On the basis of the known underlying chemistry either method can be scaled to the levels required for commercial application. Further

research to provide a firmer basis for such an application would be directed towards

- (a) the elucidation of the primary reactions in a corona discharge,
- (b) the rate and mechanism of the I_2-O_3 reaction, and
- (c) additional fundamental properties of the iodine oxides.

A new mass spectrometer system capable of sampling directly from the corona discharge volume and capable of detecting negative ions will be used to study the elementary reactions responsible for the decomposition of the organic iodides and the final fixation of the released iodine in a corona scrubber. As mentioned previously, a pilot plant is currently under construction to test large-scale removal of radioiodine from air.

The rate-determining step(s) in the reaction of I_2 with O_3 is estimated to be endothermic by $\approx 34 \pm 12$ kJ/mol:



Thus, the reaction is expected to be faster at higher temperatures. A faster rate would yield a higher D.F. with less O_3 and reaction time (V/f_v), according to Equation (5.14). Also, the more stable I_2O_5 product will be formed at higher temperatures. For these reasons the I_2-O_3 reaction will be studied as a function of temperature up to $\approx 175^\circ\text{C}$.

Experiments are under way to determine the structure of the I_4O_9 and I_2O_5 using infrared and laser Raman scattering spectroscopy. Structural information will provide supplementary information on the thermal stability and chemistry of these iodine oxides.

The underlying principles of the observed heavy-light separation in binary mixtures will be studied in more detail to assess the applicability of the method for large-scale separation of ^{85}Kr and other radionuclides, from air.

An increased effort will also be placed on the development of selective, continuous monitors for I_2 and Kr. Optical methods, such as absorption or resonance fluorescence, are particularly suitable for this application.

6. SUMMARY

The program for underlying chemical research in the AECL Nuclear Fuel Waste Management Program is concerned with developing the basic chemical knowledge and understanding required in other parts of the program. It is described under four headings: Waste Form Chemistry, Solute and Solution Chemistry, Rock-Waste-Water Interactions and Advanced Methods of Abatement and Monitoring of Gas-Phase Radionuclides.

The Waste Form Chemistry Program includes work in four main areas. The first area consists of electrochemical studies of the dissolution of UO_2 . Surface oxidation proceeds through a complex series of steps. With neutral solutions, oxidizing potentials result in rapid dissolution and precipitation of hydrated UO_3 , whereas reducing potentials result in little dissolution. With acidic solutions, or solutions containing complexing agents, dissolution is extensive. The second area is the determination of phase relationships with respect to liquid immiscibility and hydrothermal crystallization of complex borosilicates. Seven quaternary borosilicates were investigated and the size of the miscibility gap in these systems was correlated with the radii of the alkali metal or alkaline earth cations. Hydrothermal devitrification of sodium zinc borosilicate glasses was studied and hydrated zinc silicates were observed. The third area is a study of the interactions of fission products with container

materials. The experiments involve studies of the interaction of TcO_4^- and I^- with copper and lead metal and oxides. These studies are barely underway. Finally, the fourth area is a study of novel "tailored" waste forms for the anion-forming radionuclides. Phase relationships are being determined in the system $\text{Bi}_2\text{O}_5\text{-BiI}_3\text{-H}_2\text{O}$. The system $\text{Bi}_2\text{O}_3/\text{Bi}_5\text{O}_7\text{I}$ seems promising for iodide waste form development.

The Solute and Solution Chemistry program is divided into three research areas. The first, fission product chemistry, presently consists of a study of the solution chemistry of iodine and technetium, with studies of selenium and palladium solutions to be done later. Contrary to what has been generally assumed, the chemistry of technetium in a deep geological system should be dominated by the lower oxidation states. A self-consistent data base has been assembled for the iodine/water system and has been used to predict the species present. Various electrochemical techniques have been used to characterize this system further. The second research area is actinide solution chemistry, which entails a study of the solution chemistry of uranium, neptunium and plutonium. Data bases have been assembled to predict the solubilities of these actinides, both alone and with complex-forming anions. Uranium complexation is being studied experimentally. Uranium dioxide is quite stable under reducing conditions, but complex formation becomes important under oxidizing conditions. Plutonium solubility is important only at extremely acidic or oxidizing conditions. The final area of research for this program is a thermodynamic study of aqueous solutions at moderately elevated temperatures. Experimentally, apparent molar heat capacities have been measured at 50°C and 75°C for some sodium salts of geochemical interest. These heat capacities, along with enthalpies and free energies at 25°C allow calculation of the free energies of the ions up to 75°C. From such free energies the solubilities of various systems can be calculated. Various theoretical models are also being examined to allow extrapolation of room-temperature free energies to elevated temperatures, and to calculate activity coefficients for the ionic species.

The Rock-Waste-Water program is divided into three areas. One area is the dissolution of feldspars. Commonly, non-linear kinetics have

been observed in such dissolutions, but careful microscopy has shown that very small particles are responsible for much of this non-linearity. Hydrothermal alteration of minerals has been studied by surface techniques and infrared spectroscopy, and the products of alteration have been identified. The second area involves using a surface microcalorimeter as a convenient tool for studying the surface properties of solids. Such an instrument is being commissioned and will be used to determine mineral surface areas, cleaning procedures and adsorption of ions. Finally, the third area is a study of colloidal transport of radionuclides. Studies will be conducted on uranium hydrolysis and the interaction of radionuclides with mineral particulates.

The final research program is a study of Advanced Methods of Abatement and Monitoring of Gas-Phase Radionuclides. The radionuclides considered are radioiodine and krypton. The sub-program on radioiodine has four identifiable parts. A corona discharge iodine scrubber has been demonstrated on the laboratory scale and also in a small pilot scale on the ⁹⁹Mo facility at CRNL. A photochemical scrubbing method has also been demonstrated on a laboratory scale. Both methods show decontamination factors of around 1000. Both methods produce solid iodine oxides and thermochemical studies have shown that these solids are stable below 125°C. Finally, two optical methods for the detection of iodine, resonance fluorescence and light absorption, are being investigated. A compact dual-beam spectrophotometer has been constructed and is undergoing tests with various off-gas streams.

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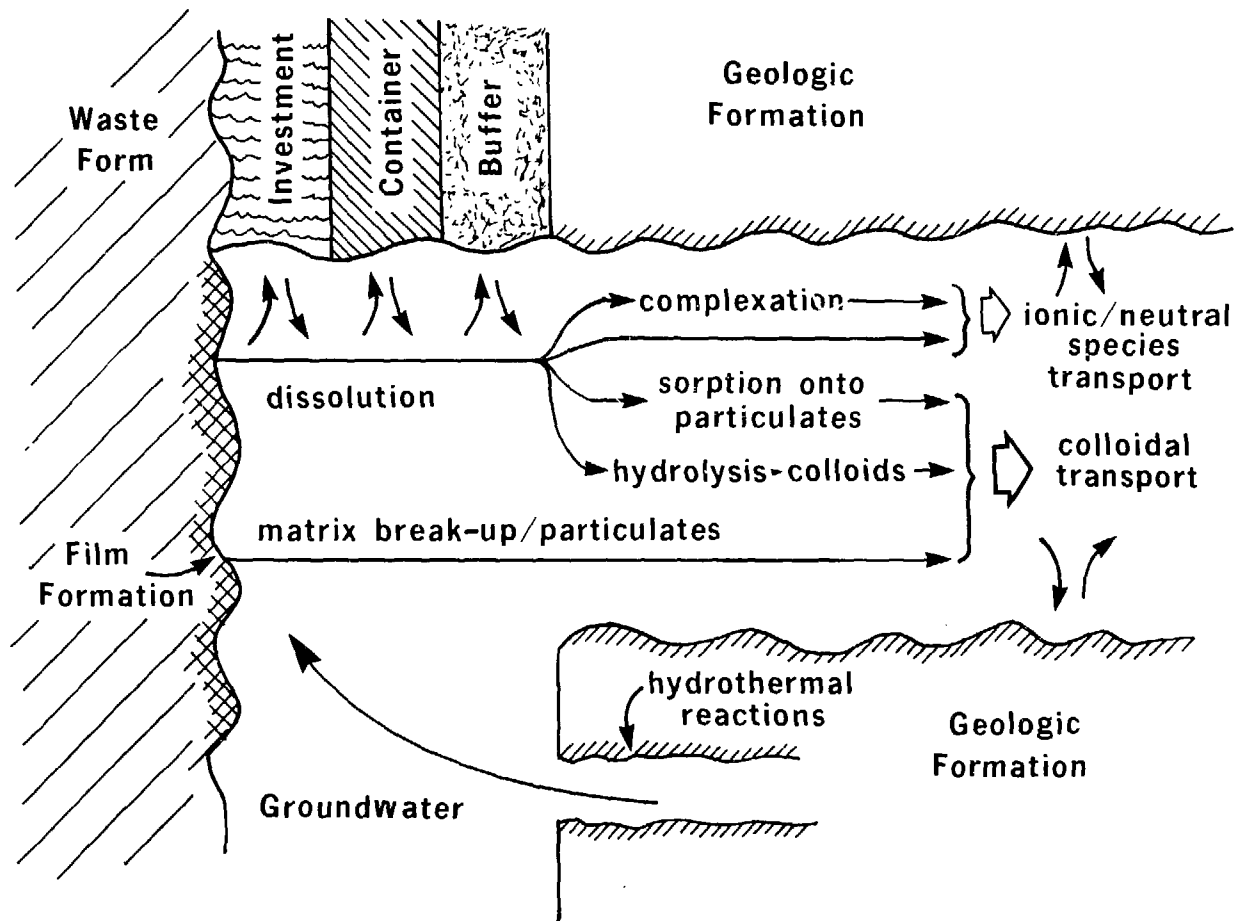


FIGURE 1-1: Schematic of Chemical Phenomena in a Waste Vault

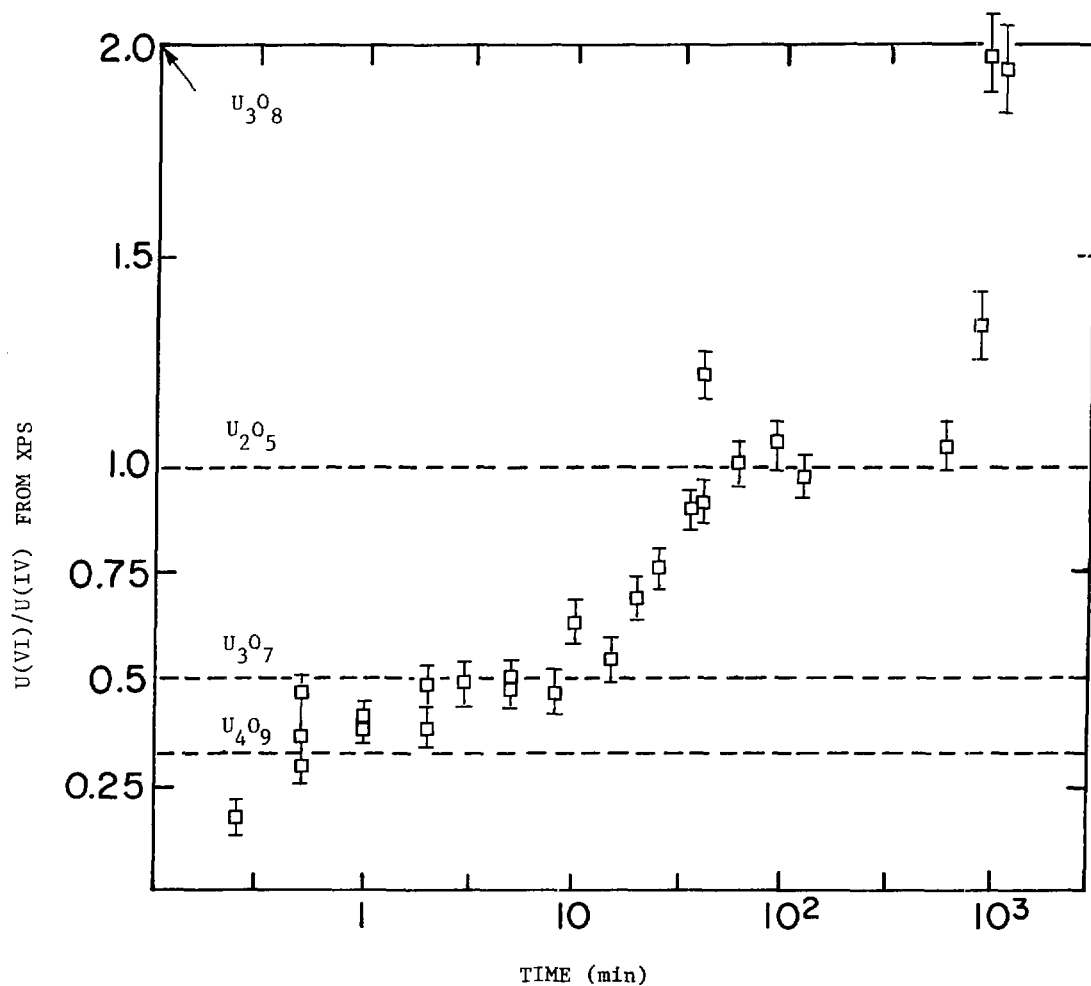


FIGURE 2-1: The Ratio of U(VI) to U(IV) in the Surface of a UO_2 Electrode Electrochemically Oxidized at a Potential of +300 mV (vs. SCE) in $0.5 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4$ (pH = 7) for Varying Times

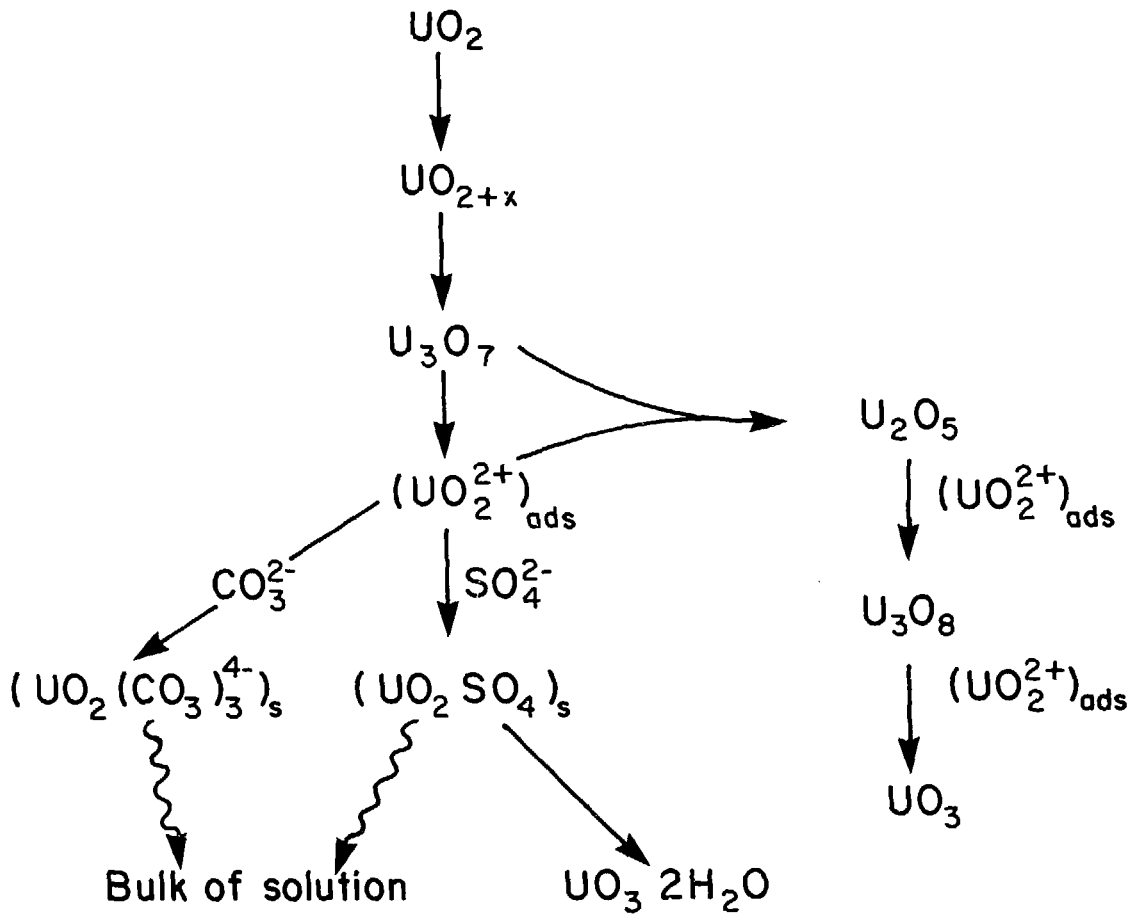
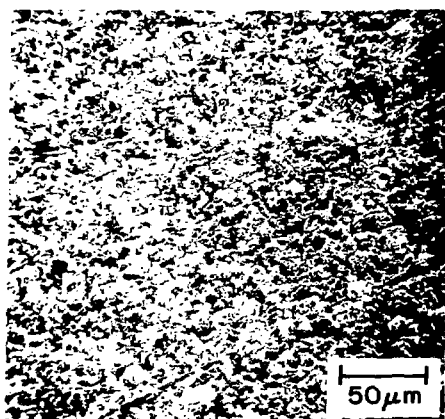
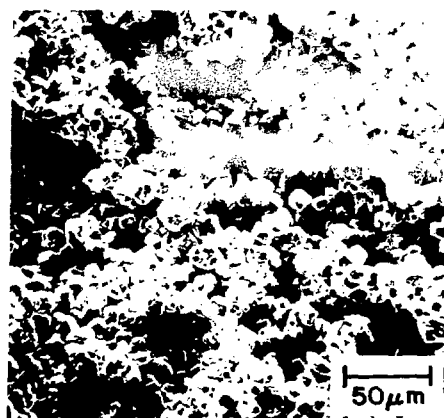


FIGURE 2-2: Reaction Scheme for Oxidative Dissolution of UO_2 in Neutral Solutions



A. ORIGINAL SURFACE



B. SURFACE AFTER 78 DAYS

FIGURE 2-3: Surface of a UO_2 Electrode Before and After Extensive Electrochemical Dissolution (+10 μA); (a) Before; (b) After Dissolution in $0.5 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{SO}_4$ Plus $0.01 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{CO}_3$

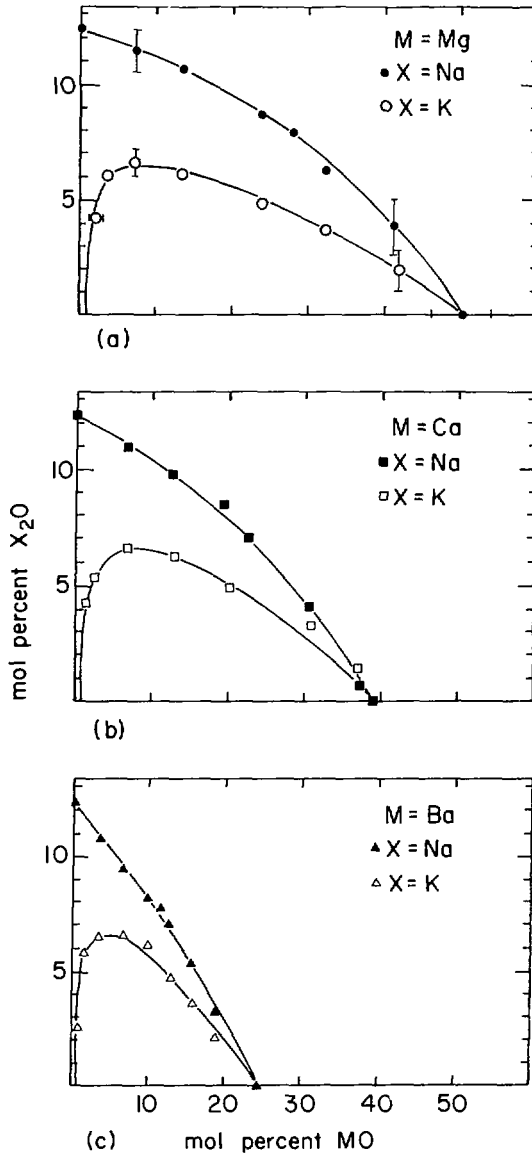


FIGURE 2-4: Limits of Miscibility in the Systems $\text{Na}_2\text{O-MO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{K}_2\text{O-MO-B}_2\text{O}_3\text{-SiO}_2$ at 650°C . (a) $M=\text{Mg}$, (b) $M=\text{Ca}$, (c) $M=\text{Ba}$, $\text{SiO}_2/\text{B}_2\text{O}_3 \cong 1.07$ (molar); ZnO Behaves Similarly to MgO

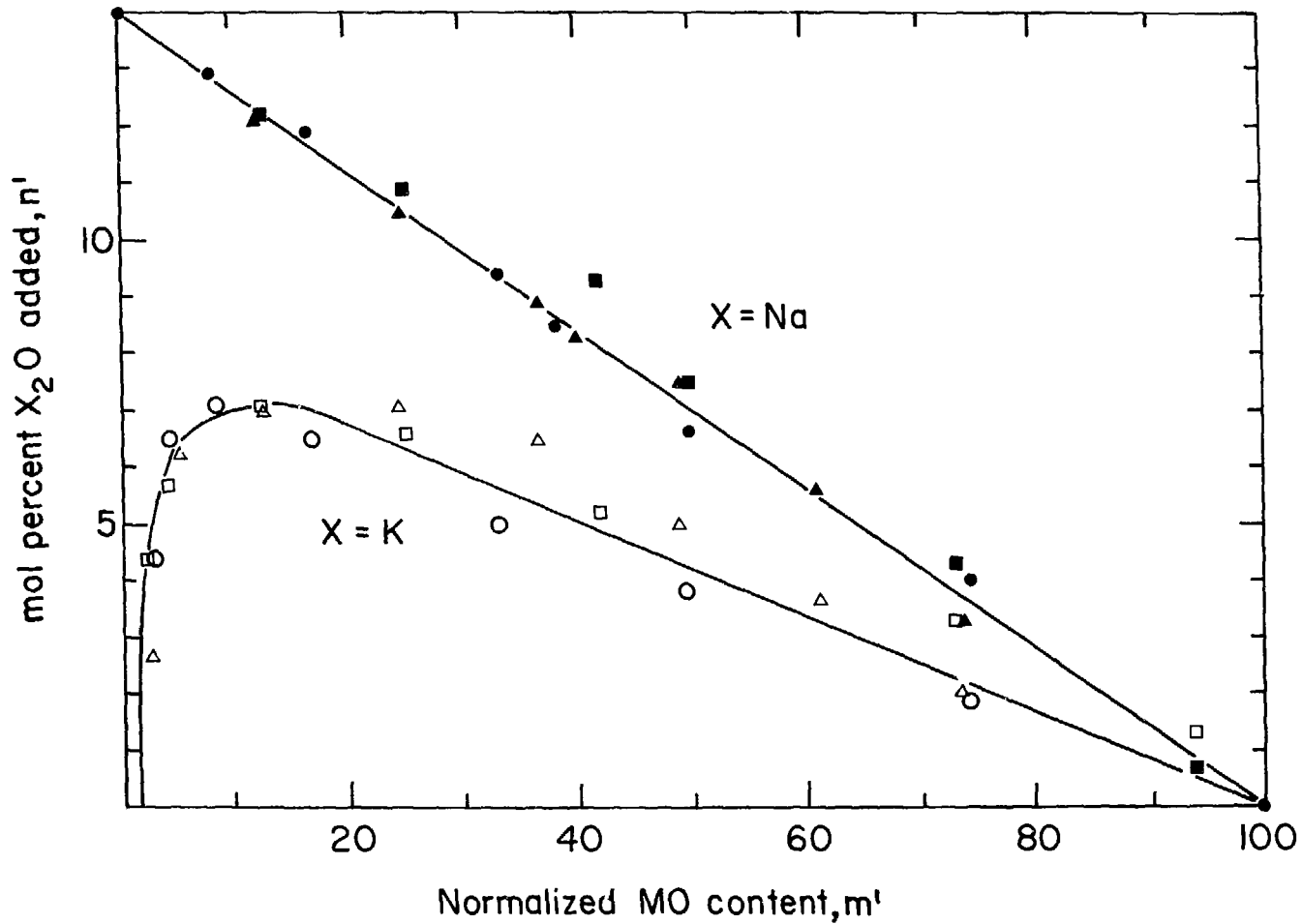


FIGURE 2-5: Data from Figure 2-4, Normalized with Respect to the Extent of the MO-B₂O₃-SiO₂ Miscibility Gap, and with Alkali Oxide Content Expressed as $n' = \frac{X_2O \times 100}{(MO + B_2O_3 + SiO_2)}$

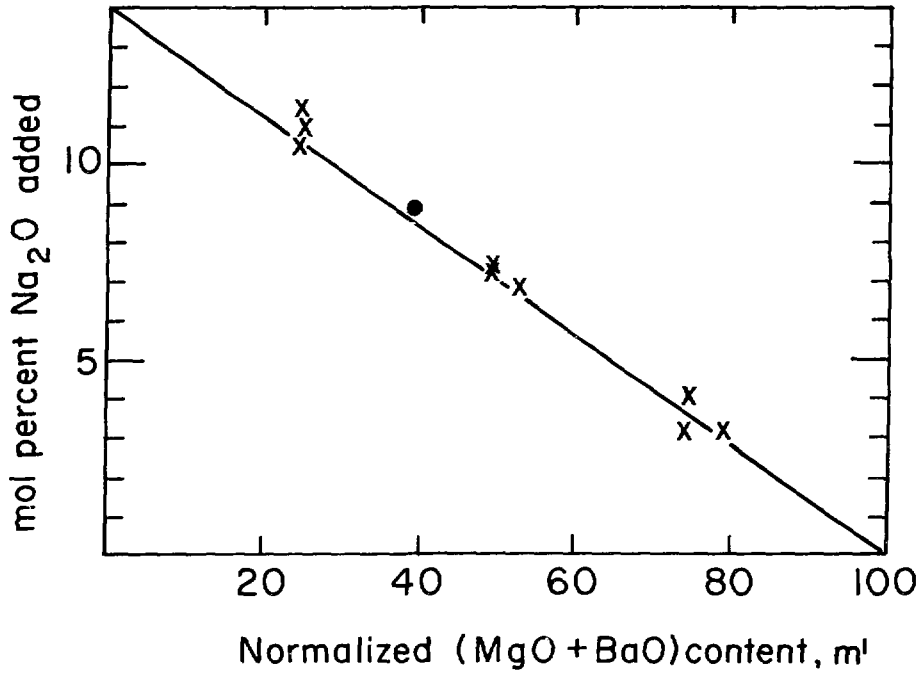


FIGURE 2-6: Miscibility Limit Data for 12 Compositions (* represents three coincident data points) in the System $\text{Na}_2\text{O}-\text{MgO}-\text{BaO}-\text{B}_2\text{O}_3-\text{SiO}_2$, Superimposed on the "Master Line" for $X \cong \text{Na}$ from Figure 2-5

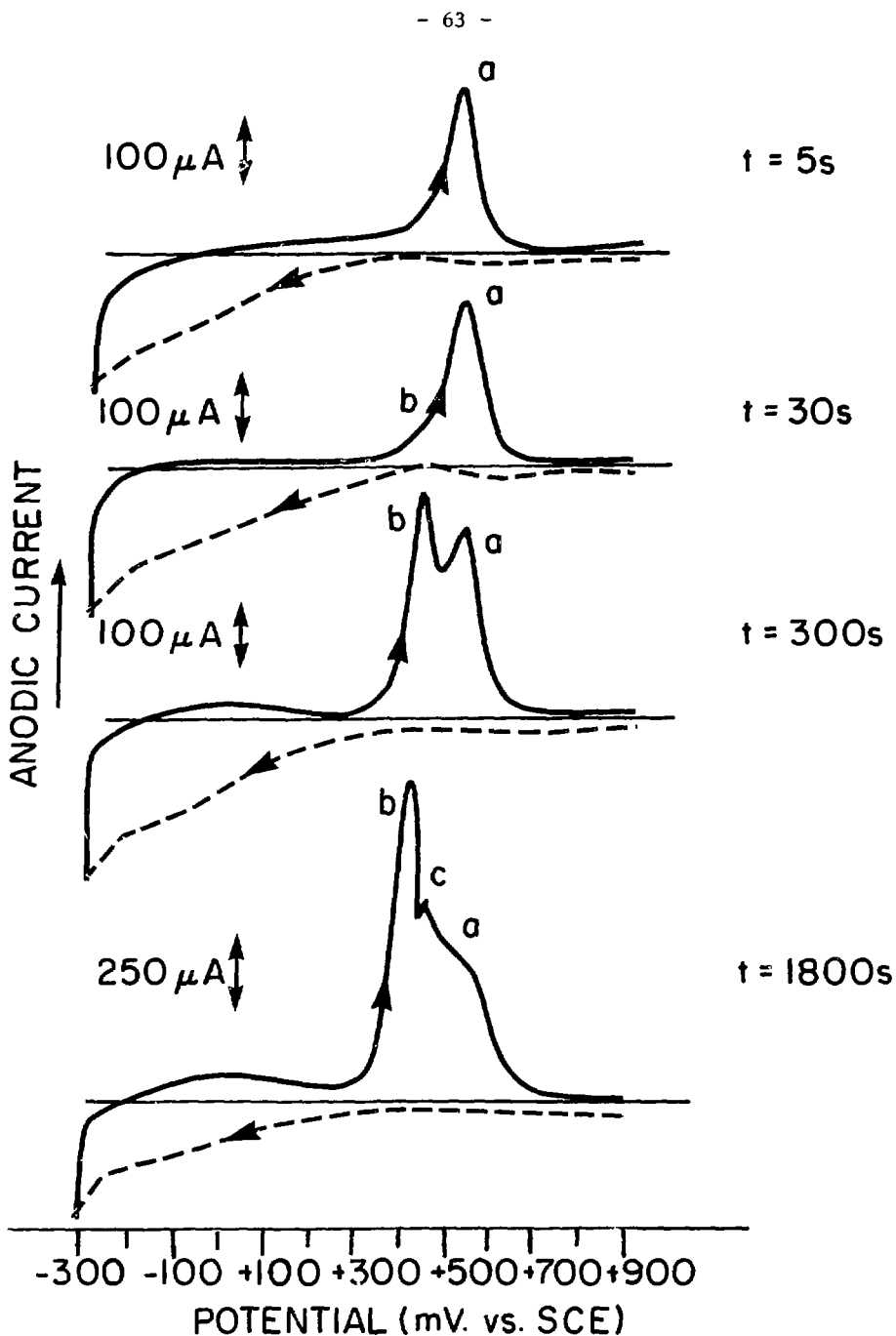


FIGURE 2-7: Anodic Stripping Voltammograms (at $20 \text{ mV}\cdot\text{s}^{-1}$) for Films Potentiostatically Deposited from Pertechnate Solutions at -300 mV . (vs. SCE) for varying times; $[\text{TcO}_4^-] = 1.2 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$; $[\text{HCl}] = 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$

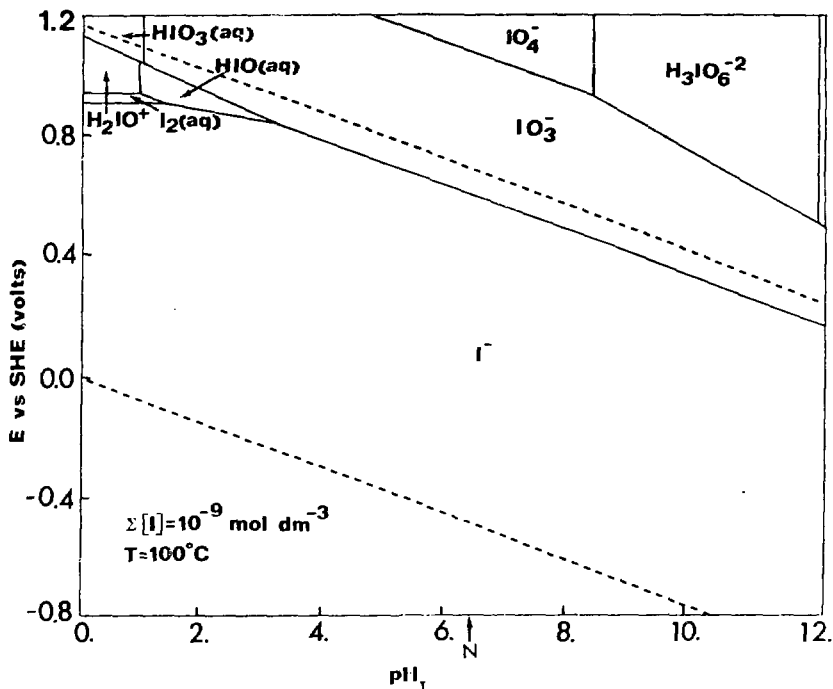


FIGURE 3-1: Potential-pH Diagram for the Iodine/Water System $\Sigma[\text{I}]_{\text{aq}} = 10^{-9} \text{ mol}\cdot\text{dm}^{-3}$, $T = 100^\circ\text{C}$

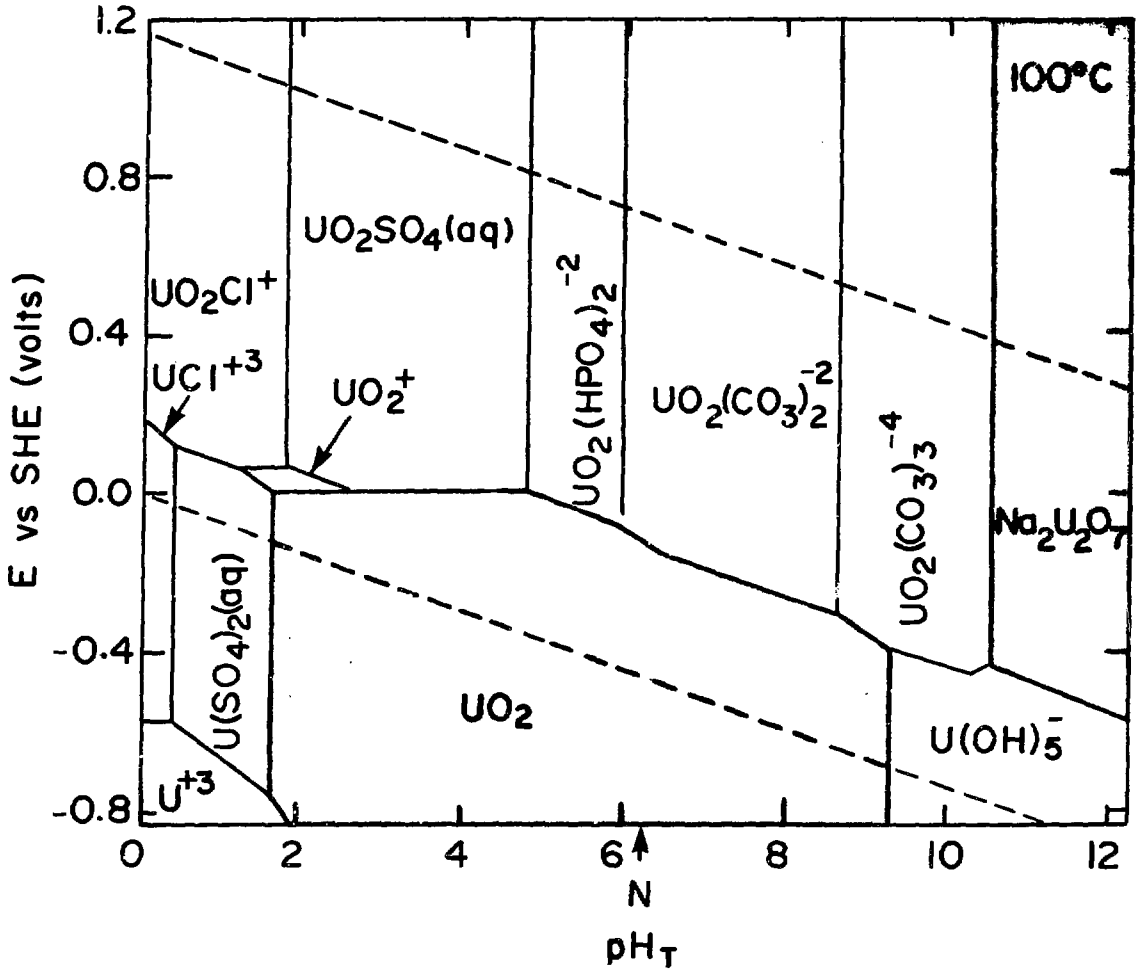


FIGURE 3-2: Potential-pH Diagram for the Uranium Model Groundwater ($[CO_3^{-2}]_T = 0.01$, $[F^-] = 0.00005$, $[Cl^-] = [Na^+] = 0.1$, $[SO_4^{-2}]_T = 0.01$, $[PO_4^{-3}]_T = 0.000002$ mol.dm⁻³) at 100°C. Boundaries are for 10^{-3} mol.dm⁻³. (N ≡ a neutral solution)

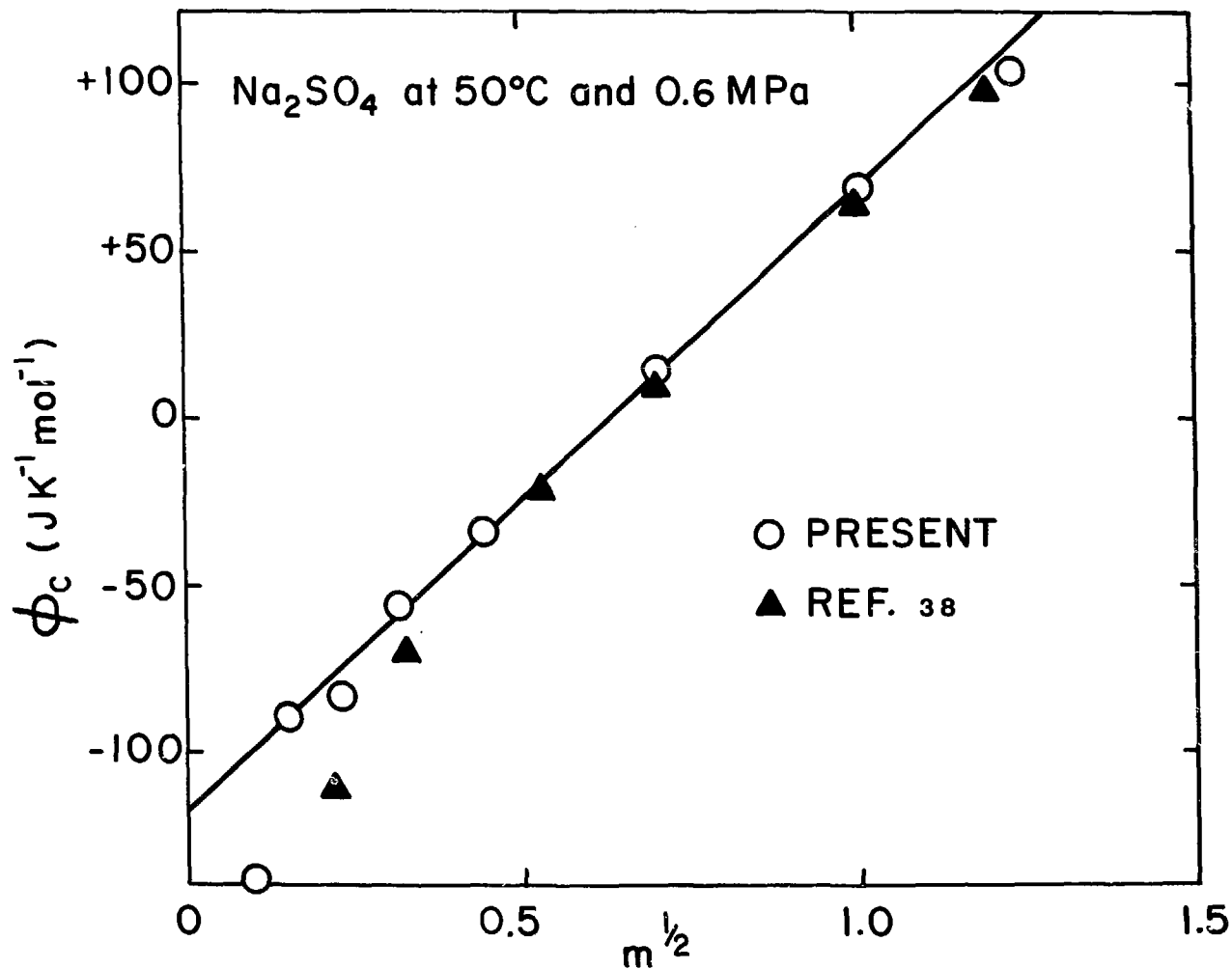


FIGURE 3-3: Apparent Molal Heat Capacities, ϕ_c , as a Function of the Molality^{1/2} ($m^{1/2}$) of Na_2SO_4 Solutions at 50°C and 0.6 MPa Compared with Literature Values of Rogers and Pitzer [38]

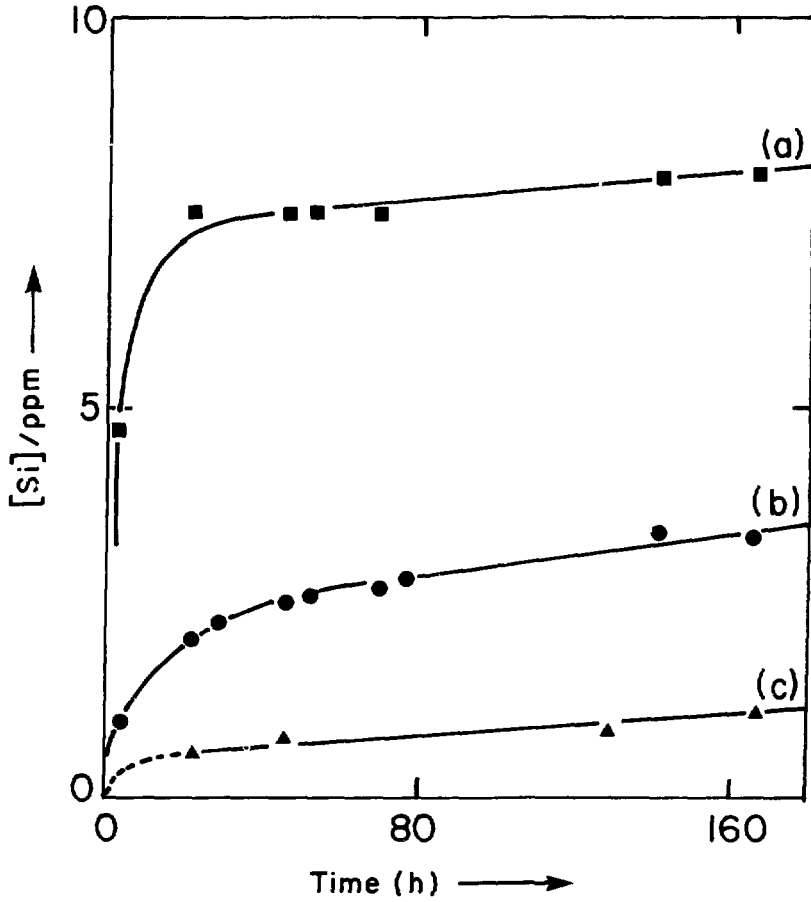


FIGURE 4-1: Release of Silicon from Microcline in Deionized Water at 80°C as a Function of Time. Key: (a) > 400 mesh, washed in water; (b) > 400 mesh, ultrasonically cleaned and washed in water; (c) 40 - 60 mesh, treated as in (b).

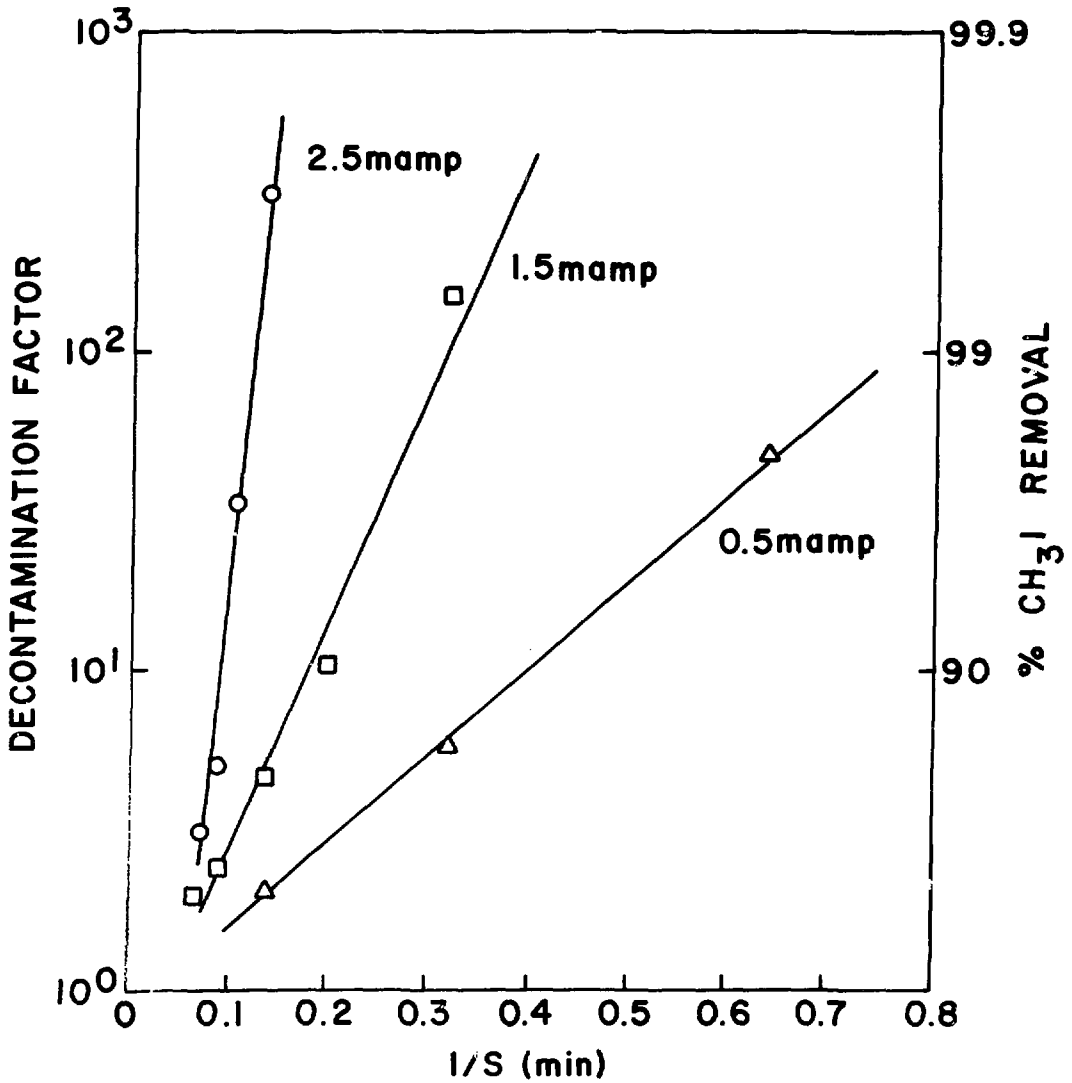


FIGURE 5-1: Methyl Iodide Removal from Air as a Function of Discharge Current and Contact Time in the Corona Discharge Tube. DF = concentration of CH_3I entering tube/concentration of CH_3I leaving tube. S = space velocity = volume flow rate/scrubber volume.

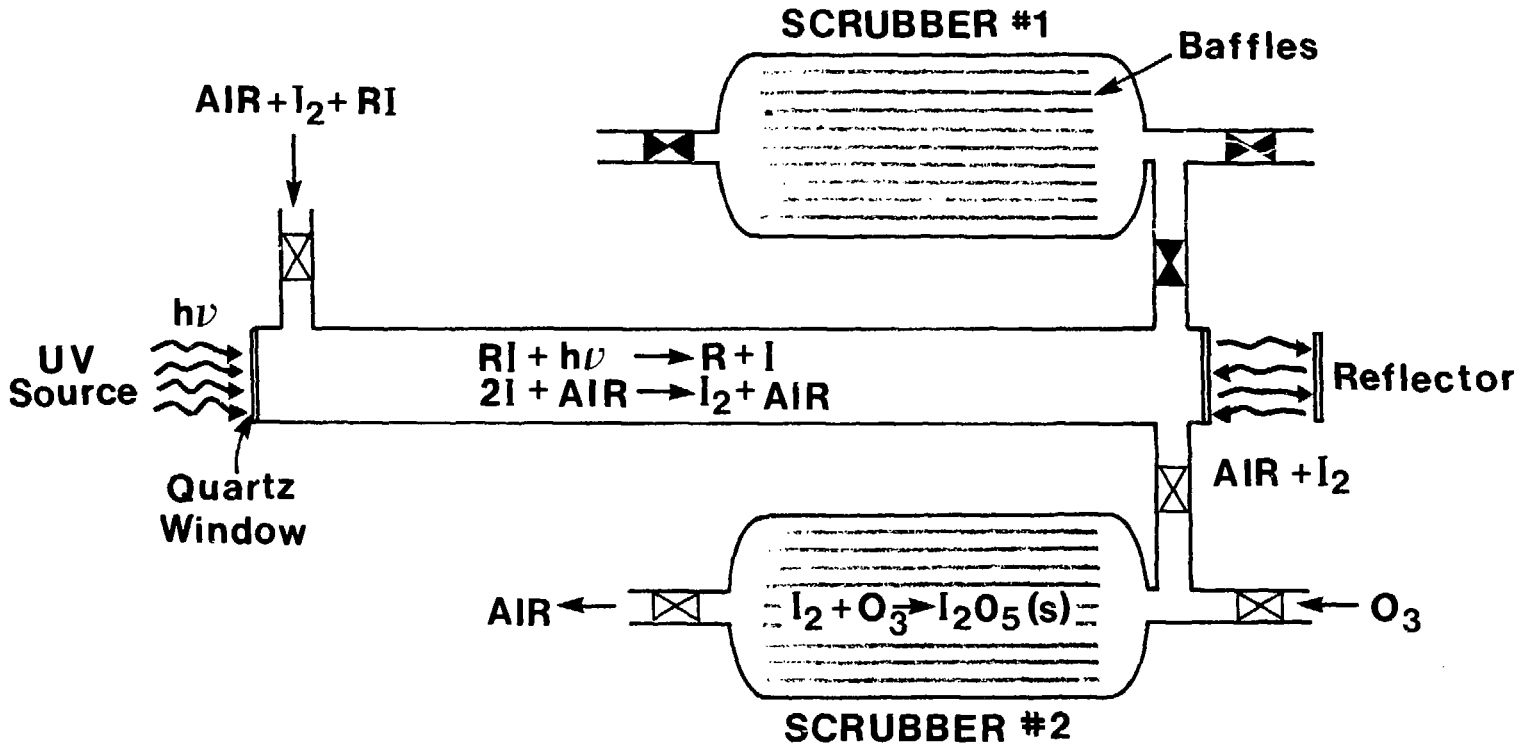


FIGURE 5-2: Photochemical Radiiodine Scrubber (Schematic)

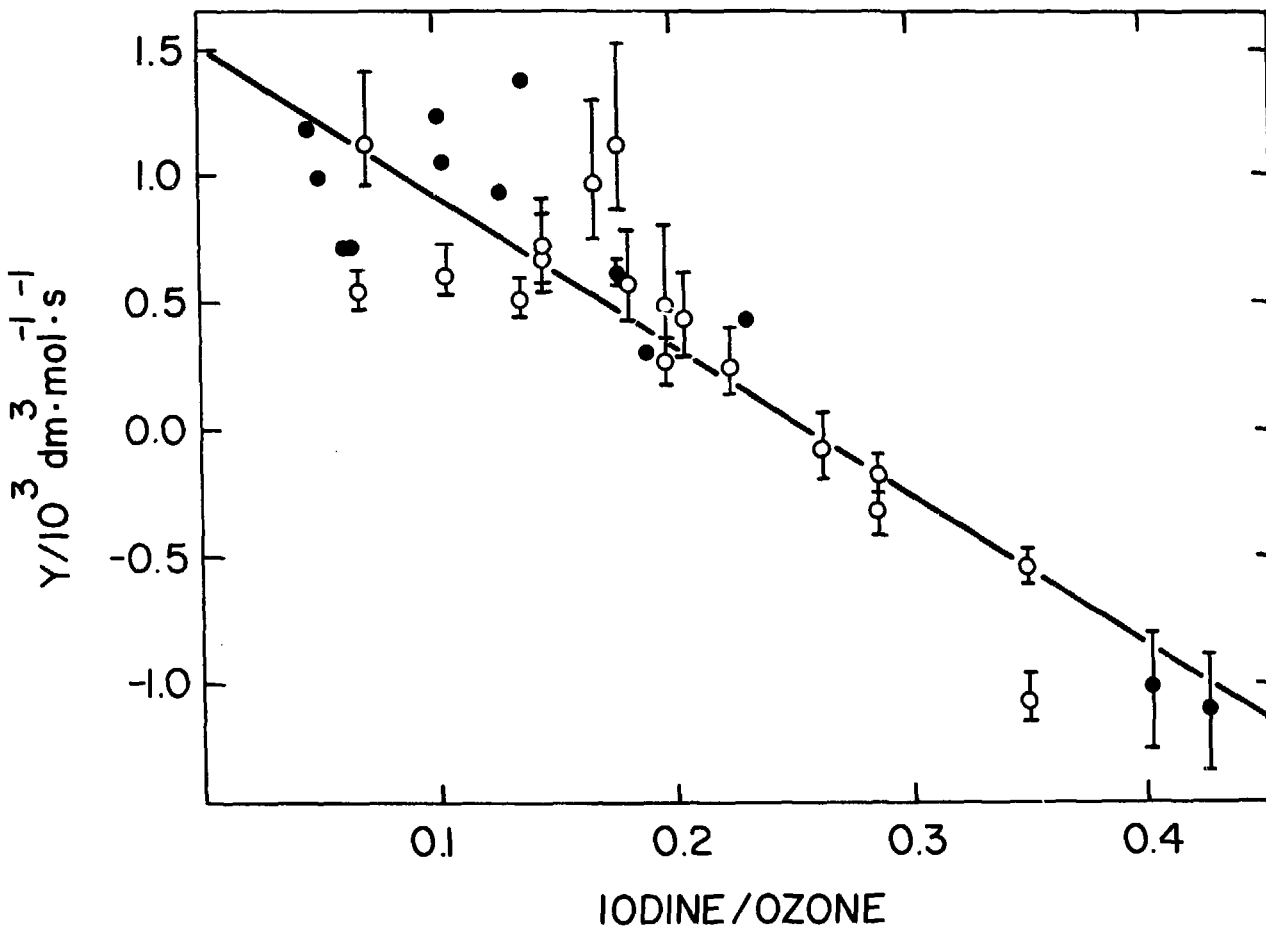


FIGURE 5-3: Rate Measurements of the Reaction of I₂ with O₃. (The ordinate, Y, is equal to

$$([O_3]_i t)^{-1} \ln \frac{[I_2]_i [O_3]_t}{[I_2]_t [O_3]_i} .$$

Measurements of O₃ consumption are shown by ϕ and those of I₂ consumption by \bullet .

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