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Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

GEOCHEMICAL ASSESSMENT OF NUCLEAR WASTE ISOLATION
Report of Activities During Fiscal Year 1982

July 1982

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GEOCHEMICAL ASSESSMENT OF NUCLEAR WASTE ISOLATION

Report of Activities During Fiscal Year 1982

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1983

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EXECUTIVE SUMMARY**TASK 1**

The purpose of this task is to investigate, by laboratory experiments, the migration of representative nuclides in proposed engineered barrier materials, at conditions comparable to those expected in a repository environment. In FY 1982 a radial-flow diffusion cell was constructed and tested which permits uniform hydration of the material being tested by the nuclide-bearing water. To test the cell, a 0.01-molar cesium solution was introduced to an agar gel, and an ion profile was obtained after 28 hours. There was close concordance of this profile with results of a stirred-cell experiment, indicating that the radial-flow cell is designed and operating properly.

Theoretical investigation of ion diffusion in montmorillonite gels indicates the presence of two porosity - spatial regions, one occupied by the micropores, one by macropores. The diffusion rates of ions in the gels are influenced by the abundance of the two porosity regions and their configuration, as well as by the ion-exchange kinetics and electrical exclusion effects. Anions, such as technetium, are electrically excluded from the micropore domains; they migrate readily through macropores in the gel. Cations also move readily through the macropores, but also divert into the micropores where they exchange on clay surfaces. This latter process is not described well by considering only distribution coefficients. The recognition of the presence of porosity domains and their effect on ion exchange is critical in the evaluation of candidate engineered barrier materials.

TASK 2

During FY 1982, a research program was conducted under Task 2 which addressed several topics pertinent to the licensing of a nuclear waste repository. The research focused on both chemical (speciation studies, analytical approaches for the detection of radionuclides) and geochemical problems (spectroscopic states of metal ions in basalt and metal ions bonded to mineral surfaces).

Significant results from the research in FY 1982 include:

- Studies of the fluoride ion complexed on feldspar; this ion is found in high concentration in the groundwater of the Hanford basalt and has been shown to be highly important in the movement of radionuclides such as plutonium in geological materials. Studies of this type are very important in understanding solubility of radionuclide complex species with the fluoride ion.
- Proof that bonding of multiple-oxidation-state metal ions to minerals can differ, depending on temperature (this case considers potassium feldspar, a component of granitic rock and Nevada Test Site tuff). These different chemical species and oxidation states of radionuclides can affect their release rates into the surrounding environment. Cobalt is particularly important as a role model for two reasons: it is a radionuclide that has been shown to migrate from radioactive waste repositories, and it has been shown to migrate by the same mechanism as plutonium, americium, and other long-lived radioactive ions.
- Investigations of the $[(\text{UO}_2^+)_2(\text{OH})_2]^{2+}$ dimer, a uranium hydrolysis product whose sensitivity to air and moisture makes it difficult to study;

its spectroscopy has been studied by cation-stabilization for the first time.

- An effective technique for the detection of important radionuclides such as uranium in fairly high aqueous concentrations that would be found in the near-field environment of a water-breached repository; the collection technique has been shown previously to be effective under geologic conditions. Analyses of this type are mandatory for site characterization, since state-of-the-art analytical techniques will have to be used to monitor breached repositories. This is especially true of radionuclides such as uranium, which will migrate from the immediate site into surrounding environments and groundwaters. Other analytical techniques which also work under the geologic conditions found in the Hanford basalt formations, will have to be developed in order to detect other actinides and fission products.

- Investigations of the chemical and spectroscopic properties of uranium hydroxide and its ability to chemisorb (and subsequently react with) carbon dioxide and form mixed hydroxy/carbonato uranium complexes; these two anions play an extremely important role in the complexation chemistry of uranium in geological environments. Research of this type is useful in furnishing information on solubilities of uranium carbonates and hydroxides, two of the most important uranium species mentioned in studies of uranium migration in groundwaters.

TASK 3

The purpose of Task 3 is to define geochemical processes in the far field host rock-groundwater system which will influence radionuclide transport and retardation.

Investigations of sorption processes include: the nature and evolution of rock and mineral surface substrates, irreversible sorption processes including solid state diffusion and chemical incorporation, and modeling of complex surface speciation and sorption phenomena. In addition, the influence of water chemistry on radionuclide solubilities is also being investigated, including geochemical controls on speciation, pH, Eh and dissolved oxygen. The results of this research will aid NRC in defining the current far field geochemical processes on a site specific basis, and will enable prediction of how geochemical controls will affect radionuclide transport under perturbed repository conditions.

Significant results in research in FY 82 include:

- Experimental weathering reactions simulated development of natural sorption substrates on associated minerals of basalt and tuff. Results indicated that extensive $Al(OH)_3$ or $Fe(OH)_3$ surface coatings do not occur, supporting the use of fresh rock and mineral substrates in radionuclide sorption experiments.
- The role of irreversible radionuclide sorption processes was investigated. Observed long term Cs uptake into obsidian implies that incorporation of this element into the hydrated surface structure of glass, an important component of basalt and tuff, can occur. Solid state volume diffusion processes were found to be too slow to be effective in crystalline silicates.

• Mechanisms and reaction rates controlling dissolved oxygen concentrations were experimentally investigated. Uptake rates are important in light of high dissolved O_2 concentrations purportedly measured in old groundwater systems such as at NTS. Results indicate kinetics are controlled by diffusion and by ferrous iron in the oxides and silicates. A model was developed which can be used to predict uptake rates for oxygen resulting from repository induced perturbations.

• Investigations were conducted on controls and buffering of Eh in basalt and tuff-water systems, and measuring methods were evaluated. Concurrent measurements by Pt electrode, Fe^{++}/Fe^{+++} couples and dissolved oxygen, and modeling by computer speciation codes gave poor agreement between methods. Results show, that in rock/water systems, Eh may be controlled by kinetic reaction rates which must be well defined to calculate meaningful Eh values.

• Methods and techniques were developed to use potentiometric titrations to characterize intrinsic surface ionization constants. Such parameters are critical in the use of computer codes being developed by NRC and DOE (MINEQL and MINTEQ) to model radionuclide sorption on host rocks.

TASK 4

This task is part of the larger investigation of issues related to assessing and measuring geochemical interactions in a repository environment between radionuclides, water, engineered barriers, and near-field and far-field host rock to assure that HLW repositories will be sited and designed with proper geochemical consideration. In particular, this task is directed toward assessing the adequacy of currently applied methods for solving geochemical problems of the migration of radionuclides, recommending improvements, and providing better understanding of chemical processes operative during transport of radionuclides. The principal issue being addressed is the level of complexity required of geochemical algorithms of transport models to adequately predict radionuclide migration.

In FY 1982, the computer code, CHEMTRN, was extended to include additional geochemical algorithms, and was tested. The code is based on chemical and thermodynamic principles and incorporates a system of simultaneous, non-linear, partial differential equations coupled to a set of mass action equations and a site constraint equation. Considerations include: one-dimensional dispersion/diffusion, advection, complexing in the aqueous phase, sorption of ions and complexes by ion exchange or surface complexation, dissociation of water and precipitation/dissolution reactions.

Results of simulations with several chemical algorithms in CHEMTRN indicate that one cannot assume that use of a constant distribution coefficient (K_D) for interphase mass transfer will adequately account for changes in the bulk or trace-element composition of ground water. A higher level of chemical complexity must be addressed, as with CHEMTRN, incorporating

considerations of thermodynamic equilibrium constants, activity corrections using activity coefficients, changes in ionic strength, finite exchange or sorption capacity of the solid phase and competition for sorption sites among aqueous species, complexation of aqueous species, varying pH, and precipitation/dissolution equilibria of secondary solid phases. A simulation of a field test, using CHEMTRN and incorporating these considerations, resulted in an excellent match with field observations.

During FY 1983, the CHEMTRN code will be transferred to NRC. The code will be applied to simulation of chemical transport in systems that are analogues of repository behavior. These systems include natural analogues investigated in Task 5, uranium ore bodies in Australia, and other site and laboratory investigations. Experimental data developed in Tasks 1, 2, and 3 will be used in the CHEMTRN code to verify and further implement mass transfer mechanisms and chemical reactions.

TASK 5

The purpose of Task 5 is to determine the chemical retentivity over time of rock types that might be candidates for repositories, and the movement of radionuclides in the fracture-controlled hydrologic systems encompassed by these rocks. To accomplish this, the chemical contents of intrusive rocks and their host country rock, chemical gradients at and away from the contacts between them, and the loci of radioelements in the rock matrix and fracture-filling minerals are investigated.

Activities in FY 1982 emphasized investigations of the effects of a monozonitic intrusive into tuffaceous terrane. In contrast to earlier investigations of a contact zone in crystalline rock where only a conductive thermal regime pertained, a strong circulating hydrothermal system was active in response to the intrusion of the monozonite into the tuff. Whole-rock neutron activation analyses of samples from a ~ 60m-wide zone encompassing the monozonite - tuff contact indicates high concentrations of many trace elements in the monozonite compared to the tuff. There are indications of gradients of Cs, Th, and Co in the tuff, with abundances of these elements increasing towards the contact. Other elements, including uranium, show no evidence for migration between the intrusive and the tuff.

Preliminary results of analyses of whole-rock samples from a contact zone between a rhyodacite dike and a Columbia River basalt flow also indicate the lack of mobility of uranium, as well as the absence of migration of U from the dike into the basalt. More detailed investigation of the distribution and abundance of U and other trace elements in the fractures in the basalt

and dike will be accomplished. Preliminary whole-rock analyses of radioelement contents of bedded salt in contact with a kimberlitic dike also suggest the lack of mobility of U, as well as the absence of migration of this element from the dike into the salt.

These observations, though preliminary, agree with results of earlier investigations of contacts between granitic rocks in suggesting that uranium and some other trace elements may not migrate readily over long time periods from intrusive rocks into tuff, basalt, and salt, in hydrologic and thermal conditions comparable to those expected in repository environments.

The emphasis of the project in Fiscal Year 1983 will shift from examination of "fossil" occurrences to investigation of active hydrothermal systems. Sites will be selected that are well documented, i.e., where rock types are well described, hydrologic and thermal conditions are well known, there is a good base of water chemistry data, and where samples of material from zones of circulation as well as from relatively impermeable zones are available. Investigation of the differences in mineralogy and in the concentration of key elements between these zones will be definitive in disclosing the geochemical behavior of candidate rock types in the near field of a repository.

1. TASK 1. INVESTIGATION OF CANISTER/OVERPACK-BACKFILL CHEMICAL INTERACTIONS AND MECHANISMS (C. J. Radke and F. M. Jahnke, Chemical Engineering Department, University of California, and J. E. Apps, Geochemistry Group, Earth Sciences Division, LBL)

1.0 Introduction

The ultimate isolation of high-level radioactive waste materials is a critical natural problem. Although many schemes have been proposed, including deep-space disposal, a most promising method is underground storage in impermeable geologic formation (1). This disposal technique involves burying spent fuel rods, most likely in an unreprocessed state, several thousand feet below the ground, as shown in Fig. 1-1. Once in place, the waste material should be protected by as many barriers as possible to prevent the escape of harmful and long-lived radioactive elements (2). Thus, the geologic environment must be chosen carefully for impermeability to water encroachment and thermal stability; considerable effort is being directed towards choosing suitable sites (3-5). Likewise, the canister material should resist corrosion. Much study is directed toward elucidating the corrosion mechanisms of materials containing radioactive waste (6). Finally, even if the first two barriers fail, it is possible to retard radioactive ion transport by ion exchange with solid fines located in the small fracture of the host formation. This too, is being studied (5, 7-11). Unfortunately, prediction of transport processes within the host formation is complicated by the fracture heterogeneity of natural porous media. If an additional, highly sorptive ion containment barrier could be deposited around the canister, a greater confidence level arises from the entire geologic waste storage scheme. Thus, as shown in Fig. 1-1, the backfill (or engineered barrier) concept is now under active consideration. Our work focuses on understanding nuclide ion transport behavior in engineered barriers.

Figure 1-1. Generalized concept of engineered barriers in basalt.

An engineered barrier material should be inexpensive, readily available, compatible with the host rock, relatively impermeable, thermally stable, highly sorptive to toxic ions, easily applied and, if possible, a fissure sealant (12). One material that apparently meets many of these qualifications is smectite or swelling clay (e.g., montmorillonite). However, since pure montmorillonite gels are not mechanically strong a likely barrier material might be a mixture of fine silica and bentonite. It might also be necessary to spice the montmorillonite with anionic getters. The purpose of this project is to investigate experimentally, under realistic conditions, the migration of representative nuclides in proposed barrier materials and to formulate a quantitative model allowing the prediction of the effectiveness of such an engineered barrier. Thus, the ultimate goal of this study is to provide reliable tools for evaluating a given backfill material and for designing the requisite amount and configuration of that backfill. We emphasize that our experimental program is general in that any backfill material can be evaluated for its ability to hinder radionuclide migration.

1.1 Diffusion in Compacted Clay Backfills

The first question which arises in modeling the transport of radionuclides released from the waste canister through a clay-based engineered barrier is that of the major mode of ion transport. That diffusion dominates over convection as the means of ion transport has been shown by Neretnieks (13), as described in our previous annual report (14). This is an important conclusion, because it indicates that nuclide migration rates through engineered barriers will indeed be slow.

Unfortunately, Neretnieks' analysis is unlikely to provide a reliable tool to design the requisite amount and configuration of backfill. His analysis is based upon the solution to the following differential equation:

$$\epsilon \left(1 + \frac{1-\epsilon}{\epsilon} K \right) \frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where ϵ is the system porosity, c is the ion concentration, t is the time and x is distance. This equation assumes instantaneous sorption equilibria, a linear sorption isotherm and a constant binary diffusion coefficient, both of which are uninfluenced by multicomponent and electrical effects, and, most critically, a homogeneous, nonporous, reasonably symmetric porous medium. Eqn. (1) does not reflect the fact that montmorillonite gels are composed of highly asymmetric, highly charged platelets, the interaction of which results in a gel structure, due to electric double layer, van der Waals and coulombic forces. The arrangement of individual particles within the montmorillonite gel has been studied widely (15-18), but is by no means fully understood. Nonetheless, application of Eqn. (1) to such a structured system would likely result in erroneous predictions.

Some workers have used Eqn. (1) (without the convection term) to predict diffusion rates in montmorillonite gels. Turk (19) found reasonable success in fitting his data with Eqn. (1), but his systems were limited to moderate compactions (about 30 w/o) at very high ionic strengths (0.7 M background ionic strength). His results may not be valid if used directly to show the applicability of Eqn. (1) for an engineered barrier for two reasons. First, the structure of the montmorillonite gel is very sensitive to background ionic strength (17), and the ionic strength at which he conducted his

experiments is significantly higher than that of 10^{-3} to 10^{-2} M found in typical basaltic groundwaters (20). Secondly, compactions on the order of 50 w/o are expected in a repository due to the considerable lithostatic head exerted on the backfill.

Torstenfelt et al. (21, 22), studying diffusion of radionuclides through a highly compacted montmorillonite at reasonable ionic strengths, recently found that Eqn. (1) cannot fit the migration behavior for any of the ions they consider. The cations Cs and Sr do not diffuse according to Eqn. (1) and they migrate more rapidly than expected considering their sorption isotherms (i.e., using K_d values from the disaggregated clay). In fact, the ionic diffusion coefficients of Cs and Sr found by Torstenfelt et al. are even higher than those in bulk water! For the anion, Tc, Torstenfelt et al. report that it migrates almost unhindered through the compacted montmorillonite.

These results indicate the failure of Eqn. (1), which is perhaps not surprising, but, nevertheless, is disconcerting. We feel that it is critically important to obtain reliable and well defined measurements of ion diffusion in actual compacted barrier materials. Only then can physically correct models be established to permit reliable backfill design.

In Section 1-2 we report the preliminary testing of our newly constructed radial flow diffusion cell, and in Section 1-3 we present further thoughts on modeling diffusion in a montmorillonite gel.

1.2 Diffusion Cell Design

The backfill material surrounding a nuclear waste canister will initially not experience significant loading. However, if the site is enclosed, the barrier material may eventually experience forces as large as the difference between the lithostatic and hydrostatic heads. Therefore, to understand ion migration in backfills representative of those in the field the barrier material must be studied at various known degrees of compaction. The experimental cell must also allow sampling to determine uptake by the clay barrier must permit ion concentration profile measurements and must include some means of monitoring continuously structural changes of the clay into which the ions diffuse. Finally, the apparatus must not impose a resistance to mass transfer such that experiments are either too lengthy in duration or insufficiently sensitive to the properties of the gel.

In the previous annual report (14), we proposed a diffusion cell which separated a solute chamber containing the ion whose diffusion was being studied and the backfill by two membranes: a Nuclepore membrane (~10 μm in thickness) of small pore size which confines the clay particles and a sintered metal disk which provides the required structural support for the fragile Nuclepore membrane. Unfortunately, calculations (23) showed that the resistance imposed by these dual membranes to diffusion through them into the clay gel proved to be sufficiently high to mask the sensitivity of the ion uptake to parameters of the barrier.

The culprit was the high mass transfer resistance of the sintered metal support disk. This problem has been alleviated by designing a radial flow

cell (23), shown in Fig. 1-2. The key feature of the new cell is the reduction of the mass transfer resistance due to convective transport through the sintered metal disk. The calculated mass transfer resistance is now confined to the thin Nuclepore membrane and the concentration boundary layer in the porous disk adjacent to the Nuclepore membrane. Because of convective flow, the concentration boundary layer thickness is small. Hence, it offers a significantly lower mass transfer resistance when compared with molecular diffusion through a porous disk of the same thickness.

The radial flow configuration also allows the sintered metal disk to be supported throughout its entire length. A much greater compaction of the gel within the clay chamber is permitted. The maximum load the membrane can withstand is now a function of the strength of the support plate, which can be made as thick as desired.

The cell is also unique in its handling of the barrier clay gel. The clay is always in contact with water, so uniform hydration is assured. Our design permits measurement of both ion uptake from an external solution and the ion profile within the gel. Thus, meaningful diffusion data from this new cell is possible due to a reduction of mass transfer resistance and due to the ability to compact the backfill under realistic pressures.

1.3 Diffusion Cell Performance

To establish that our radial flow-cell design can indeed quantify diffusion rates in a gelled material, unencumbered by external mass transfer resistances, we chose to measure ion concentration profiles in a noncompacted gel. In this case a simple stirred-cell diffusion experiment can be performed

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Figure 1-2. Schematic of the radial flow-cell.

in addition to the radial flow-cell diffusion experiment. In the simple, stirred-cell no porous support is necessary so there are negligible external mass transfer resistances. Then, if the ion profiles measured by both experiments are identical, our radial flow-cell is designed and operating properly.

Figure 1-3 gives ion profiles in a 4 weight percent agar gel by the two diffusion experiments (agar was chosen only for ease of handling). The solid line gives the radial flow-cell profile and the dashed line reports the simple stirred-cell result cesium is the diffusing ion and its concentration at the gel surface is fixed during the course of the experiment at 0.01 molar. The solution pH is 10 and the background ionic strength is 10^{-3} molar sodium chloride.

Note that the two cesium profiles in Fig. 1-3 agrees extremely well. The only significant deviation is in the initial region (i.e., $0 \leq \bar{x} \leq 0.1$) of the stirred-cell profile. This is due to minor sampling error and, therefore, can be accounted for. We conclude that our radial flow-cell, which can probe compacted barrier materials, is properly designed. This is heartening news.

Our first task is to study ion diffusion rates in mixtures of quartz and bentonite at various degrees of compaction and with various background ionic strengths and background pH values. Next we will investigate illite, bentonite and quartz since illite is a diagenesis product of montmorillonite and can be expected to form from montmorillonite under prolonged temperature exposure. Finally we need to study the role of temperature and possibly even temperature gradients on ion migration rates.

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Figure 1-3. Cesium profiles in agar.

1.5 Ion Diffusion Theory

In our last annual report (14) we suggested that compacted montmorillonite gel has a micropore-macropore structure (see Fig. 1-3 of reference 14). That is, there are local domains in which the clay platelets are reasonably well aligned by electrical double layer forces in a regular parallel array. The void space in these aligned domains constitute the micropores. A given micropore domain does not extend through the gel. Rather they are randomly arranged in space. The voidage separating the local micropore domains from each other is designated as macropore.

The micropore-macropore clay structure was suggested by Chi (24) from some very simple, stirred-cell ion diffusion experiments with uncompact bentonite. There does exist also some low-angle X-ray scattering results that yield a similar conclusion for the geometry of montmorillonite gels (25). Our attempts at directly observing such structures by fast-freeze SEM examination proved unsuccessful because of ice formation which destroyed the local structure. Thus, there remains no conclusive, direct evidence for such structuring in montmorillonite gels.

We believe, nevertheless that a micropore-macropore picture or something like it is the key to understanding ion diffusion rates in compacted barriers containing a significant portion of bentonite. The results of Torstenfelt et al. (21, 22) can be rationalized, at least qualitatively.

Anions, such as Tc, are partially excluded by electrical effects (see following sections) from the micropore domains. They are relegated only to the macropores and they migrate through the gel relatively unscathed. Cations also move faster than expected because they travel through the

macropores. However, along their journey, the cations must take side trips into the micropores where they exchange on the clay surfaces. Apparently this latter process, according to the results of Torstenfelt et al., is not described well by disaggregated K_d values.

To understand ion diffusion in clay gels we are attempting to quantify the micro-macro picture. Aside from our earlier modeling (14), we are considering two additional questions. First, what is the tortuosity within the micropore domains, and second, how do we understand the ion exclusion effects? These two questions are briefly addressed below.

Tortuosity

The presence of clay particles within the gel imposes a tortuous path upon the diffusion of ions. If the particles are segregated such that a micropore/macropore structure results, we have to consider two tortuosities: that through the micropores and that through the macropores. Here we will consider the tortuosity imposed by a structured microporous clay region comprised of parallel platelets with a concentration gradient normal to the platelets, as shown in Fig. 1-4. We consider the steady-state tortuosity imposed by such a structure by solving Laplace's Eqn. in two dimensions for one unit cell, which repeats throughout the region of consideration. The boundary condition of the unit cell are six no-flux conditions, four along the impermeable particle surfaces and two symmetry conditions, and a periodicity condition, which states that the flux and higher order derivatives of concentration are equal at the inlet and outlet of the unit cell. Thus, we have a uniquely specified problem from which we may obtain a tortuosity by the relation

$$\tau^2 = \frac{1}{\int_{\text{inlet or outlet face}} \frac{\partial c}{\partial y} dx} = \frac{1}{\int_{y=0} \frac{\partial c}{\partial x} dy}$$

Tortuosity Calculation

Idealization

Transport Equation

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0$$

Boundary Conditions

- 6 no flux conditions (shaded regions)
- Periodicity

Calculate

$$\tau^2 = \frac{1}{\int \frac{\partial c}{\partial y} dx}$$

Figure 1-4. The tortuosity calculation.

The solution for this problem is numerical.

Electrical Model

Within the microprocesses of highly compacted montmorillonite gels, it is likely that the coions will be excluded from the highly electrically charged interlamellar regions. This would affect ion transport by limiting anions (in the case of montmorillonite) to macropore regions, while cations would be free to migrate into the micropore regions within the clay gel. How the uptake rate into the microporous regions within the gel is affected by coion exclusion is elucidated by the following problem, originally due to Helfferich (26), as shown in Fig. 1-5. Consider two platelets of negative charge (q) separated by distance $2H$. Initially, the interplatelet region is sodium exchanged, and cesium is diffusing from the bulk solution, displacing sodium, which must back diffuse into the bulk to maintain electroneutrality. We use the Nernst-Planck relation to describe the mass transfer of an ion in an electrical field, and impose the electroneutrality relation that, at any time, the number of sodium and cesium ions in the interlamellar region must equal the surface charge.

These relations, as well as the final result, is also shown in Fig. 1-5. Here, ϕ = electrostatic potential in volts, U_i = electrical mobility of species i in $\text{cm}^2 \text{ mole}^{-1} \text{ j}^{-1} \text{ sec}^{-1}$, Z_i = valence of species i , F = Faraday's constant in c/equiv , C_i = concentration of species i in mol/dm^3 , t = time, D_i = the diffusion coefficient of species i , cm^2/sec , x = distance and ∇ is the gradient operator, $1/\text{cm}$. We notice that the diffusion coefficient is now a function of platelet separation distance, the charge of the platelets, the individual diffusion coefficients and the concentration

Electrical Model

Mass Transfer

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (z_i u_i F c_i \nabla \Phi - D_i \nabla c_i)$$

Electroneutrality

$$\frac{q}{FH} = \langle C_{\text{Cs}} \rangle + \langle C_{\text{Na}} \rangle$$

Result

$$\frac{\partial \langle C_{\text{Cs}} \rangle}{\partial t} = D_{\text{Cs}} \frac{\partial}{\partial x} \left[\frac{D_{\text{Na}} q}{F(D_{\text{Cs}} - D_{\text{Na}}) \langle C_{\text{Cs}} \rangle H + q D_{\text{Na}}} \right] \frac{\partial \langle C_{\text{Cs}} \rangle}{\partial x}$$

Figure 1-5. Ion exclusion model.

gradient of the ion entering the platelets. Thus, the diffusion coefficient is not constant, which is in stark contrast to Eqn (1). The solution to the electrical model presented here is also numerical.

Conclusions

Isolation of high-level nuclear waste is a critical national, and international problem. Underground storage in impermeable geologic media appears promising. To give confidence in the waste-package design, as many barriers to radionuclides escape as feasible should be employed.

We focus on the particular barrier of a montmorillonite-based backfill. Because ion migration rates in compacted backfills are not well understood, we have constructed a radial flow diffusion cell which can measure diffusion rates of any nuclide or mixtures of nuclides, for any proposed backfill under known and varying degrees of compaction. Preliminary diffusion measurements with an uncompacted gel establish that the radial flow-cell is free of external mass transfer resistances and can correctly monitor gel diffusion rates.

Compacted montmorillonite gels apparently consist of macro and micro-porous spatial regions. Ion diffusion rates are influenced by both the amount and configuration of the two porosity regions, along with ion exchange kinetics and electrical exclusion effects.

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2. **TASK 2. INVESTIGATE BACKFILL AND NEAR-FIELD HOST ROCK CHEMICAL INTERACTIONS MECHANISMS** (D. L. Perry, Geosciences Group, Earth Sciences Division, LBL).
- 1) **Surface Studies of Fluoride Ions on Feldspar: Initial Study of Radionuclide Complexation with Fluorides Found in Hanford Basalt.**

1. INTRODUCTION

A considerable interest has been expressed recently in experimental studies simulating dissolution kinetics and mass transfer rates of silicate mineral weathering. One problem which has arisen in such experiments has been the preparation and characterization of silicate surfaces which are representative of natural weathering processes. The work of HOLDREN and BERNER (1979), GRANDSTAFF (1980), and HOLDREN (1981) has shown that a distortion of the surface structure and the creation of fine particles during grinding and crushing of silicates have lead to anomalous experimental results. Previous studies citing parabolic dissolution rates for crystalline silicates may have resulted from such sample preparation effects. One recent approach to solving this problem has been to leach the crushed silicate with hydrofluoric acid (HF) to remove both the distorted surface layer of particles and the adhering microparticulate matter on the surface (HOLDREN and BERNER, 1979). Leaching with HF has also been used by WHITE (1982) to depth profile the surface layers of glassy silicates and by BERNER et al. (1979) to simulate natural dissolution features in pyroxenes and amphiboles.

This type of research is quite vital to the licensing procedure involving a basalt repository in the Grand Ronde basalt formation. The groundwater in that formation has been shown to have an excessively high fluoride content which apparently plays a major role in the transport of

radionuclides such as plutonium. Further studies will be able to demonstrate the role of either chemisorbed or inherent fluoride on basalt or tuff in the retention or migration of these radionuclides in a waste repository.

In an ongoing study of the effects of weathering reactions on silicate surface chemistry, a significant decrease has been noticed in the sorption capacity of minerals treated with HF relative to untreated samples. The question therefore arises as to the possible effects of HF treatment on silicate surfaces, in particular irreversible surface reactions between silicate and fluoride which may influence experimental kinetic studies. The present report describes a preliminary Auger surface study of the potential influence of the HF and HF/H₂SO₄ reactions with new K-feldspar surface layers that result from this chemical interaction. The Auger technique has been coupled with argon ion etching in an attempt to determine the depth of migration of the fluoride ion into the mineral bulk.

II. EXPERIMENTAL

K-feldspar samples were obtained commercially (Wards Natural History Establishment) and gave the following bulk analysis (percent by weight): FeO, 0.010 ± 0.001 ; Al₂O₃, 21.2 ± 0.2 ; CaO, 0.48 ± 0.05 ; Na₂O, 3.7 ± 0.2 ; K₂O, 9.0 ± 0.2 ; MgO, 0.010 ± 0.001 ; SiO₂, 65.0 ± 0.2 ; H₂O, 0.13 ± 0.01 ; total carbon 0.026 ± 0.005 ; total sulfur, 0.003 ± 0.001 ; inorganic carbon, 0.005 ± 0.005 . The samples were then chemically treated in the following two ways that are similar to that of HOLDREN and BERNER (1979). The first sample was reacted with an aqueous 10% HF solution for 20 min with mild stirring. It was removed from the reaction solution and washed several

times with jets of distilled, deionized water. It was then dried in air overnight at approximately 100°C. The second sample was prepared in the same manner except that the original reaction solution was a 50% mixture of aqueous 10% HF and 0.1 N H₂SO₄.

Auger spectra were recorded using a working vacuum chamber pressure of approximately 10⁻⁹ torr on a Physical Electronics Industries Model 590 scanning Auger microprobe. Samples were studied using a primary beam energy of 3 keV and a primary beam current of 0.12 μA; these experimental parameters were found to minimize charging and specimen damage while yielding an acceptable signal-to-noise ratio. The peak-to-peak modulation in the lock-in amplifier was 6 eV throughout.

III. RESULTS AND DISCUSSION

The Auger spectra of K-feldspar "as received", treated with 10% HF, and treated with a 50% mixture of 10% HF/0.1 N H₂SO₄ are shown in Figs. 2.1 and 2.2. Figure 2.1 shows the resulting Auger spectra of the feldspar sample that was treated with only the 10% HF solution. Figure 2.1a is a survey Auger spectrum (0-1000 eV) of the untreated, "as received," feldspar sample. After treatment with hydrofluoric acid, however, several major changes appeared in the spectrum (Fig. 2.1b). The surface concentration of potassium decreased dramatically (see Table 2.1) as shown by the O/K ratio. Sodium, which was almost not detectable on the original surface layer, was then quite visible. (It should be remembered that this chemical treatment removes layers of the feldspar sample; what is being observed spectroscopically, then, is the chemical state of the remaining surface). Additionally,

XBL 821-1639

Figure 2.1. Auger spectra of HF-treated K-feldspar. a) untreated, "as received," b) treated with 10% aqueous HF for 20 min., then washed with distilled, de-ionized water, c) HF-treated sample after 15 sec argon ion sputtering, and d) HF-treated sample after 30 sec argon ion sputtering.

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Figure 2.2. Auger spectra of HF/H₂SO₄-treated K-feldspar. a) untreated, "as received," b) treated with a 50% aqueous mixture of 10% HF and 0.1 N H₂SO₄ for 20 min., then washed with distilled, de-ionized water, c) HF/H₂SO₄-treated sample after 15 sec argon ion sputtering, and d) HF/H₂SO₄-treated sample after 30 sec argon ion sputtering.

Table 2.1. Elemental Auger line intensity ratios for feldspar and acid-treated feldspar

Feldspar Sample		O/Si	O/K	O/Na	Si/Na	Si/F	Al/F	Si/Al
I	Untreated	6.4	3.5	33.3	5.3	*	*	1.8
II	Treated with 10% HF	5.5	23.4	15.6	2.8	1.8	1.1	1.6
III	Treated with 10% HF, ion sputtered for 15 sec	6.5	30.9	14.5	2.2	2.2	1.5	1.5
IV	Treated with 10% HF, ion sputtered for 30 sec	4.3	29.9	14.1	3.2	3.9	1.6	2.4
V	Treated with 10% HF/ 0.1 N H ₂ SO ₄	5.4	14.3	*	*	1.0	0.4	2.5
VI	Treated with 10% HF/ 0.1 N H ₂ SO ₄ , ion sputtered for 15 sec	4.7	14.0	*	*	2.1	1.1	1.9
VII	Treated with 10% HF/ 0.1 N H ₂ SO ₄ , ion sputtered for 30 sec	5.2	7.9	*	*	2.6	1.8	1.5

*One of the elements not detected

the fluoride ion could also be detected on the new surface. Argon ion sputter etching, performed at the rate of 600 Å/min. relative to Ta₂O₅, was then used to depth profile the sample. After 15 sec of sputtering (Fig. 2.1c), the concentration of fluorine had diminished; after 30 sec (Fig. 2.1d), the fluorine concentration was even lower. The sodium content, on the initially HF-etched sample and on the subsequently argon ion-sputtered surface, remained fairly constant.

Similar results were also observed for the sample subjected to the HF/H₂SO₄ (Fig. 2.2). The major difference was the lack of sodium observed on the subsequent spectra of the acid-etched surface, presumably due to exchange in the much stronger acid solution. The fluoride was very evident on this treated surface, too, but the concentration of the fluoride ion, which was initially much greater on the surface of this sample than the feldspar sample treated with 10% HF alone, diminished as the ion-sputtering proceeded into the mineral bulk. In addition to the fluoride ion, sulfur could also be detected (Fig. 2.2b). The sulfur, however, had not migrated into the bulk of the feldspar to as great an extent as the fluorine and was completely removed with only light ion-sputtering (Fig. 2.2c); after 30 sec of sputtering, there was no remaining trace of the initially observed sulfur (Fig. 2.2d). The Al/F intensity ratio for the surface of this sample was also markedly lower than it was for the surface of feldspar treated with HF alone; the Si/F ratio was somewhat similar in going from the feldspar/HF to the feldspar/HF-H₂SO₄ system. Thus, it appeared that in the stronger HF/H₂SO₄ acid, more aluminum was lost from the surface than silicon. This is in agreement with those results reported for dissolution of glassy silicates (WHITE, 1982).

The sample depths being observed in the spectra of the argon ion sputtered samples in this study could not be determined accurately, since sputter-etch profiling rate data for feldspars are not available. The profiling rate for quartz, however, is approximately 30% of the rate of Ta_2O_5 (TAYLOR, private communication), or 180 Å/min for the sputtering rate used here. Assuming a similar rate for feldspars, a 30 sec argon ion bombardment would be equivalent to a penetration of about 90 Å into the mineral bulk. While it should be emphasized that the feldspar value will probably vary somewhat from that of quartz, it would still represent a 45 Å/30 sec value at even half the rate of quartz. When one then considers the 10-15 Å mean free path of the emitted electrons for the 300-800 eV range (ALLEN, 1978), a 30 sec sputtering period would represent a roughly 60 Å depth that is being observed with respect to the fluorine Auger signal. It must also be remembered that elemental sputtering yields are different; this can result in altered surface layers enriched in elements that exhibit low sputtering yields (HOFMAN, 1980). In any case, however, the sputtering rate for feldspar will have to be known with certainty before the depth of penetration for the fluoride ion in this reaction system can be accurately determined.

In an attempt to determine the nature of the sulfur and fluorine species formed on the feldspar surface, x-ray photoelectron spectroscopy has also been used. In the case of sulfur, the sulfate anion is readily identified on samples that had been subjected to 1.0 M sulfuric acid in order to increase the surface sulfur concentration. Spectra of the 10% HF/1.0 M H_2SO_4 - treated feldspar, however, reveal that the species

involving sulfur on the surface is much more complex; the sulfur-2p photoelectron line indicates at least two sulfur species to be present.

The fluorine-1s line spectrum representing the surface of feldspar treated with 10% HF/1.0 M H_2SO_4 is shown in Fig. 2.3. Clearly, the spectrum indicates more than one species to be present. Two shoulders at 686.6 and 687.9 eV are present, along with the main photoelectron line centered at 687.2 eV. Additionally, the linewidth (the full width at half maximum, or FWHM) is 4.0 eV; this is considerably wider than simple fluoride salts (compare this width, for example to that of ~2.0-2.3 eV for LiF). While multiple chemical species may indeed be responsible for these peaks and the broad line, preferential surface charging may also be responsible. Further research is thus warranted.

Clearly such HF treatments complex the surface in a manner that might be difficult to reverse; the extent of this chemical alteration is a function of the time of surface treatment and the concentration of the acid system being used. It is therefore suggested that such a treatment either not be applied to studies involving sorption measurements on silicate mineral surfaces or that this chemical treatment be extensively studied in order to thoroughly understand its effect on silicate mineral dissolution kinetics.

XBL 827-2318

Fig. 2.3 The fluorine 1s photoelectron spectrum of feldspar treated with HF/H₂SO₄

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2) Surface Studies of Cobalt on Feldspar: A Model System for the Chemisorption of a Variable Oxidation State Migrating Radionuclide.

I. INTRODUCTION

Recent studies have shown that two important processes which affect radionuclide migration in natural rock-water systems are adsorption on minerals and metal oxides and complexation with organic ligands. Manganese oxides, for example, have been shown to be associated with mobile radionuclides such as californium, americium, cobalt, and plutonium^{1,2}. Several other researchers have also documented this relationship between trace metals and metal scavenging oxide minerals, particularly those of manganese and iron. Tamura³ has shown iron oxide minerals (specifically, limonite) to be important in strontium retention in soils. One worker⁴ has demonstrated the manganese oxide-controlled solubility of lead in rivers. Uranium has been shown to adsorb on iron oxides such as hematite.⁵ Although several investigations of trace metal adsorption by hydrous manganese oxides have been made,⁶ the actual mechanisms which govern the adsorption process are not well understood;² adsorption of metal ions on iron and other metal oxides has not been completely explained, either. Very few of these systems have been rigorously studied using state-of-the-art spectroscopic techniques.

Another mechanism which has been proved to be operable in radionuclide ion migration is that of complexation with organic ligands. Recent studies⁷ have shown radioactive isotopes such as cobalt mobilize as complexes of ethylenediaminetetraacetic acid (EDTA) that has been introduced into radioactive disposal sites by decontamination procedures. Other naturally

occurring chelating ligands such as humic and fulvic acids also contribute to migration.⁸ Several other studies have also been reported related to the adsorption and desorption of other radionuclides, including cesium,⁹ strontium,¹⁰ and cobalt.¹¹

Although many descriptions exist of the phenomena of mineral and metal oxide adsorption and organic complexation of radionuclides, there is very little understanding of the bonding characteristics and surface chemical processes that occur between the organic ligands, metal ions, and minerals. In order for radionuclides migration to occur by these mechanisms, there must first be an interaction between the metals ions and the mineral/metal oxide substrate with subsequent complexation (adsorption or metal ion exchange involving lattice sites, for example). A similar reaction process between metal ions and organic compounds must also occur for the mechanism of migration enhancement via metal ion/organic complexation to be a viable factor in transport processes.

The phenomena of adsorption, complexation, and migration between metal ions and solid geological substrates have been shown to be important in a number of other geological processes, too. It is postulated, for example, that humic acids (which represent a major portion of carbonaceous rocks) act as cation exchangers and are responsible for the fixation of uranium¹²⁻¹⁶ and other trace elements.¹⁷⁻²⁰ Strontium-87 diffusion plays an important role in the re-homogenization in minerals and rock after a thermal event; this allows the determination of the isochron ages and the changed values of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Several studies of mineral ages in the region of well-defined igneous contact of younger intrusives into older

formations have been conducted.²¹⁻²³ Surface/lattice metal ion concentrations of feldspars are also important in the study of the dissolution kinetics of these minerals.^{24,25}

The necessity of studying the solution and surface chemistry of cobalt on geological surfaces as it relates to licensing is very high. While cobalt has a relatively short half-life, it is an important radionuclide to study for several reasons. First, it is a documented migrating radionuclide as shown by previous studies^{1,2}, even though it has a short half-life, the long term effects of a metal radionuclide such as this one on the biosphere in general must be addressed. Second, cobalt is a good example of a variable oxidation state (+2,3) radionuclide that has been shown to have a variable chemistry with geological material under elevated temperature conditions such as those found in a repository set in Hanford basalt. Finally, the mechanisms for the migration of cobalt from a radioactive waste repository and through the soil is similar to that for plutonium, americium, and californium.^{1,2}

II. EXPERIMENTAL

X-ray photoelectron spectra were obtained using a Physical Electronics Model 560 ESCA SAM spectrometer equipped with a Mg K α (1253.6 eV) x-ray source and a double pass cylindrical mirror analyzer. The energy scale of the instrument was calibrated against the gold-4f $_{7/2}$ peak, assuming a value of 83.8 eV. All photoelectron lines were referenced to the adventitious carbon-1s line at 284.6 eV. The main chamber was kept at a pressure of 10⁻⁸-10⁻⁹ torr during the acquisition of data. Spectra were recorded

using analyzer band pass energies of either 25 or 50 eV; these energies were found to give adequate spectral resolution within a reasonable collection time.

Feldspar samples were prepared by reacting them with a 0.1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution in polyethylene bottles. They were then washed with cold distilled, de-ionized water to remove the remaining original solution present and any loosely bound material. The samples were air dried at $\sim 100^\circ\text{C}$ overnight and then mounted on aluminum backed tape as thin wafers before placing them in the chamber for analyses.

III. RESULTS AND DISCUSSION

Recent studies in this laboratory have concentrated on the initial studies of the reaction of metal ions such as iron, uranium, tin, and cobalt on K-feldspar, a constituent of granitic, basaltic, and tuffaceous rock. Chemisorption (or reaction to form identifiable, isolable products) of these metal ions, all important fission products, actinides, and radionuclides that have been documented as having migrated from nuclear waste repositories most assuredly will play some role in the transport mechanism of these radionuclides at some pH.

Figure 2.4 shows the spectrum of cobalt (II) that has been reacted with K-feldspar. The cobalt was reacted with feldspar in the form of a 0.1 M CoCl_2 aqueous solution, the reaction being effected at an initial pH of 8.0 at 95°C for 312 hours. The spectrum of the cobalt-2p photoelectron lines (both the $2p_{1/2}$ and $2p_{3/2}$ lines, resulting from spin-orbit coupling, are shown) represents the resulting species of cobalt that has been

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Fig. 2.4 The cobalt 2- photoelectron spectrum of cobalt reacted with feldspar

formed on the surface. Several conclusions can be drawn from this spectrum as well as other spectra of the feldspar surface.

- 1) One of the predominant species present is cobalt (II); this is confirmed by the presence of the satellites to the high binding energy side of the main photoelectron peaks.²⁶ These lines do not appear in the cobalt-2p spectra of compounds of cobalt (III) that are diamagnetic (such as CoOOH).
- 2) There is a small amount of chlorine present on the surface, either as a contaminant from the original salt or as a very minor new complex; preliminary Auger data show it to be unreacted CoCl_2 .
- 3) One product is the complex Co(OH)_2 . The separation of 16.1 eV for the $2p_{3/2}$ - $2p_{1/2}$ spin orbit lines is virtually identical with that previously reported for this compound.²⁶ The oxygen-1s line value of 531.8 eV is in reasonable agreement with 531.2 reported for Co(OH)_2 ,²⁷ also, it is identical with those values reported for a cobalt hydroxide species²⁸ and other transition metal hydroxide species.^{28,29} Visual examinations of some feldspar samples that have been reacted with cobalt (II) have also resulted in the observation of colored species that are probably one form of Co(OH)_2 . Additionally, the satellite observed in Fig. 2.4 is located 5.5 eV to the high binding energy side of the main photoelectron line; this is identical to the value reported²⁷ for Co(OH)_2 .
- 4) Shoulders on the high binding energy side of the main peaks would tend to indicate multiple species. This is also possibly due to charging on the surface of what is basically an insulating sample.

In Fig. 2.5, however, one sees a different situation. In this example, the feldspar has again been reacted with cobalt (II); the initial pH, however, was 5.0. Several changes in this spectrum from the spectrum shown in Fig. 2.4 are evident, along with changes in other spectral parameters. Taken together, these changes indicate a change in the chemistry of the feldspar surface as a function of the pH.

- 1) Instead of 16.1 eV, the spin-orbit splitting is 15.3 eV; this represents a change in the electronic state of the principal cobalt (II) species.
- 2) The oxygen-1s binding energy for the surface is 532.4 eV; this value is indicative of adsorbed water.²⁹ One other possibility is a hydrated cobalt hydroxide, since hydrated metal oxides/hydroxides exhibit oxygen-1s binding energy values in this range.³⁰
- 3) Small amounts of chlorine were also observed on the surface of this sample; in Fig. 2.6, this chlorine is shown to be associated with segregated cobalt on the surface. Thus, even under these reaction conditions, some of the original Co(II) is un-hydrolyzed.
- 4) The amount of "charging" observed for this sample was different from the one depicted in Fig. 2.4: 3.6 eV for this sample vs. 5.0 eV for the sample which was reacted at an initial pH of 8.0. This, too, implies two distinctly different surface chemistries.

When one then conducts the reaction of 0.1M CoCl_2 with the feldspar at 250°C for 48 hours, similar results are observed. Figure 2.7 shows the magnified (500x) surface of a feldspar sample that has been treated in this manner. The morphological surface characteristics of the feldspar have been

XBL 827-2316

Fig. 2.5 The cobalt 2p photoelectron spectrum of cobalt reacted with feldspar

X008 820-9594

Figure 2.6.

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Figure 2.7

totally changed; instead, one sees a ring of the complexed cobalt on the surface. Again, chloride can be seen on the mineral, also. While cobalt seems to be uniformly spread over the mineral, this is not the case with chlorine. As can be seen in Figure 2.7, segregations of both chlorine and aluminum are identical, possibly, indicating either a reaction of the chloride ion with the mineral aluminum or a complexation of the CoCl_2 with the aluminum on the surface.

Even less rigorous reaction conditions than those of elevated temperature described above result in the chemisorption of cobalt on the feldspar. Figure 2.8 represents the x-ray photoelectron survey scan (0-1000 eV) of the surface of feldspar that has been reacted at pH = 10 with CoCl_2 (0.1 M) for only one hour at 25°C. Clearly, the initial CoCl_2 has been chemisorbed even under these relatively mild conditions. Not only has the cobalt reacted with the surface, but it has also migrated a rather substantial distance into the bulk. Figure 2.9 depicts the atomic percentage concentration of various elements in the bulk of the feldspar from this reaction as a function of sputtering time (using argon ion sputtering). Assuming a sputtering rate of 30 Å/min., that of quartz, Fig. 2.9 would indicate the penetration of the Co^{2+} and Cl^- ions to be ~90 Å. One alternate explanation for these data is that the reaction product formed at the surface has formed a ring of this thickness, and one is merely profiling through this ring. This would seem unlikely in view of the mild reaction conditions. Also, it would not be expected that this ring would not be as silicon rich as the species shown here: the silicon atomic concentration, not shown here, is in the 60-70% range.

Figure 2.8.

XBL 6210-2583

Figure 2.9.

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3) Infrared and X-Ray Photoelectron Evidence for a Cation Stabilized Hydroxy-Bridged Uranyl Species, $[(\text{UO}_2^{2+})_2(\text{OH})_2]^{2+}$.

This laboratory recently reported the synthesis and structure of the uranium dimer complex, di- μ -aquo-bis(dioxobis(nitrato)uranium(VI)) di-imidazole [1] (Fig. 2-10). Although the hydrogen atoms between the imidazole molecules and the bridging oxygen atom species were not located during the least-squares refinement of the crystal structure, they were assumed to be associated with the oxygen to form a water bridge; subsequent additional attempts using electron density difference maps to find the hydrogen atoms were also unsuccessful. This assumption of the hydrogen atoms being part of water molecules was made, because previous structurally documented hydrolysis products of uranium [2] were unstable outside the reaction medium in which they were formed. Complex (I) is stable with respect to both air and moisture and can be stored without special precautions. This report details experimental infrared and x-ray photoelectron data that would indicate the hydrogen atoms could instead be localized on the "pyridine" nitrogen of the imidazole, thus affording a bridged hydroxy uranyl complex that is stabilized by imidazolium cations that are adjacent to hydroxy ligand bridges.

Experimental

The same group of crystals used for the x-ray crystallographic structure work [1] was used for the present study. Infrared spectra were taken as Nujol mulls between KBr plates using a Perkin-Elmer Model 283 infrared spectrophotometer, and x-ray photoelectron spectra were obtained on a McPherson Model 36 spectrometer using Mg K_α (1253.6 eV) radiation. The

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photoelectron spectra were recorded as previously reported [3], assigning the contaminant principal carbon 1s photoelectron line a value of 285.0 eV. Samples were ground to fine powders and applied to double-sided Scotch brand sticky tape before being placed in the vacuum chamber for analysis. Samples were checked visually for decomposition after spectra were taken, but none was detected. The spectra were also time-independent, indicating a lack of decomposition of the samples in the x-ray beam.

Results and Discussion

As reported earlier [1], the dimeric compound (Fig. 2-10) consists of two uranyl ion centers that are joined by either aquo (as originally postulated) or hydroxy bridging ligands. The two uranium atoms are 3.93 Å apart. If the bridges are indeed water molecules, the complex is a co-ordination isomer of uranyl nitrate hexahydrate. In uranyl nitrate hexahydrate, the two coordinated terminal water molecules are trans to each other [4]; the two bidentate nitrate anions are also trans to each other. Compound I, however, presents a case in which the nitrate ligands are cis to each other, while the water ligands are also cis to each other and bridging (Fig. 2-10).

Two possibilities exist for the position of the hydrogen atoms between the imidazole molecules and the bridging oxygen species. In Fig. 2-11(2), the hydrogen atoms are associated with the bridging oxygen group; this would yield a bridging aquo complex with the water molecule hydrogen bonded to the imidazole (the originally postulated complex [1]). Fig. 2-11(1), however, shows an alternate situation in which the hydrogen atoms are associated with the "pyridine" ring nitrogens of the nearby imidazole

Figure 2-11. Two possible bonding modes involving the imidazole-oxygen bridge.

molecules. This results in a hydroxy-bridged uranyl complex in which anionic OH^- bridges are presumably stabilized by imidazolium cations.

There is substantial, although not unequivocal, evidence for the bonding scheme depicted in Fig. 2-11(1) in the infrared (Fig. 2-12) and x-ray photoelectron data (Table I), coupled with the previously reported infrared, luminescence, and structural results [1]. The arguments for this case are as follows:

- a) The two uranium-oxygen bonds, $\text{U-O}(6)$ (Fig. 2-10) are 2.35(1) and 2.37(1) Å. The corresponding bond strengths, calculated according to Brown [5], are 0.57 and 0.55 valence units, respectively [6]. The sum, 1.02 v.u., is extremely large for an H_2O molecule; however, this value would be in good agreement with a bridging hydroxide group.
- b) The nitrogen-carbon bond lengths (the bonds involving both ring nitrogen atoms with adjacent carbon atoms) in complex (I) are equivalent [1], indicating that both nitrogen atoms are similar in their bonding. This is the situation in the imidazolium- $\text{UO}_2\text{Cl}_4^{2-}$ complex [7].
- c) The bond distances and angles involved in the uranium-oxygen-uranium bridge in complex (I) are virtually identical to those reported for the $[(\text{NO}_3)_2\text{UO}_2(\text{OH})_2\text{UO}_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ [8] and $\text{Cl}(\text{H}_2\text{O})_3\text{UO}_2(\text{OH})_2\text{UO}_2(\text{H}_2\text{O})_3\text{Cl}$ [2] hydroxy-bridged dimers. The uranium-uranium "bond" lengths in the complexes are also similar, being 3.927, 3.939, and 3.944 Å, respectively.

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Figure 2-12. Infrared spectrum of Complex (I).

- d) The initially reported infrared spectrum of (I) revealed two N-H stretching bands at 3350 and 3160 cm^{-1} . While both bands are in the region reported for other complexes of imidazole with transition metal ions [9], the 3350 cm^{-1} band has also been attributed to a hydroxy-bridged copper complex [10]. Another assigned OH-bridge band at 3480 cm^{-1} in the same copper system also appears in the spectrum of (I) (Fig. 2-12). A further study of the spectrum revealed additional bands at 355, 426, and 1090 cm^{-1} that are almost identical to those previously reported for hydroxy-bridged cobalt [11] and copper [12] complexes. Band sets involving bands at 3580, 3520, 3100 and 3400, 3220 cm^{-1} which have been reported [13] for water ligands in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, respectively, were absent.
- e) The oxygen-1s x-ray photoelectron spectrum (Table I) of complex (I) consisted of a peak that could be de-convoluted into two peaks with binding energies of 533.1 and 531.6 eV. A similar doublet could also be resolved for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the binding energies being 533.4 and 531.8 eV (compared to a single, "averaged" value of 533.3 eV that has been published [14] for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Accordingly, the 533.1 eV peak in (I) can be assigned as resulting from the NO_3^- oxygens; this is in excellent agreement with reported values for other nitrates [15]. The 531.6 eV peak in (I), however, can easily be assigned to an OH^- functional group. It is in good agreement with the values of 531.9-532.2 eV observed for the oxygen-1s spectra of NaOH-hydrolyzed uranyl salts [16]; also, it

Table I. X-Ray Photoelectron Data for Complex (I) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Compound	<u>Binding energies^{a,b} peak widths, and intensity ratios</u>		
	O_{1s}	FWHM ^c	Intensity ratio
Complex (I)	533.1	2.4	2
	531.6	2.6	1
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	533.4	2.3	2
	531.8	2.3	1

^aBinding energies and peak widths reported in electron volts, eV.

^bCalibrated against the carbon 1s line taken as 285.0 eV.

^cFull width at half maximum, in eV.

is quite similar to the 531.5 eV value reported for the alkoxide oxygen in uranyl alkoxide compounds [3]. Values of $\sim 531.2 - 531.8$ eV have been observed for several other metal hydroxide compounds [17,18]. The intensity ratios reported in Table I for these lines are also in excellent agreement with these assignments.

If the bridging species are in fact hydroxy groups rather than water groups, this would be one possible explanation for the difference in the luminescence spectra of (I) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ which were reported by Brittain and Perry [19]. These studies showed that while the emission spectra for the two compounds are the same at room temperature, significant differences are observed on cooling to 77°K; vibronic structure is observed for (I), but none is evident for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The existence of this hydroxy bridge, however, would still not unequivocally exclude three other possibilities for these differences: weak coupling of the two UO_2^{2+} species with the imidazole molecule in (I), coupling of the lattice waters in $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the central UO_2^{2+} ion, or interaction of the two uranyl centers with each other in (I).

The possibility of an imidazolium-stabilized hydroxy bridge in (I) represents a potentially new approach for the study of solid-state uranyl hydrolysis products that are stable outside the reaction solution in which they are formed. The coordinated ligands about the uranyl ions could be chosen (sulfates, acetates, etc., or, as in the present case, nitrates), then mild hydrolysis of that compound be effected using imidazole as the base. One restriction to this approach might be that the compound being hydrolyzed must also contain water molecules in two coordination sites (or

have two vacant coordination sites) which can then be replaced with OH^- groups to form the bridges in the dimers. In any case, complex (1) serves quite well as a spectroscopic model for a uranyl hydrolysis dimer of the nitrate salt; this is irrespective of which representation in Figure 2-11 is the correct one.

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4) Detection of Uranium in Aqueous Samples Using X-Ray Photoelectron Spectroscopy: A Method of Detecting Uranium in Groundwater Samples from a Breached Repository

Introduction

Over the last several years, several advanced analytical techniques have been used by researchers for the detection of uranium in natural geologic systems. The direct measurement of uranium in surface and groundwaters has been reported using atomic absorption spectroscopy (1), atomic emission (2), and fluorescence (3); enrichment or separation techniques such as ion-exchange, precipitation, and extraction have also been combined with absorption spectroscopy (4), neutron counting (5), and x-ray fluorescence to make these determinations. Ultratrace levels of uranium in aqueous samples have been detected using a combined coprecipitation/laser-induced fluorescence technique (6). Some studies have been directed at comparing multiple approaches on the samples in order to check the degree of experimental agreement (7).

Techniques for the detection of uranium at relatively high concentrations are highly important, since uranium and other radionuclide concentrations in intruding groundwater will be the highest in the near field region of the repository, the first area where containment of the radioactive species would be most desirable. The first line of warning and subsequent defense in a licensed repository against any such breach would be the rapid and accurate detection of radionuclides that would migrate from the repository by way of a groundwater flow. A technique should also be versatile enough so that it can be used to detect as many radionuclides as possible in the same sample.

Several methods for the qualitative analysis of uranium in aqueous samples involved a preconcentration of the uranium in an inert matrix followed by the use of some spectroscopic technique to detect it. One scheme developed here involves the coprecipitation of uranium into barium fluoride, BaF_2 ; the precipitate is then studied using x-ray photoelectron spectroscopy (XPS).

The uranium samples are prepared in the following manner. All glassware is prewashed with dilute nitric acid followed by repeated rinsing with quartz-distilled water in order to remove any possible contaminant metal ions on the glass surfaces. One milliliter of a $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution of appropriate concentration is added to a 250-mL beaker with 5 mL of 1 M $\text{Ba}(\text{NO}_3)_2$ and 14 mL of distilled, deionized water. Thirty milliliters of a 0.3 M NH_4F solution is then added dropwise with stirring using a magnetic stirring bar over a period of 55-60 s, giving a final solution volume of 50 mL. The concentration of uranium is expressed with respect to the final solution volume prior to precipitation. The above solutions are then covered with "Parafilm" and allowed to precipitate and settle for one day. The BaF_2 precipitates are centrifuged and dried in the centrifuge tubes at 105°C for 2 h. The precipitate is removed from walls of the centrifuge tubes with a stainless steel spatula and crushed. The samples are fired in porcelain crucibles for 3 h, usually at 800°C (Lindberg Model 51333 box furnace accurate to $\pm 1^\circ\text{C}$), allowed to cool to room temperature in the open air, and crushed again in a vibrating ball mill (a mortar and pestle were initially employed, but the vibrating ball mill produces a more homogeneous powdered sample and better reproducibility in the spectra).

The BaF_2 samples are then pressed into 200-mg pellets 1 cm in diameter and 1 mm thick.

X-ray photoelectron spectra are recorded on a McPherson Model 36 spectrometer using Mg , K_α radiation (1253.6 eV). Samples are checked visually for decomposition after each set of spectra is collected, but none has been detected. The stability of the samples to radiation has been further corroborated by the spectra being time-independent.

Figure 2-13 shows a spectrum of the uranium $4f_{7/2}$, $5/2$ lines of uranium in BaF_2 that was precipitated from an aqueous sample that was 10^{-4} in uranium. This method can detect uranium at or above this concentration level with no interference problems from other ions that can lead to quenching problems such as those involved in fluorescence techniques. Trace metal ions found in groundwater, for example, will not interfere with the x-ray photoelectron emission from the uranium $4f$ level after the uranium has been coprecipitated into the BaF_2 matrix. The variation of the calcination temperature of the pellets also seemed to have no effect on the photoemission properties.

The binding energies (calibrated against the adventitious carbon $1s$ photoelectron line which was assigned a value of 284.6 eV) for the uranium $4f_{7/2}$, $5/2$ lines as 379.1 and 391.6 eV, respectively; the values for the barium $3d_{5/2}$, $3/2$ levels are 779.4 and 793.7 eV, respectively. The barium values are identical to those reported for BaF_2 by Wagner (8), while the binding energy for uranium is somewhat low for uranium (VI) in comparison to those values reported by Perry (9) and other workers (10, 11).

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Figure 2-13. X-ray photoelectron spectrum of uranium in BaF₂. The barium fluoride was precipitated from 10⁻⁴ molar UO₂(NO₃)₂·6H₂O.

These techniques need not necessarily be restricted to only uranium but can also probably be used to detect other radionuclides that can be coprecipitated from aqueous solutions. Thorium, for example, has been shown (12) to coprecipitate with CaF_2 , as have plutonium and americium (13). Since BaF_2 also exhibits a fluorite (CaF_2) lattice structure and is thus isostructural, it would seem logical that ions that can be occluded in one of the salts can also be introduced into the other. This has already been shown to be true for uranium (6).

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5) Spectroscopic Studies of Uranium Hydrolysis Products Found Under Repository Conditions: Uranyl Hydroxides

INTRODUCTION

The solid state hydrolysis products of uranium have been the subject of several studies. The compounds, formed by the hydrolysis of uranyl salts by bases such as sodium and ammonium hydroxide, exhibit variable chemical compositions that are heavily dependent on the method of preparation; parameters which have been shown to affect these compositions include aging of the precipitates under carefully controlled conditions approaching equilibrium (1), temperature (2) or pressure (3) experienced by several forms of the solid hydrolysis precipitates, and the hydroxide/uranium ratio used (1). As a result, not only are different chemical compositions formulated for these compounds (among them, $\text{Na}_2\text{O} \cdot 8\text{UO}_3$ (4), $\text{Na}_2\text{U}_7\text{O}_{22}$ ("uranates") (1), $\text{U}_3\text{O}_8(\text{OH})_2$ (5), and $3\text{UO}_3 \cdot \text{NH}_3 \cdot 5\text{H}_2\text{O}$ (6)), but also mixtures of various pure compounds and contaminated compounds almost unequivocally result in these precipitates in many cases. The chemistry of these compounds has been discussed extensively in a review (7), however, and they have been structurally documented as being uranyl hydroxides; uranium oxides have also been shown to be present in the mixture of hydrolysis products (5).

The present study is one which further attempts to obtain a clearer and more complete picture of the chemistry of these compounds. Because of the rather large number of compounds and compound mixtures produced by varying the preparative procedure, two standard sets of products have been prepared and used for all measurements for the present study. First, two different concentrations of the uranyl ion solution being hydrolyzed were used in order to determine if there is any initial uranyl ion solution con-

centration dependence on the final product. Second, variable counterions such as chloride, nitrate, and acetate were used in preparing the uranyl solutions at the two different concentrations so as to check for an anion dependency. The same hydrolysis precipitate for a given synthetic route was used to perform all analyses and spectroscopic studies in order that data for a particular preparation were comparable to those data for other different synthetic routes. All isolable products have been characterized by elemental analyses, infrared spectroscopy, thermolysis mass spectrometry, x-ray photoelectron spectroscopy, scanning electron microscopy, and luminescence spectroscopy.

EXPERIMENTAL

All hydrolysis products were synthesized by the slow, dropwise addition of 1.0 M aqueous solution of sodium or ammonium hydroxide to a vigorously stirred solution of either a 0.1 or 1.0 M solution of uranyl chloride, nitrate, or acetate. The addition of base was continued until all precipitation had ceased. The samples were then filtered on a Buchner funnel, washed with cold distilled, de-ionized water in order to remove any unreacted base or uranyl salt, and allowed to air dry on the filter bed. Elemental analyses were performed by the microanalytical laboratory of the chemistry department at the University of California, Berkeley. The analytical data for the series of compounds used in the present studies were as follows:

Sample A [Hydrolysis of 0.1 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 71.1; Na, 3.14; C, 0.03; H, 0.97. % U/% Na = 22.64.

Sample B [Hydrolysis of 0.1 M $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 73.1; Na, 3.66; C, 0.04; H, 0.04; N, 0.91. % U/% Na = 19.97.

Sample C [Hydrolysis of 0.1 M $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 70.6; Na, 4.38; C, 0.03; H, 0.97. % U/% Na = 16.11.

Sample D [Hydrolysis of 1.0 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 72.2; Na, 4.32; C, 0.05; H, 0.98. % U/% Na = 16.71.

Sample E [Hydrolysis of 1.0 M $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 71.4; Na, 3.48; C, 0.04; H, 0.97. % U/% Na = 20.52.

Sample F [Hydrolysis of 1.0 M $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 1.0 M NaOH].

U, 72.3; Na, 3.56; C, 0.03; H, 0.92. % U/% Na = 20.31.

Sample G [Hydrolysis of 0.1 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1.0 M NH_4OH].

U, 72.9; C, 0.05; N, 1.38; H, 1.33. % U/% N = 52.83.

Sample H [Hydrolysis of 0.1 M $\text{UO}_2(\text{Cl}_2 \cdot 3\text{H}_2\text{O})$ with 1.0 M NH_4OH].

U, 71.2; C, 0.04; N, 1.35; H, 1.36. % U/% N = 52.74.

Sample I [Hydrolysis of 0.1 M $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 1.0 M NH_4OH].

U, 71.7; C, 0.06; N, 1.35; H, 1.37. % U/% N = 53.11.

Infrared spectra were obtained as both Nujol mulls and KBr pellets on a Perkin-Elmer Model 283 infrared spectrometer. Scanning electron microscopy data were taken using an AMR Model 1000 scanning electron microscope equipped with an energy dispersive x-ray spectrometer. A

McPherson Model 36 spectrometer using Mg K_{α} radiation (1253.6 eV) was used to collect x-ray photoelectron spectra. The photoelectron peaks were fitted using a standard least-squares fitting program, and all binding energies were charge referenced to the contaminant (adventitious) carbon 1s line using a value of C 1s = 284.6 eV. Finely powdered samples were dusted on Scotch-brand tape and checked visually for decomposition after each set of spectra was obtained, but none was detected. The stability of the samples to radiation was further corroborated by the spectra being time-independent within the time frame for collecting data.

All luminescence spectra were obtained on a high-resolution spectrometer. The samples were excited by the 325 nm output (10 mW power) of a He-Cd laser (Liconix), with all the plasma lines being filtered out by a UV-transmitting filter. The emission was collected at 90° to the exciting beam and analyzed by a one meter grating monochromator (Spex Model 1704). All data were obtained at 5 Å resolution, and further increases in resolving power of the system did not yield further improvement in the emission features. The luminescence was finally detected by a cooled (-20 °C) photomultiplier tube (EMI Model 9558, S-20 response), the output current converted to voltage on the Spex digital photometer, and displayed on a strip-chart recorder.

None of the uranyl hydrolysis products exhibited luminescence at room temperature, but cooling the samples to 77 °K did lead to the observation of measurable emission in the green region of the spectrum. Further cooling of the samples to 10 °K in a closed-cycle refrigerator system (Lake Shore Cryotronics Model LTS-21) provided the maximum luminescence quantum

yields. The samples were found to be quite photosensitive; accordingly, each determination of any spectroscopic property was repeated a minimum of three times on a fresh sample. The photodecomposition proved to be most efficient in the high vacuum of the refrigerator system, and a comparison of the photodecomposed material with known uranium oxides indicated that the photoreaction was probably a dehydration of the hydrolysis product.

Measurements of the emission lifetimes of the uranyl hydrolysis products were obtained by exciting the samples with a pulsed UV source, converting the photomultiplier current to voltage via a 200 K load resistor, and then photographing the decay curve off a storage oscilloscope. The source of UV pulses was a nitrogen laser (200 kW output in 250 psec at 37 nm), and the decay curves were processed to yield the luminescence decay time with standard least-squares analysis. The lifetime of each peak in the emission spectrum was obtained separately and found to be identical to within experiments error for a given compound. In no case was it found that the decay curves contained anything other than a simple exponential decay.

RESULTS AND DISCUSSION

As expected, the complexes that resulted from the hydrolysis of the parent uranyl salts were of variable composition. Elemental analyses showed the precipitates to contain variable amounts of sodium or ammonium cations, while the thermolysis of the solids (monitored by mass spectrometry) also showed a variable water content for each of the samples. The elemental analyses substantiated a bulk chemical formulation of the type $\text{UO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$

and/or $\text{UO}_3 \cdot x\text{H}_2\text{O}$ for the NaOH-effected hydrolysis products, with small amounts of sodium ions being occluded in the lattice. X-ray photoelectron, infrared and luminescence data (discussed below) also supported formulas of this type.

The analytical data for the NH_4OH -effected hydrolysis products are consistent with the previously reported complex of stoichiometry (8) $3\text{UO}_3 \cdot \text{NH}_3 \cdot 5\text{H}_2\text{O}$ (6); again, however, this principal product was also found to be $\text{UO}_2(\text{OH})_2$ contaminated with the ammonium cation, and the amount of water varied from sample to sample.

All attempts to prepare one synthetically pure sample of uranyl hydroxide product which was contaminant-free were unsuccessful. All NaOH--hydrolysis compounds contained approximately 3-5% sodium, regardless of the rate at which NaOH was added to the solution of the parent salt, the concentration of the parent salt, or the anionic counterion. The only exception to this was the hydrolysis of $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, in which the final hydrolysis product also always contained traces (1% or less) of the chloride ion. An examination of infrared spectra, wet chemical analyses, and other analytical and spectroscopic data failed to show any acetate or nitrate species after hydrolysis. The most consistently reproducible analytical results were obtained for the NH_4OH -effected compound; the hydrogen and nitrogen analyses, for example, were virtually identical for all three samples studied here. Also, the x-ray photoelectron and luminescence spectral data discussed below would be consistent with minor amounts of other hydrolysis products being present as contaminants.

As a result of the lack of exact reproducibility in preparing the samples, a set of samples was prepared in which three parameters were varied:

initial concentration of the uranyl ion solution, the counterion used with the uranyl ion, and the base used to hydrolyze the uranyl ion. These samples were then used for the present study in which all spectroscopic studies were conducted on the same preparative batch of that sample. Unlike many previous studies involving this class of compounds, data taken using these techniques could then be directly compared to one another.

X-Ray Photoelectron Spectroscopy

Uranium 4f lines

Values of the binding energies for the series of hydrated uranyl hydroxides are given in Table I, along with the binding energies of the parent uranyl salts. The oxygen 1s lines are reported as well as the uranium 4f spin-orbit doublet. The values recorded for $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are virtually identical to those reported by Chadwick (10), while the uranium 4f lines for $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ exhibit a binding energy of approximately 1.5 eV higher than that previously reported for this compound. While there is no apparent explanation for this observation, typical sample reactions such as photoreduction that often occur under an x-ray beam can be ruled out due to the positive increase in the binding energy. Again, the sample was of the highest analytical purity, and no other visible or spectral evidence exists that the sample decomposed during the course of the experiment. The spectrum of $\text{UO}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ reported here has not been previously reported, but the values for the principal photoelectron lines are in good agreement with those expected for a $\text{UO}_2^{2+}/\text{Cl}^-$ salt. The chlorine 2p binding energy (198.8 eV) is typical for a chloride ion with a divalent cation (11, 12).

The maximum 4f binding energies for the products exhibit a narrow range of values of 381.5-381.8 eV. These values agree quite well with the ones reported by Teterin et al. (13) (382.0 eV) and Allen et al. (14) (381.7 eV) for uranium(VI) species such as $\gamma\text{-UO}_3$ (15). In light of the rather marked effect on binding energies of the uranium 4f level that a variation in the water content of uranium-oxygen systems such as will exhibit (16) and the large variation of hydration for this oxide (17) and the present uranyl hydroxides, this small range of only 0.3 eV is somewhat surprising.

Another characteristic of the uranium 4f spectrum which is helpful in establishing the electronic character of the central uranium species is that of the satellite structure found on the high binding energy side of the principal photoelectron lines. Pireaux and co-workers (18) have shown that these satellites (due to charge transfer from the ligand oxygen-uranium bonding band, of dominant oxygen 2p character, to the empty uranium 5f level (19,20)) can be used to "fingerprint" the oxidation state of uranium present in a number of oxides. In the present set of hydrolysis products, this area of the spectra of the uranium 4f_{7/2} region consists of either poorly defined or weak peaks for most of the samples which could not be fitted by the least-squares program (non-convergence). Two samples, however, B and E, exhibited pronounced doublets in this area. The spectrum of B contains peaks at 3.8 and 9.9 eV, while the spectrum of E contains peaks at 3.9 and 9.6 eV (Fig. 2-14). These values are quite similar to those reported by Perry (21), the values in that study being ~3.7 and ~9.8 eV for those structurally documented uranyl compounds.

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Figure 2-14. The uranium $4f_{5/2}$ photoelectron lines and associated satellite structure of 1) Sample E (hydrolysis of 1.0M $UO_2Cl_2 \cdot 3H_2O$ with NaOH) and 2) Sample B (hydrolysis of 0.1M $UO_2Cl_2 \cdot 3H_2O$ with NaOH).

The satellite features shown in Fig. 2-14 would be in reasonable agreement with a hydrated uranyl hydroxide if the assumption were made that varying in the coordination sphere of the dioxouranium(VI) metal ion center could shift the satellite positions. The effect on these satellites of varying the amounts of contaminants such as sodium or ammonium ions in a systematic fashion is unknown. Unfortunately, there is no way to systematically study such an effect, since the amount of sodium or ammonium ion remains essentially constant for this type of precipitate.

Oxygen 1s Lines

The oxygen 1s binding energies for the hydrolysis products, shown in Table I, range from 530.8 to 531.9 eV. Their width is approximately 3.0 eV, or considerably broader than either the parent $\text{UO}_2\text{C}_2\text{H}_2\text{O}$ or $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ salts (22). In the case of the oxygen lines for the NaOH-effected hydrolysis products, this line can be deconvoluted into two separate lines (Table II). The first line, at a binding energy of ~ 531.5 eV, is consistent with an hydroxyl group and would be compatible with the formulation of these compounds as $\text{UO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ species which truly contains both uranyl and hydroxide species rather than a designation such as $\text{UO}_3 \cdot x\text{H}_2\text{O}$ which would imply simple lattice oxides exclusively. This oxygen line at ~ 531.5 eV is the predominant line in each of the doublets (Table II), indicating its importance to the overall photoelectron line. The second line, with a binding energy of ~ 530.1 – 530.4 eV, can be attributed to lattice oxide species involving oxygens interacting with uranium atoms that are next nearest neighbors or, more likely, the lattice oxides of UO_3 .

One other explanation exists for the major "hydroxyl" peak in the doublet. Those binding energies in Table II also correspond to the oxygen binding energy of the carbonate functional group, the range being 531.0-531.6 eV (25). Other researchers (26) have observed the absorption of CO_2 by plutonium(IV) polymers formed by the NaOH-effected hydrolysis of plutonium(IV) salts in aqueous solutions; this in effect forms Pu(IV) carbonate complexes.

Indeed, there is tentative evidence in this study to support such a phenomenon with the present series of hydrolysis products. First, the elemental analyses always indicate a certain amount of bulk carbon to be present in the samples, the carbon content increases slightly upon standing in the open air for several weeks. Second, small infrared bands or inflections at 890 and 1350 cm^{-1} that appear in the spectra of the Pu(IV) polymers also appear in the infrared spectra of the uranyl hydroxide samples studied here.

A reaction of this type should not be unexpected for the basic uranium hydrolysis products studied here, especially in light of their similarity to the Pu(IV) polymers. Also, many metal hydroxides such as $\text{Pb}(\text{OH})_2$ also exhibit carbonate layers in their x-ray photoelectron spectra (27).

Luminescence Spectroscopy

The luminescence associated with the uranyl hydrolysis products is fundamentally different from that obtained in similar studies on the parent uranyl ion salts. Whereas the luminescence spectrum of uranyl nitrate hexahydrate at cryogenic temperatures consists of a series of well-defined sharp emission bands (1), the analogous spectra of the hydrolysis products

obtained from uranyl nitrate are fairly broad in character, do not contain any vibrational fine structure, and the wavelengths of the emission are considerably red-shifted relative to the spectrum of the uranyl salts. Representative spectra of three hydrolysis products obtained from uranyl nitrate may be seen in Figure 2-15.

Furthermore, while the luminescence spectra of uranyl nitrate (28), chloride (29), and acetate (30), are all dissimilar, the spectra of the three hydrolysis products obtained from each of these sources are essentially identical. In each case, the lineshape observed is that as shown in Figure 2-16: each spectrum contains two well-defined peaks which actually are quite broad in comparison to the luminescence spectra of most uranyl salts at these cryogenic temperatures (10°K). The spectra do exhibit qualitative differences in that the wavelength maxima of the peaks do vary somewhat with the identity of the counterion present in the original uranyl salt used to prepare the hydrolysis product and with the nature of the base used to hydrolyze the uranyl ion. The wavelength positions of the observed luminescence maxima and the energies of these have been collected in Table III.

A fundamental question which must be answered concerns whether both peaks observed in the emission spectrum of a given hydrolysis product actually originate from the same uranium ion, or whether they reflect the presence of different uranyl species. This question can be resolved by measurement of the emission lifetime associated with each band. The luminescence lifetime was obtained at each of the maxima listed in Table III,

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Figure 2-15. Luminescence spectra obtained for the uranyl ion hydrolysis products prepared from uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. 1) Sample A (hydrolysis of 0.1M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by NaOH, 2) Sample D (hydrolysis of 1.0M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by NaOH), and 3) Sample G (hydrolysis of 0.1 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by NH_4OH).

and it was found that in every case the lifetime of both peaks was absolutely identical to within experimental error. The lifetimes may be found in Table IV. This observation provides very strong evidence to indicate that the two luminescence peaks observed in the spectrum of each hydrolysis product are due to emission from a single emitting uranyl species, and do not reflect the presence of multiple emitting species in the hydrolysis products.

Given that the two peaks listed in Table III for each uranyl species originate from the luminescence of a single uranyl species, one is then able to interpret the energy spacing between the peaks as reflecting a ground state vibrational energy associated with hydrated uranyl hydroxide species. In simple uranyl salts, this progression is based on the totally symmetrical uranyl ion stretching mode, and energy values for this mode have been tabulated by these workers for a variety of uranyl salts (28). For the simple salts, an average value of 860 cm^{-1} is obtained. The energy differences obtained from the spectra of the hydrolysis products are shown in Table V, and it may be immediately seen that all ground state vibrational energies significantly smaller than those obtained for the uranyl salts.

With both uranyl nitrate and acetate, three emission band systems are found; they exhibit origins at approximately 486 nm, 507 nm, and 530 nm (28, 30). A comparison of these values to those shown in Table III for the hydrolysis products reflects the degree of red-shifting in which the luminescence has undergone. The lifetime values are also significantly shorter than those obtained with the simple parent uranyl ion salts; a lifetime of 660 μsec for UO_2^{2+} in uranyl nitrate hexahydrate was observed, for instance. The luminescence data thus provides very strong evidence for the

existence of a new uranium species in the hydrolysis products, which is quite different in nature from the parent uranyl species. The luminescence data thus strongly agree with the marked change in the luminescence spectrum of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ when two water molecules are replaced with hydroxy groups (28, 31).

The lifetime and ground state vibrational energy data (Tables IV and V) contain data which permits a classification of the hydrolysis products. In several instances, a lifetime of 100-115 μsec is obtained, and a ground state vibrational energy of $700\text{-}730\text{ cm}^{-1}$ for these compounds was calculated from the emission data. For other products, the emission lifetime was measured as being significantly smaller, and the ground state vibrational energies of these hydrolysis products were also found to be much reduced below 700 cm^{-1} . This behavior was most pronounced for the uranyl hydroxide products obtained from NaOH addition to 1.0M uranyl ion solutions. These data imply that significant counterion effects exist in the formation of several of the hydrolysis products.

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Table I. Binding Energies^{a,b} of Uranyl Salts and Their Hydrolysis Products.

Sample	O 1s	U 4f _{7/2}	U 4f _{5/2}	ΔE_{4f} ^d
UO ₂ Cl ₂ ·3H ₂ O	531.9 (2.3) ^c	382.3 (2.4) ^c	393.0 (2.4) ^c	10.7
UO ₂ (NO ₃) ₂ ·6H ₂ O	532.1 (2.8)	382.1 (3.9)	392.8 (3.9)	10.7
UO ₂ (CH ₃ COO) ₂ ·2H ₂ O	531.9 (2.4)	382.5 (3.2)	393.3 (3.3)	10.8
A	530.8 (2.8)	381.5 (2.9)	392.3 (2.6)	10.8
B	530.8 (2.6)	381.5 (2.9)	392.4 (2.5)	10.9
C	531.1 (3.0)	381.8 (2.7)	392.6 (2.7)	10.8
D	531.1 (3.0)	381.8 (2.6)	392.5 (2.5)	10.7
E	531.0 (2.9)	381.8 (2.8)	392.4 (2.6)	10.6
F	530.9 (3.1)	381.6 (2.5)	392.4 (2.4)	10.8
G	530.8 (2.9)	381.7 (2.6)	392.2 (2.6)	10.4
H	531.2 (3.0)	381.8 (2.7)	392.0 (2.6)	10.2
I	531.9 (3.0)	381.8 (2.7)	392.4 (2.6)	10.6

^aElectron volts, eV.^bCalibrated against the adventitious carbon line taken as C 1s = 284.6 eV.^cNumbers in parentheses represent the full width at half maximum (FWHM) of the photoelectron line, in eV.^dDifference in the binding energies of the uranium 4f_{7/2} and uranium 4f_{5/2} photoelectron lines.

Table II. Binding Energies^{a,b} of the Deconvoluted Oxygen 1s Photoelectron Lines of NaOH-Promoted Uranyl Hydrolysis Products.

<u>Sample</u>	O 1s (I) ^c	O 1s(II) ^d	Width ^e	Area Ratio (I/II)
A	(f)	(f)	(f)	(f)
B	530.4	531.1	2.3	1:2.2
C	530.1	531.5	2.1	1:1.7
D	530.2	531.4	2.3	1:2
E	530.2	531.5	2.3	1:1.4
F	530.2	531.3	2.7	1:1.7

^aElectron volts, eV.

^bCalibrated against the adventitious carbon line taken as C 1s = 284.6 eV.

^cLattice "oxide" value; please see text.

^dLattice "hydroxide" value; please see text.

^eFull width at half maximum, FWHM, eV.

^fCould not be fitted as two peaks.

Table III. Wavelength Maxima and Energies for the Luminescence Transitions of Uranyl Hydrolysis Products.

Sample ^{1,2}	Wavelength, Å	Energy, cm ⁻¹
A (NO ₃ ⁻ , 0.1 M)	5,334	18,749
	5,551	18,015
B (Cl ⁻ , 0.1 M)	5,373	18,611
	5,566	17,965
C (CH ₃ COO ⁻ , 0.1 M)	5,409	18,488
	5,623	17,783
D (NO ₃ ⁻ , 1.0 M)	5,379	18,031
	5,546	18,031
E (Cl ⁻ , 1.0 M)	5,327	18,772
	5,490	18,215
F (CH ₃ COO ⁻ , 1.0 M)	5,411	18,480
	5,594	17,876
G (NO ₃ ⁻ , 0.1 M)	5,331	18,758
	5,545	18,036
H (Cl ⁻ , 0.1 M)	5,351	18,688
	5,503	18,172
I (CH ₃ COO ⁻ , 0.1 M)	5,399	18,522
	5,611	17,822

¹The uranyl counterion and the concentration [UO₂²⁺] of the hydrolyzed solution are in parentheses.

²

Samples A-F were hydrolyzed with 1.0 M NaOH, while G-I were hydrolyzed with 1.0 M NaOH.

Table IV. Emission Lifetimes of the Uranyl Hydrolysis Products.¹

Sample	Counterion	Concentration, M	Lifetime, μ sec
A	NO_3^-	0.1	102 ± 2
B	Cl^-	0.1	115 ± 3
C	CH_3COO^-	0.1	102 ± 2
D	NO_3^-	1.0	78 ± 2
E	Cl^-	1.0	99 ± 4
F	CH_3COO^-	1.0	87 ± 1
G	NO_3^-	0.1	103 ± 3
H	Cl^-	0.1	74 ± 3
I	CH_3COO^-	0.1	100 ± 3

¹Samples A-F were NaOH-hydrolyzed; samples G-I were NH_4OH -hydrolyzed.

Table V. Ground State Vibrational Energies for the Uranyl Hydrolysis Products.¹

Sample	Counterion	Concentration, M	Energy Separation, cm^{-1}
A	NO_3^-	0.1	734
B	Cl^-	0.1	646
C	CH_3COO^-	0.1	705
D	NO_3^-	1.0	561
E	Cl^-	1.0	557
F	CH_3COO^-	1.0	604
G	NO_3^-	0.1	722
H	Cl^-	0.1	516
I	CH_3COO^-	0.1	700

¹ Samples A-F were NaOH-hydrolyzed; samples G-I were NH_4OH -hydrolyzed.

TASK 3: FAR FIELD HOST ROCK GEOCHEMICAL INTERACTIONS (Art. F. White,
Geochemistry Group, Earth Sciences Division, LBL)

a) Introduction--Application to NRC Licensing Needs

The far-field host rocks surrounding a nuclear waste repository represent the final barrier between potential radionuclide release from the near-field to the biosphere. The extent of migration within this region will be strongly influenced by the extent and nature of chemical interaction between the host rock and ground water. Parameters determined by water/rock interaction and affecting radionuclide migration include weathering of mineral substrates which influence sorption behavior, ground water pH and Eh conditions. These in turn affect oxidation states and sorption capacities, chemical speciation and finally the complexation of radionuclides. The emphasis of Task 3 is to evaluate the effects of far field geochemical water/rock interactions and processes occurring at ambient temperature on radionuclide transport and sorption. The principal goals of the task are:

- (1) Develop predictive capability to judge what reactions are significant in influencing sorption and migration for site-specific cases.
- (2) Evaluate the validity of laboratory experimental approaches in measuring sorptive capacities and in setting upper bounds on estimates under actual aquifer conditions.
- (3) Develop and verify additional methods and approaches that can be used to measure and characterize relevant site specific far-field geochemical processes.

The principal areas of research undertaken in FY 82 and reported in the following sections are:

- 1) The nature of sorption substrates present in the far field and determination of how these surfaces are influenced by geochemical reactions in the far field, either due to natural disequilibrium conditions or repository perturbations.

The investigation of specific effects include as incongruent dissolution, the formation of oxide and hydroxide coatings and radionuclide diffusion as related to mineral surfaces.

2) The determination of aqueous parameters that are critical to the solubility of various radionuclides. This investigation has focused thus far on the measurement of Eh and geochemical factors controlling it. Rates of oxygen uptake were measured and modeled using Eh and basalt, tuff and associated minerals as the substrate.

These results and additional ongoing research should be useful to NRC with regard to licensing consideration of far-field radionuclide migration.

b) Tuff, Basalt and Related Mineral Surface Chemistries of Far-Field Host Rocks

A fundamental difficulty in characterizing the sorption capacity of rocks surrounding a repository lies in defining the composition and chemistry of aquifer substrates. The bulk mineralogy of basalt and tuff consists of silicates that are thermodynamically unstable with respect to ground water and have the potential to be extensively altered by weathering reactions. Altered substrates can have considerably different sorption capacities than the bulk host rock and significant changes in radionuclide retardation may occur.

Although certain secondary mineral phases, such as clays and zeolites, are being characterized by DOE in site specific investigations on basalt and tuff few data exist on the chemical composition of surfaces ($< 1\mu\text{m}$) of weathered host rocks. Sorption mechanisms are predominantly influenced by near surface phenomena such as charge imbalance. Heterogeneous mineral surfaces (relative to the bulk primary or secondary mineralogy) may develop either by precipitation of surface coatings such as $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$, discussed below or by surface dissolution reactions.

Previous investigators have used aqueous dissolution data and suggested that a general incongruent weathering of mineral surfaces does occur (see White and Claassen, 1979). Figures 3-1 and 3-2 show this type of apparent incongruent weathering for Hanford basalt and NTS tuff reacted at pH 7 in deionized water for several months at 25°C. The weathering appears to occur in two steps, an initial rapid release of cations and silica which is essentially complete in 24 hours, followed by longer term slower release rates. Note however, in both basalt and tuff dissolution experiments that the final aqueous solutions contain much higher ratios of cations, relative to silica and aluminum (not shown) than those reported for bulk basalt or tuff. This implies that basalt and tuff surfaces may become depleted in cations which would result in the postulated incongruent dissolution mechanism. If such incongruent dissolution does occur, weathered mineral surfaces are expected to be compositionally different from the bulk host rock; consisting of essentially an Al_2O_3 - SiO_2 rich phase which probably possesses different sorption characteristics than the bulk tuff or basalt.

To test whether such sorptive substrates do form, a number of long term experiments were conducted in order to simulate far-field weathering conditions. The host rock was characterized by individual mineral phases common to basalt and tuff. The experimental apparatus and chemical analyses for the aqueous solutions were reported in FY 81. The final phase of these experiments, completed this year, consists of analysis of surface substrates using XPS and Auger spectroscopy. Detailed discussions concerning the specific effects of weathering reactions on iron containing minerals and incorporation of ions into the structure of hydrated glass are presented in following sections. The analytical data show that no major changes in the overall chemical composition

Fig. 3-1. Reaction of Umtanum Basalt in water at pH 7 and 25°C

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Fig. 3-2. Reaction of Bullfrog Hills Tuff in water at pH and 25°C.

of the silicate surfaces seem to occur during weathering. Furthermore, as shown in Figures 3 and 6, no major change in sorptive capacities of radio-nuclides were found during these experiments except in the case of glass hydration, to be discussed in a later section.

The photo electron emission spectra for Na, Ca, Al and Si for plagioclase feldspar, a common mineral in basalt and tuff is shown in Figure 3. The horizontal axes, corresponding to the binding energy of the element in approximately the upper 20 Å of the surface are plotted against relative intensity or amount. As indicated, little difference in intensity for Ca, Al and Si are seen between the unreacted sample (D) and samples reacted upwards of 9 months (A and B). Sodium shows some decrease with extended reaction. The atomic percentage of Al relative to Si are shown for several minerals by multiple XPS data in Figure 3-3. As indicated, virtually no change occurs in the Al content with time indicating that a $\text{Al}(\text{OH})_3$ rich phase does not form on the minerals surfaces as proposed by Helgeson (1971) and others. An initial drop in sodium is found for all the silicate minerals investigated. This decrease corresponds to the initial rapid increase in cation concentrations shown in Figures 3-1 and 3-2 for basalt and tuff and can be related to rapid surface ion exchange with the aqueous solutions and not to a long term weathering mechanism.

These results, along with previous work by Holdren and Berner (1979), support the conclusion that natural weathering of silicate mineral and rock surfaces is essentially a congruent process in which the surface chemistry does not change. The important ramifications are that these results support the general applicability of using fresh silicate surfaces as analogues to natural aquifer substrates for the determination of sorption and exchange constants provided that the bulk primary and secondary mineralogy is the same.

Fig. 3-3a. XPS spectra for i) Si, ii) Al, in the surface layer of plagioclase feldspar weathered at pH 7 - and 25°C. D is unreacted, B is weathered 1 month, A is weathered 9 months.

Fig. 3-3b. XPS spectra for iii) Ca, and iv) Na in the surface of plagioclase feldspar weathered at pH 7 - and 25°C. D is unreacted, B is weathered 1 month, A is weathered 9 months.

Fig. 3-4. Multiplex XPS data showing Al/Si ratios in the surface layers of minerals reacted up to 9 months at pH 7 and 25°C.

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c) Incorporation of Radionuclides in the Surface Structure of Silicate Minerals and Glass under Far-Field Conditions

In addition to reversible ion exchange on surface sites of silicates, a potential exists for radionuclides, under long term far-field conditions, to be permanently immobilized by structural incorporation into near surface layers of minerals by chemical reaction and/or solid state diffusion. Many examples of apparently non-reversible ion exchange involving " K_d " measurements exist in the literature, and at least some anomalies may be due to such mechanisms.

An example of such non-equilibrium sorption process occurred during the long term open system weathering experiments, is shown in Figure 3-5 by the continual uptake of Cs by obsidian over a nine month period. Similar experiments involving Ca and K-feldspar and plagioclase show a general steady-state Cs sorption (Fig. 3-5). The XPS peak for Cs in the obsidian indicates that substantial amounts of Cs are found in the top 20 Å of the obsidian surface (Fig. 3-6b). Interestingly no Cs was detected in the two feldspar surfaces reacted for similar time intervals.

Additional experiments involving Sr, Cs, Rb and Ba interactions with silicate surfaces were performed. After equilibrating the spiked aqueous solutions for 2 weeks, the minerals were filtered and separate splits re-equilibrated with solutions of deionized water (D.I.) and 0.1 N HCl. The object of these experiments was to determine the extent to which the exchange process was reversible and the extent of incorporation into the surface by an exchangeable process. Figure 3-7 shows an example of the XPS peak for Ba sorption on obsidian, K-feldspar and plagioclase feldspar. As expected for an exchange process, the 0.1 N HCl solution stripped virtually all of the Ba off of the silicate surface. Similar results occurred for the acid

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Fig. 3-5. Amount of cesium sorbed on surfaces of K feldspar ($\square$), plagioclase feldspar ($\circ$) and obsidian (Δ) during reaction at pH 7-8 for approximately 9 months.

Fig. 3-6. XPS spectra showing C_{1s} uptake in the surface layers of obsidian and feldspar (a) obsidian reacted 2 weeks and reequilibrated with H_2O and 0.1 N HCl, (b) obsidian reacted 9 months untreated, (c) K-feldspar and plagioclase reacted 2 weeks and reequilibrated with H_2O and 0.1 N HCl.

Fig. 3-7. XPS spectra show Ba sorption on silicate surfaces reequilibrated with H_2O and 0.1 N HCl
 a) obsidian
 b) K-feldspar
 c) plagioclase

treatment of Cs in the feldspar samples. However, the 0.1 N ECl solution failed to remove a significant portion of the Cs from the obsidian sample (Fig. 3-6a). This data coupled with the long-term Cs uptake by obsidian shown in Figure 3-5 implies that Cs may be irreversibly incorporated into the structure of natural glass, probably during a surface hydration process. Because glass is an important component in both basalt and tuff, the extent of such a mechanism should be investigated in greater detail.

d) Formation of Iron Oxide-Hydroxide Coating on Repository Host Rocks and Minerals

One potential mechanism for radionuclide retardation in far field host rocks is retention by secondary phases which may coat aquifer surfaces. In basalt the formation of iron hydroxide and oxide coatings may occur on weathered Fe-silicates. These coatings would have large surface areas capable of adsorbing radionuclides as well as as coprecipitation in hydroxide and oxide structures.. Siever and Woodford (1979), postulated that formation of phases such as $\text{Fe}(\text{OH})_3$ on silicate surfaces that was due to the oxidation of ferrous iron would result in the formation of an oxide rind. These rinds would be capable of further dissolution and weathering of basalt by requiring diffusion of silica, cations, and oxygen through a surface barrier. They also demonstrated that such a precipitate scavenges silica and cations out of solution. Their experiments show that the rates and extents of dissolution in an oxygen free system are much greater than the oxygen present. One of the goals of research in FY 82 was to evaluate under simulated repository conditions, the stability and morphology of such coatings and to assess their kinetic rates of formation.

Long-term open system weathering experiments similar to those described in the FY 81 annual report were conducted on iron silicates under both low (<0.1 ppm) and high (9.0 ppm) dissolved oxygen (D.O.) conditions. These conditions simulate natural low D.O. conditions found in basaltic groundwater and

conditions perturbed by the intrusion of oxygen during repository construction and closure. Figure 3 showed that the amount of Cs sorbed in moles/m² of surface area into hornblende and biotite, two common iron rich minerals, from spiked aqueous solutions increased only slightly during the weathering process over 9 months. This increase is due principally to a small increase in surface areas due to abrasion of mineral particles during agitation as documented by B.E.T. surface area measurements. Of perhaps greater significance is the observation that the concentration of sorbed Cs is slightly higher for biotite and hornblende reacted at low O₂ (O₂ <ppm) than at higher O₂ (= 8.5 ppm). These results are counter to the hypothesis that iron hydroxide and oxide coatings, formed on iron silicate minerals under oxidizing conditions, possess high sorption capacities and the ability to scavenge cations, including radio-nuclides out of solution.

To investigate the formation of Fe-hydroxides and-oxides coatings on iron silicates under simulated far field repository conditions, surface chemical compositions and profiles were compared for fresh and reacted minerals. The methods used included XPS and Auger spectroscopy, the applications of which were developed and described in FY 81. XPS spectra were obtained for unreacted dry mineral powders and powders reacted for 9 months at neutral pH under both high and low O₂ conditions. Figure 3-8 and 3-9 show results for biotite and hornblende plotted as intensity versus electron binding energy for iron. The iron spectra is taken from the top 20 Å of the mineral surfaces. Superimposed on the iron spectra are peak positions expected for Fe³⁺. The separation of the 2p orbital peaks for Fe³⁺ should be 13.6eV. The calculated shifts are 3.9 eV for biotite and 2.4 eV for hornblende. These results indicate that ferric iron is the dominant iron phase on the mineral surfaces for both unreacted and reacted phases.

XBI 8210-2539

Fig. 3-8. XPS spectra of unreacted biotite and biotite reacted with H_2O at pH 7.

XBL 8210-2540

Fig. 3-9. XPS spectra of unreacted hornblende and hornblende reacted with H_2O at pH 7.

Even though ferric iron is the dominant phase it is not present in any significant amount as an oxide or hydroxide coating formed during experimental weathering. Figure 3-10 shows multiplexed quantitative analysis by XPS of the amount of iron present on the mineral surface, its ratio against silica and as the square root of reaction time. As indicated, the iron content is essentially constant with possibly slightly more iron on the surface with increasing time and lower O_2 conditions. The relatively constant iron content is also demonstrated by the constant peak heights shown for the iron spectra in Figures 3-8 and 3-9.

In addition to characterization of the surface layer (top 20 Å) of Fe-silicates, individual cleavage surfaces were also depth profiled using a combination of argon sputtering and Auger spectroscopy to document chemical distributions with depth beneath the surface. Figure 3-11 shows the composition in atomic percent as a function of depth (100 Å) in biotite for both unreacted and reacted surfaces under high and low D.O. conditions. The most striking feature of the profiles is the remarkable similarity in elemental distributions. This suggests that aqueous weathering over the reaction interval (9 months) has virtually no effect on bulk near-surface compositions. The profiles indicate that both aluminium and iron in biotite are actually depleted near the surface. Yet there is a build-up of iron beneath this surface layer suggesting a compositional redistribution away from the surface through solid-state diffusion. Figure 3-12 shows similar depth profiles for hornblende. The profiles again suggest that there isn't a build-up of iron on the surface. A coating of $Fe(OH)_3$ could result in increased sorption capacities.

As has been previously documented (annual report FY 81), significant increases in dissolved species indicating incongruent dissolution do occur in aqueous solutions during the aforementioned weathering experiments. The fact that the basal crystallographic plane of biotite shown in the profile in Figure

Fig. 3-10. XPS Multiplex shows ratios of Fe to S_i on surfaces of biotite and hornblende reacted in water at pH 7 up to 9 months.

XBL 8210-2533

Fig. 3-11. Auger depth profile for biotite (total depth is approximately 100 Å)

Fig. 3-12. Auger depth profile for hornblende (total depth is approximately 100 Å)

3-11 shows virtually no compositional change indicates that reaction and dissolution must occur at defect or edge sites on the biotite. The fact that similar lack of compositional changes also occur on the hornblende cleavage surfaces supports the suggestion that reaction and dissolution must occur at defect sites. Once Fe and Al are released from defect sites in minerals into the aqueous double layer interfacing the solid surface, they may form insoluble hydroxide precipitates at these sites, or they may be transported into the bulk solution and left to nucleate as discrete hydroxide phases. In either case, the mineral surfaces themselves do not seem to become coated with monolayers of $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ which presumably would increase the sorption and coprecipitation capacity of mineral phases reasonably quickly.

e) Kinetics and Rates of Oxygen Consumption in Ferrous Iron Containing Repository Host Rocks and Minerals

Until recently relatively old deep groundwaters such as those at proposed repository sites in tuff and basalt have been assumed to be anoxic i.e. partial pressures of dissolved oxygen are extremely low. Few data exist on D.O. measurements in deep groundwater systems Winograd and Robertson (1982). Winograd and Robertson measured significant D.O. (2-8 mg/l) concentrations in water several thousand to more than 10,000 years BP and at distances as great as 80 Km from recharge areas suggesting that oxygenated conditions may persist much longer than previously thought. Dissolved oxygen has also been measured in deep groundwaters from the Hanford basalt but this condition is assumed to have resulted from contamination during pumping. Because D.O. is a critical parameter in controlling redox (Eh) potentials and therefore oxidization states, solubilities and sorption properties of radionuclides in groundwater, additional research is needed in defining the mechanisms and rates of O_2 consumption during rock/groundwater interactions. Initial work, centering on using Fe-

silicates as an oxygen sink was begun in FY 82. Experiments consisted of saturating deionized water at various O_2 and CO_2 pressures, then reacting these solutions with minerals and rocks in closed system flasks as described in the FY 81 annual report. More detailed experiments performed in FY 82, consisted of using a closed glove system so that sample preparation (i.e., final grinding, separation and addition of minerals and rocks to the flasks) could be done under an inert argon atmosphere. No reactions between the fresh mineral surfaces and CO_2 and O_2 were permitted to occur prior to the water/rock contact.

Figure 3-13 shows variations in dissolved oxygen as a function of time for a number of minerals as well as Hanford basalt and NTS tuff. At 25°C and sea level pressure has a saturated solution has a D.O. of about 8.5 ppm. After months, no leakage or microbial activity is observed in silicate minerals in the pure H_2O system. Solutions containing silicate minerals with low ferrous iron contents (such as obsidian and feldspar), show a slight oxygen decrease. In contrast, solutions with Fe-rich silicates (such as biotite and hornblende) show a decrease of about 2.0 ppm D.O. The NTS tuff result in decreases by 6 ppm while the Hanford basalt solution dropped the full 8.5 ppm, below detection limits (< 0.1 ppm) in less than 2 days.

The long term uptake of O_2 by iron silicates, hornblende and biotite, is shown in Figure 3-14 in which the moles of oxygen uptake per unit mineral surface area is plotted against the square root of time. As indicated, uptake rates for the two minerals are nearly identical. This is believed to involve transport across an oxidized surface zone and into the bulk unreacted mineral containing Fe^{2+} . Similar oxidization studies of metals, such processes are generally diffusion controlled. The simplest diffusional model (Crank 1955), assuming one-dimensional diffusion with constant boundary conditions, would

XBL 8210-257

Fig. 3-13. O_2 partial pressures of selected rocks and minerals in solution as a function of reaction time under closed system conditions.

XBL 8210-2529

Fig. 3-14. Oxygen taken per unit area of mineral surface plotted as a function of reaction time. Solid lines are fit of experimental data. Dashed line is diffusion model assuming D_{O_2} diffusion coefficient of $3 \times 10^{-20} \text{ cm}^2/\text{s}$.

result in a parabolic relationship between time and dissolved oxygen concentrations (linear for Fig. 3-14 for $t^{1/2}$ versus D.O. uptake). As shown in Figure 3-14, this condition is not observed in the concave upward trend in data. Such a lack of agreement is not unexpected for a closed system situation in which oxygen concentrations at the mineral interface decreases with time.

A numerical approximation for the observed distribution of O_2 in aqueous solution and adjacent solid material was obtained using a modified Crank-Nicholson method and a numerical solution presented by White and Classen (1980). At time $T=0$, the concentration of O_2 in the solid at the aqueous-solid interface is equal to dissolved O_2 in solution. O_2 elsewhere in the solid is assumed to be zero. The diffusion equation is then solved at each node and the total oxygen concentration which has diffused into the solid is then calculated. This concentration is subtracted from the initial aqueous O_2 concentration and the process repeated

The fit of the theoretical model (dashed line) to the experimental rates of oxygen uptake is shown in Figure 3-14 using a diffusion coefficient for biotite and hornblende of $3 \times 10^{-20} \text{ cm}^2/\text{s}$. This apparent diffusion rate can be compared to extrapolated high temperature volume diffusion rates found by Gilletti and Anderson (1975) for phlogopite mica. Use of their data and an activation energy of 29 kcal/g for the range 500 - 800°C yields results a linear Arrhenius extrapolation of about $1 \times 10^{-30} \text{ cm}^2/\text{s}$ at 25°C, which is comparable to solid state monovalent and bivalent cation diffusion in silicates. These diffusion rates are much slower than calculated for the present experiments at 25°C which appear to more closely fit grain boundary or micro porosity types of diffusion documented by Holdren and Berner (1979) as controlling crystalline silicate weathering at 25°C.

Based on the rate data in Figure 3-13, O_2 diffusion in Fe-silicate minerals appears to be a slower mechanism than O_2 uptake in bulk tuff and basalt, even though the total ferrous iron, may be much lower than in the iron silicates. Thus, it appears that secondary iron oxide minerals present in the basalt and tuff samples, may control the oxygen depletion in the rock samples. The rapid reaction of minor secondary phases may be a short term process, and limited to the number of fresh surfaces available. As shown in Figure 3-13, for tuff, the rate of O_2 appears to level off with longer time suggesting that reaction with such phases may have been exhausted. Note that the process of O_2 uptake by the iron silicates continues to proceed. Additional experiments are being planned in FY 83 to quantify O_2 uptake rates which in turn can be incorporated in chemical transport codes.

f) Influence of Host Rock Water Interactions on Redox Potentials and Eh Measurements of Ground Water

The oxidization-reduction potentials in ground water surrounding a repository are generally recognized as having a strong control on radionuclide transport by influencing both solubility and sorption characteristics. To date, little information exists on how geochemical rock/water interactions control ground water Eh and how these interactions would buffer a system during waste employment where oxygen or metallic (Fe) compounds may be introduced.

Experiments to date have been conducted on a number of iron-containing silicate minerals and tuff and basalt. Experimental methods are identical to those closed system methods described in the previous section on oxygen uptake. The Eh of the water/rock systems were characterized by three separate methods, Pt electrode, activities of Fe^{++}/Fe^{+++} and dissolved oxygen (D.O.). Because considerable uncertainties involving the calculation of Eh have been demonstrated

by numerous workers. consistency between the methods are vital in order to document Eh trends. One of the goals of this years work was to develop a method which both detects dissolved iron concentrations at very low levels ($\sim$ ppb) and distinguishes between the Fe^{++} and Fe^{+++} oxydation states. A method was adapted using the chromagen, Ferrozine, which reacts with the ferrous ion, forming a colored species which can be detected by a spectrophotometer. Because only Fe^{++} is sensitive, two samples are run, one for Fe^{++} and another to which a reducing agent is added and total dissolved iron determined. The Fe^{+++} component is then calculated by the difference.

The latest U.S.G.S. geochemical speciation code, PHREEQE, was also brought on line this year. This code is being used to compare calculated redox conditions in closed system experiments using various combinations of D.O., Eh and the $\text{Fe}^{++}/\text{Fe}^{+++}$ couple measurements. Such codes will also be of value in comparing relative redox measurement techniques both in laboratory experiments using host rocks and minerals and also for application to the in situ field monitoring.

Figure 3-15 shows Eh calculated by PHREEQE using the three analytical methods, Pt electrode, $\text{Fe}^{++}/\text{Fe}^{+++}$ couple and D.O., plotted against pH. As indicated the pH of the closed system runs was buffered by initial saturation of the solution with a given partial pressure of CO_2 , ranging between 0.8 atm and 5×10^{-4} atm. The initial dissolved O_2 partial pressure of all experiments was 0.2 atm, comparable to atmospheric conditions. The various partial pressures were produced by mixing proportions of N_2 , O_2 and CO_2 using micrometer-type flow meter systems.

Also shown in Figure 3-15 are the stability fields for various aqueous and solid iron phases and for upper and low stability reactions for water,

Fig. 3-15. Eh-pH stability of aqueous and solid iron containing phases.

i.e., O_2-H_2O and H_2-H_2O . As discussed by Krauskopf (1967) the dominant equilibrium control on iron concentrations in neutral groundwater conditions is

This reaction was solved for Fe^{++} concentrations representative of the upper and lower concentration ranges of most groundwaters, is also shown in Figure 3-15.

Eh values measured by Pt electrode techniques generally produce values which are much lower than other methods. These measurements show a progressive Eh decrease with length of reaction which also corresponds to qualitative decrease in dissolved oxygen. The upper limit of the Pt electrode measurements correspond to the Pt - PtO couple cited by Natarjan and Iwasaki (1974) as resulting from the formation of an oxidized layer on the electrode surface. The fact that with D.O. is also in agreement with the condition that if redox species in solution are not present in sufficient concentrations, the measured potential may be influenced by the mixed potential involving the oxygen species.

Eh values calculated by WATEQF from dissolved oxygen measurements plot near the upper stability limit water controlled by the redox reaction

Reactions involving tuff and hornblende, maintained appreciable levels of dissolved oxygen in solution throughout the experiments. Reactions involving basalt resulted in an extensive reduction of D.O. levels, to below detection limits. In the calculation, the D.O. of these reactions was assumed to be a maximum i.e., 0.1 ppm. Therefore as long as the D.O. is relatively high, due partly to the inability to measure very low D.O., the calculations will yield a

dominance of reaction 2. In reality, the actual control of oxidation reactions involving O_2 may be more complicated than indicated above, possibly involving a kinetic step in which traces of hydrogen peroxide act as an intermediate complex.

The final method of calculating Eh is by measured Fe^{++}/Fe^{+++} concentration in aqueous solution. These values plot reasonably close to the Eh values calculated by the D.O. measurements metastable Fe^{++}/Fe^{+++} boundary extended to the right of the Fe^{+++} stability field, but is independent of pH. In an equilibrium system, the dominant phases are the aqueous species Fe^{++} and the solid phase $Fe(OH)_3$. Since only very low concentrations of Fe^{+++} exist in natural solutions. Therefore the Eh based on the $Fe^{++} - Fe(OH)_3$ reaction would be expected to fall at a much lower Eh, along the $Fe(OH)_3/Fe^{++}$ boundary. However in the experimental system, both Fe^{++} and Fe^{+++} are measurable at relatively high concentrations which result in an Eh controlled by the Fe^{++}/Fe^{+++} couple. This metastable relationship implies that the Eh of the basalt, tuff and hornblende experimental systems are therefore controlled by kinetic parameters associated with water/rock reactions rather than by equilibrium constraints involving $Fe(OH)_3$ solubility and the oxidization of Fe^{++} . The high concentrations of both Fe^{++} and Fe^{+++} indicate that their release rates from the solid iron phases in the rocks is rapid enough to maintain a disequilibrium condition. This is substantiated by the data in Figures 3-16 and 3-17 which show respectively the extent of $Fe(OH)_3$ saturation in basalt and tuff experiments plotted as the ratios of the ionic activity product (IAP) to the solubility constant (K) for iron hydroxide against time ($t^{1/2}$, s). Also shown is the extent of aqueous Al saturation with respect to gibbsite. A IAP/K ratio of unity indicates saturated equilibrium conditions. As indicated in the case of basalt, the solutions over a pH range of 5 to 9.5

Fig. 3-16. Extent of supersaturation of aqueous solutions with respect to iron and aluminium hydroxide during reaction with basalt at 25°C.

Initial $O_2 \approx 8.5$ ppm, dissolved

○ 2.0×10^{-1} ATM CO_2 pH range 5.04-5.73

△ 4.0×10^{-2} ATM CO_2 pH range 6.55-8.07

□ 3.0×10^{-4} ATM CO_2 pH range 9.28-9.53

RBL 0211-2677

Fig. 3-17. Extent of supersaturation of aqueous solutions with respect to iron and aluminum hydroxide during reaction with tuff at 25°C.

initial $O_2 = 8.5$ ppm, dissolved

○ 2.0×10^{-1} ATMCO₂

pH range 5.41 - 6.05

become, progressively supersaturated with the solid iron hydroxide phase and eventually reach steady state conditions at approximately two orders of magnitude above equilibrium. Data for tuff of NTS shows similar steady state conditions persisting at supersaturation values of more than one order of magnitude above $\text{Fe}(\text{OH})_3$ saturation. Such steady state conditions imply that $\text{Fe}(\text{OH})_3$ is precipitating but that release of iron from the basalt phases is rapid enough to maintain a high degree of supersaturation. This rapid release rate is undoubtedly also responsible for the correspondence of the calculated Eh values to the metastable $\text{Fe}^{++}/\text{Fe}^{+++}$ boundary. Whether or not such unequilibrium Eh conditions can persist under perturbed repository conditions is a critical question which will require additional research.

g) Characterization of Silicate Sorbent Substrates by Potentiometric Titration

As discussed in the FY 81 annual report, the type, extent, and variations of electrical charge potentials present in host rock mineral and rock surfaces in association with ground water control, in large measure, the retardation capacity for radionuclides in far field aquifers. As discussed by Davis et al (1978) and Silva, White and Yee (1981) a variety of acidic, basic and amphoteric hydroxide groups are present on silicate surfaces and their characteristics control the sorption capacity of the mineral as well as response to perturbations in pH and ionic strength.

The intrinsic surface ionization and exchange constants governing surface ionization reactions can be estimated from experimental acid-base titrations obtained from aqueous suspensions over a wide range of pH and at several different electrolytic concentrations. The resulting constants can then be incorporated into existing speciation codes such as MINEQL or codes

being developed MINETEQ (PHL) to model species distribution both in the aqueous and sorbed states of a ground water system.

In order to increase overall sensitivity to relatively low exchange capacities of most silicate rocks and minerals, by decreasing the titration increments, and increasing equilibrium times, an automated titration apparatus was constructed. The principal components consisted of a Hamilton digital diluter/titrator, an Orion microprocessor/pH meter Model 811 and an Orion Model 951 printer.

A timing assembly permits sequential injection of a prescribed aliquot of acid or base into a water-rock suspension, stirring the solution for a fixed time, activating the pH monitoring mode, and printing the resulting end point pH. Titration can be varied between acid-base aliquots of 0 and 250 ml; monitoring intervals can be varied between 1 and 99 minutes. The titrations are conducted in a 3 neck, 1000 ml flask placed in a constant temperature water bath. The titrations are conducted under an inert atmosphere of helium which has been scrubbed of CO_2 and other buffering contaminants by elution through a bed of ascarite. The gas is subsequently saturated with H_2O prior to being introduced to the titration vessel. Experiments have employed 750 ml of solution and 75 grams of mineral.

In addition to continuous monitoring of pH during the course of the titrations, fluid samples were also collected automatically and analyzed for aqueous composition. Major cations, Al and Si, were monitored as well as variations in the extent of Cs and Sr sorption.

During the initial experiments, a complication to the titration techniques was encountered. In addition to inflection points in the titration curves caused by buffering capacities of the surface ionization sites, additional inflections

were caused by dissolution and precipitation reactions involving Al over the pH range 4 to 11.

Figure 3-18 shows an example of a titration for a plagioclase feldspar. The vertical axis is the solution pH and the horizontal axis the milliequivalents of base or acid added. Because the titrations start with an acidic solution, the milliequivalents are reported as OH^- . The first titration, a, represents the initial titration of the feldspar surface after pH stat equilibration. As indicated, a considerable acid-base buffering capacity is present. However, this capacity decreases markedly after the completion of the titration and the mineral has been reequilibrated at pH 3.5 and titrated in a new solution (titration b). The reason for this discrepancy is clearly shown in the third titration in which the solution from the first titration is retitrated separately from the feldspar. As shown in Figure 3-18, the principal buffering capacity resides in the aqueous solution and not as hydrogen ion sorption and desorption on the feldspar surface.

Figures 3-19 through 3-22 show corresponding aqueous composition changes for Al, Si, Cs and Sr during the course of the three titrations. The mechanism governing the aqueous buffering capacity is documented by the behavior of Al during the course of the titration. As is apparent in Figure 3-19, the Al concentration in the initial solution at the beginning of the first titration is relatively high indicating selective Al leaching from the feldspar surface. During the base titration at neutral pH's, the Al concentration decreases significantly and then increases again at basic pH. The acid titration shows that the titration process is reversible. This pattern corresponds with predicted Al solubility calculations in which

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Figure 3-18. Acid-base titration of plagioclase feldspar.

Figure 3-19. Aqueous Al concentrations during acid-base titration of plagioclase feldspar a) initial water/rock suspension, b) solution only and c) feldspar only with new equilibrated solution. Arrows to right are base titration, arrows to left are acid titration.

Fig. 3-20. Aqueous Si concentrations during acid-base titration of plagioclase feldspar; a) initial water-rock suspension, b) solution only, c) feldspar with new equilibrated solution. Arrows to right are base titration, arrows to left are acid titration.

Figure 3-21. Aqueous Cs concentrations during acid-base titration of plagioclase feldspar; a) initial water-rock suspension, b) solution only, c) feldspar with new equilibrated solution. Arrows to right are base titration, arrows to left are acid titration.

Figure 3-22. Aqueous Sr concentrations during acid-base titration of plagioclase feldspar: a) initial water/rock suspension, b) solution only, c) feldspar only with new equilibrated solution. Arrows to right are base titration, arrows to left acid titration.

Al^{+++} and $\text{Al}(\text{OH})_4^-$ species, respectively at low and high pH, result in high Al solubilities while gibbsite precipitation results in low Al solubilities at neutral pH. Figure 3-19 shows that, a second titration of the same solution without the feldspar present results in a very similar pattern of Al concentrations with pH.

The pH buffer effect in the titration documented in Figure 3-19 can be described using the following reaction

from the acid to neutral range and

in the base to neutral range. The low Al concentrations in the second solution equilibrated with the same feldspar sample (Figure 3-19) explains why a much lower buffer capacity occurs during the subsequent titration as shown in Figure 3-18). These results indicate that Al desorption or leaching from the feldspar surface is an irreversible short term reaction in even mildly acidic conditions and that the surface chemistry of aluminosilicates is permanently altered by such treatment.

Figure 3-20 shows changes in the aqueous Si concentrations as functions of pH. Because the solutions are significantly undersaturated with respect to solid silica phases, the corresponding decreases of dissolved Si in Figures 3-20a and b at neutral pH implies coprecipitation with the Al phase. However, unlike Al, the Si concentration variations are not completely reversible in the acid and base titrations when the feldspar phase is present (Figures 3-20a and 3-20c). This is due to significant dissolution of Si at pH's greater than 10 which corresponds to onset of silicic acid

disassociation. The low initial concentrations of silica in the second solution equilibrated at pH 3.5 with the feldspar also suggests that much of the Si contained in the initial solution is the result of short term irreversible reaction.

Figures 3-21 and 3-22 show Cs and Sr variations as functions of pH for the same titrations. As indicated, little correlation exists with fluctuations in Al and Si concentrations suggesting that precipitation of an aluminum hydroxide-containing phase does not significantly increase the sorption capacity of the solid as has been suggested for natural conditions. At present, the significant increase in Sr uptake at pH's > 10 has not been explained.

Although the preceding experiments have important ramifications in terms of pH controls on silicate reactions and potential influences on sorption capacities, modifications in procedures were required to isolate the specific influences of the primary mineral surface chemistry from overall water rock interactions. Longer equilibration times coupled with higher initial pH's were used in which the silicate minerals were equilibrated 1 week at pH 4.0 after which the minerals were separated from solution, washed and titrated. The procedure had the effect of weathering and stabilizing the surface relative to aluminum dissolution.

Figure 3-24 shows an example of a successful titration of albite in deionized water over two titration cycles (cycle 1 and 4). The inflexion points shown during the acidic titration cycles have been documented to represent surface exchange reactions and not dissolution precipitation effects. Figure 3-23 shows similar results for intermediate titrations in solutions containing NaCl. As evidenced the extent of the inflexion

ALBITE TITRATION IN 0.01M NaCl
0.1 ML INCREMENT, 12 HOURS/CYCLE

6/25/82

Fig. 3-23. Acid-base titration of plagioclase feldspar surfaces in 0.01 N NaCl (cycle 2) and 0.1 N NaCl (cycle 3) at 25°C.

ALBITE TITRATION IN WATER
0.1 ML INCREMENT, 12 HOURS/CYCLE

6/25/82

Fig. 3-24. Acid-base titration of plagioclase feldspar surfaces in deionized H_2O at $25^{\circ}C$.

becomes less with increasing NaCl indicating that exchange sites occupied by H^+ in diluted solutions become progressively saturated with sodium. Raw data of the data presented in Figures 3-23 and 3-24 are currently being processed using a statistical curve fitting program and the magnitude of the intrinsic exchange constants for the surface complexes will be extrapolated by the methods discussed by Davis (1978).

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GEOCHEMICAL ASSESSMENT OF NUCLEAR WASTE ISOLATION

TASK 4. VERIFICATION AND IMPROVEMENT OF PREDICTIVE

ALGORITHMS FOR RADIONUCLIDE MIGRATION

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INTRODUCTION

This report describes results of work performed through FY 1982 on Task 4 of the Geochemical Assessment of Nuclear Waste Isolation sponsored by the Office of Nuclear Regulatory Research, U. S. Nuclear Regulatory Commission. Other accounts of this research are given by *Miller and Benson [1982]* and *Miller [1982]*.

This task is part of the larger investigation of issues related to assessing and measuring geochemical interactions in a repository environment between radionuclides, water, engineered barriers, and near-field and far-field host rock to assure that HLW repositories will be sited and designed with proper geochemical consideration. In particular, this task is directed toward assessing the adequacy of currently applied methods for solving geochemical problems of the migration of radionuclides, recommending improvements, and providing better understanding of chemical processes operative during transport of radionuclides. The principal issue being addressed is the level of complexity required of geochemical algorithms of transport models to adequately predict radionuclide migration.

Model calculations of radionuclide migration will be used in assessments of the abilities of proposed repository sites to adequately isolate radioactive waste. Such geochemical modeling is an integral part of analytical and investigative activities re-

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quired by 10 CFR 60 in Sections 60.11(a), 60.21(c), 60.31(a), 60.111(c), 60.122, and 60.123.

Two approaches have been used in chemical transport modeling. One approach integrates existing codes for equilibrium distributions of species with transport algorithms in a two-step procedure. Applications of this approach can be differentiated by the manner in which transport by dispersion/diffusion is accounted for. The second approach is based on a one-step procedure which consists of solving simultaneously a system of equations describing chemical reactions and advective-dispersive transport with interphase mass transfer. In its simplest form, this approach assumes uncoupled equilibrium exchange of noncompeting solutes, each possessing a constant distribution coefficient (K_D). In this case, the system of simultaneous equations reduces to a set of independent, linear, partial differential transport equations, one for each exchanging solute. In its more advanced form, the approach is more soundly based on chemical and thermodynamic principles and leads to a system of simultaneous, non-linear, partial differential equations coupled to a set of mass action equations and a site constraint equation. The advanced form of the one-step approach was used in construction of the chemical transport model, CHEMTRN, used in this task to evaluate chemical algorithms. CHEMTRN provides a flexible framework and method of solution which facilitate attachment of different algorithms. At present CHEMTRN includes one-dimensional dispersion/diffusion, advection, complexing in the aqueous phase, sorption of ions and complexes by either ion exchange or surface complexation, dissociation of water, and precipitation/dissolution reactions.

BASIC EQUATIONS

Given a basis set of species ($A_j^{n_j}$), which are the minimum number (N_b) of species needed to define all the chemical species present, one can write a reaction for formation of a complex $B_i^{n_{ci}}$,

or a solid precipitate G

where a_{ij} and s_{kj} are the stoichiometric reaction coefficients, n_j is the charge of the basis species, and n_{ci} is the charge of the complex. Assuming chemical equilibrium, mass action expressions can be written for each of these cases. For the formation of complexes,

$$K_i = \frac{[B_i^{n_{ci}}]}{\prod_{j=1}^{N_b} [A_j^{n_j}]^{a_{ij}}}, \quad (1)$$

where the square brackets denote the thermodynamic activity of the dissolved species and K_i is the equilibrium constant. For the formation of the precipitates,

$$K_k = \prod_{j=1}^{N_b} [A_j^{n_j}]^{s_{kj}} \quad (2)$$

where the square brackets again denote activities and K_k is the solubility product. The activities of the dissolved species are approximated using the relation,

$$[A_j^{n_j}] = \gamma_j m_j \quad (3)$$

where γ_j is an activity coefficient and m_j is the concentration (molar) of solute species. Equation 1 then reduces to

$$K_i = \frac{\gamma_{c_i} m_{c_i}}{\prod_{j=1}^{N_b} (\gamma_j m_j)^{a_{ij}}} \quad (4)$$

where m_{c_i} is the molar concentration of the complex $B_i^{n_{c_i}}$.

The activity coefficients of the aqueous species (basis species and complexes) are functions of temperature, pressure, and chemical composition. For this work, they are approximated using the Davies equation [Stumm and Morgan, 1970],

$$\log_{10} \gamma_j = -\frac{1}{2} n_j^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right), \quad (5)$$

where I is the ionic strength defined as

$$I = \frac{1}{2} \left(\sum_{j=1}^{N_b} n_j^2 m_j + \sum_{i=1}^{N_c} n_{c_i}^2 m_{c_i} \right), \quad (6)$$

and N_c is the number of complexes in the the aqueous phase. The activity of water is taken to be unity. (Note that $0.3I$ has been used in the Davies equation instead of $0.2I$ as per footnote, p.83 of Stumm and Morgan [1970].)

The mass transfer of ions and complexes from the aqueous phase to the solid phase is simulated by either ion exchange or surface complexation. For an ion exchange process, the charge on the solid remains fixed with the chemical species being sorbed on a fixed number of sorption sites. The species in the aqueous phase are sorbed on the solid phase by displacing ions already on it. Because the charge on the solid matrix does not change, a species which is sorbed must replace an equivalent amount of charge. For species $A_1^{n_1}$ exchanging with species $A_2^{n_2}$,

$$n_2 A_1^{n_1}(aq) + n_1 \bar{A}_2 \rightleftharpoons n_2 \bar{A}_1 + n_1 A_2^{n_2}(aq), \quad (R3)$$

where $\bar{A}_j$ denotes the sorbed component. This reaction is described by a thermodynamic equilibrium constant,

$$K_{eq} = \frac{[\bar{A}_1]^{n_2} [A_2^{n_2}]^{n_1}}{[A_1^{n_1}]^{n_2} [\bar{A}_2]^{n_1}}, \quad (7)$$

where the square brackets again denote activities. At present, because of the lack of data for activity coefficients for the surface phase, an ideal solution is assumed where

$$[\bar{A}_j] = \frac{\bar{m}_j}{\bar{m}_T}, \quad (8)$$

$\bar{m}_j$ is the concentration of species j on the surface phase, $\bar{m}_T$ is the total concentration sorbed on the surface phase given by

$$\bar{m}_T = \sum_{j=1}^{\bar{N}_b} \bar{m}_j + \sum_{i=1}^{\bar{N}_c} \bar{m}_{c_i}, \quad (9)$$

$\bar{N}_b$ is the total number of sorbed basis species, $\bar{N}_c$ is the total number of sorbed complexes, and $\bar{m}_{c_i}$ is the concentration of sorbed complexes. The units of $\bar{m}_j$, $\bar{m}_{c_i}$, and $\bar{m}_T$ are expressed as moles/ ℓ solution. These units can be related to the more conventional ones (moles/g solid) used for the sorbed phase by dividing $\bar{m}_j$ by $\rho_s(1 - \phi)10^3/\phi$, where ρ_s is the density of the solid phase in g/cm³, and ϕ is the porosity of the porous medium. An effective equilibrium constant, K_1^2 , is used to model the ion exchange process and (7) is replaced by

$$K_1^2 = \frac{(\bar{m}_1/\bar{m}_T)^{n_2} (\gamma_2 m_2)^{n_1}}{(\gamma_1 m_1)^{n_2} (\bar{m}_2/\bar{m}_T)^{n_1}}. \quad (10)$$

In addition, it is assumed that the total number of equivalents of surface sites per ℓ solution, N_s , available for ion exchange is constant,

$$N_s = \sum_{j=1}^{\bar{N}_b} n_j \bar{m}_j + \sum_{i=1}^{\bar{N}_c} n_{c_i} \bar{m}_{c_i}. \quad (11)$$

This concentration of sites, on a solid whose surface density is constant over the pH range of interest, can be determined from the cation exchange capacity (meq/g solid),

CEC, or

$$N_s = (CEC)\rho_s \frac{1-\phi}{\phi}. \quad (12)$$

For a surface complexation model, a neutral site denoted as SOH can dissociate to give a negatively charged site, SO^- ,

where the subscript s denotes the ion at the surface, or SOH can react with a H^+ ion to give a positively charged site SOH_2^+ ,

In contrast to the ion exchange model, the charge on the solid surface changes and both cations and anions can be sorbed instead of just one or the other. In addition, because of the variable surface charge, an ion does not necessarily have to displace an equal amount of charge when it forms a complex with the surface site. For example, in an ion exchange model, the sorption of Sr^{2+} on the solid phase would require a reaction with two surface sites,

while in a surface complexation model a reaction with only one site is possible,

The subscript β denotes the plane where the Sr^{2+} ion is located when it forms a complex with the surface site. In an ion exchange model, the s and β planes are not designated because they are the same while in the surface complexation model, the β plane is displaced a distance from the solid surface.

Following the discussion by Davis et al. [1978], the equilibrium constant for reaction R4 is

$$K = \frac{[SO^-][H_s^+]}{[SOH]}. \quad (13)$$

The activity of H^+ at the surface is related to the activity in the bulk solution by

$$[H_s^+] = [H^+] \exp\left(-\frac{e\psi_i}{kT}\right), \quad (14)$$

where ψ_i is the change of potential when a species moves from the bulk phase to the solid phase. A similar expression can be written for reactions R6 and R7. However, the sorbed Sr^{2+} ion resides at the β plane and only moves through a potential difference of ψ_β . Therefore, the activity of Sr^{2+} at the β plane is related to the bulk activity by a term $\exp(-2e\psi_\beta/kT)$. The potentials ψ_i and ψ_β are functions of the charge distribution developed between the bulk fluid and the solid surface. A complete discussion of this surface complexation model for sorption is given in Davis et al. [1978].

For a velocity v and a dispersion coefficient D , both the basis species and the complexes are subject to transport by advection and dispersion/diffusion. In addition they are subject to sorption and precipitation or dissolution. One can write a mass balance for the concentration of each species. If W_j is the total concentration of species A_j in the aqueous phase, given by

$$W_j = m_j + \sum_{i=1}^{N_c} a_{ij} m_{c_i}, \quad (15)$$

and if $\bar{W}_j$ is the total concentration of the sorbed species A_j , given by

$$\bar{W}_j = \bar{m}_j + \sum_{i=1}^{N_c} a_{ij} \bar{m}_{c_i}, \quad (16),$$

and if N_p is the total number of precipitates, then

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial x} - D \frac{\partial^2}{\partial x^2}\right) W_j = -\frac{\partial}{\partial t} \bar{W}_j - \frac{\partial}{\partial t} \sum_{k=1}^{N_p} s_{kj} G_k. \quad (17)$$

The number of unknowns is $N_b + \bar{N}_b + N_c + \bar{N}_c + N_p$. Therefore, an equal number of equations is needed for solution of this system. For (17), $j = 1, \dots, N_b$,

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giving N_b equations. The mass action relations, (4), provide N_c equations for the complexes. There are $\overline{N}_b + \overline{N}_c - 1$ relationships of the form of (10); N_p relations of the form of (2); and (11) provides the final relationship needed. The activity coefficients are given by (5), and $\overline{m}_T$ is defined by (9). Therefore a sufficient number of equations exist and can be used to determine m_j , $\overline{m}_j$, m_{c_i} , m_p , and $\overline{m}_{c_i}$.

SOLUTION PROCEDURE

The partial differential equations (17) are discretized in space leading to a set of ordinary differential equations (ODE's)

$$\frac{d}{dt}W_{j,n} + \frac{d}{dt}\overline{W}_{j,n} + \frac{d}{dt} \sum_{k=1}^{N_p} s_{kj} G_k = \frac{D}{\Delta x^2}(W_{j,n+1} - 2W_{j,n} + W_{j,n-1}) - \frac{v}{\Delta x}(W_{j,n} - W_{j,n-1}) \quad (18)$$

where j denotes the species and n is the spatial position. The advection term has been expressed using an upwind differencing method. The reason for this choice and some alternative approaches will be discussed below.

Equations (2,4,10,11,13,14,18) form a set of differential/algebraic equations (DAE's) which fits the form

$$G(m, t) \frac{dm}{dt} + F(m, t) = 0. \quad (19)$$

where m is a vector which contains all the unknowns (m_j , $\overline{m}_j$, m_{c_i} , $\overline{m}_{c_i}$, m_p) at all the node points. The matrix G is singular, because $g_{j,n} = 0$ when the mass action equations (2,4,10) and the site constraint equation (11) are fit to the form of (19).

Kee and Miller [1980] have used this approach to model chemically reacting flow in boundary layers. They give a detailed procedure for solving these types of differential/algebraic problems, pointing out that there are a number of methods of discretizing m in time. For the work done here a backward Euler method was used,

i.e.

$$G(m^{\ell+1}, t) \frac{(m^{\ell+1} - m^{\ell})}{\Delta t} + F(m^{\ell+1}, t) = 0, \quad (23)$$

where ℓ denotes the old time level, and $\ell + 1$ denotes the new time level. A number of more sophisticated DAE solvers based on more than one old time level are available, including that of Hindmarsh [1980] and Petsold [1981]. However, the model developed includes precipitation and when precipitates form, the number of unknowns increases. Methods based on using derivatives at several time steps such as those employed by Hindmarsh [1980] would have to be restarted. Because of the inclusion of precipitation in this model, the simpler backward differencing method was used.

An advantage of using just two time levels is that it is possible to modify the backward Euler method slightly by evaluating the advection terms at the old time level using an upwind differencing method, maintaining the physical significance of this term; i.e., information is transported in the direction of the flow, while still evaluating the diffusion terms at the new time level. (Central differencing as well as the finite element methods of Rubin and James [1973] and those of Valocchi et al. [1981] allow information to be advected upstream.) However, the upwind differencing scheme used in CHEMTRN for the advection term does introduce artificial diffusion with a coefficient of $(v\Delta x/2)(1 - c)$, where c is the Courant number and is equal to $v\Delta t/\Delta x$. This dispersion, though, can be thought of as contributing to the physical dispersion term. It is directly proportional to the velocity in the same manner in which the physical dispersion is formulated. The numerical dispersion can be minimized by using a time step such that the $c=1$; then $\Delta t = \Delta x/v$. However, this restriction can be rather stringent. In addition, for a variable grid spacing, one cannot necessarily have $c=1$ throughout the entire grid. In this case, if numerical dispersion is comparable to or greater than physical dispersion, alternate differencing methods [Roache, 1972] may have to be used for the advection term.

To solve the system of equations, a Newton-Raphson iteration technique is used. The Newton-Raphson method solves the set of equations by first guessing the values of the unknowns at the new time level, and then calculating the residue for all the

equations for that guess, i.e.,

$$G(m^{\ell+1,k}, t) \left(\frac{m^{\ell+1,k} - m^{\ell}}{\Delta t} \right) + F(m^{\ell+1,k}, t) = R(m^{\ell+1,k}, t) \quad (21)$$

where k denotes the iteration number and R is a matrix containing the residues of the equations. A new guess is obtained by first calculating the Jacobian, J , where $J = \partial R / \partial m$, and then using the Jacobian to predict the value of the unknowns at the new time level,

$$J \Delta m = J(m^{\ell+1,k+1} - m^{\ell+1,k}) = -R(m^{\ell+1,k}). \quad (22)$$

Since one-dimensional flow is being modeled, any component of the residue vector will be a function of m at that node point and the neighboring node points resulting in a block tridiagonal Jacobian matrix. The linear system of equations (22) is solved with LU decomposition where the Jacobian is factored into lower and upper triangular matrices. A software package written by Hindmarsh [1977] was used both to perform the LU decomposition and to solve the set of equations. To save time, the Jacobian is not necessarily evaluated at every time step [Kee and Miller, 1980]. The iterations of (22) continue until the change in the new values of m are less than the specified error tolerance. If convergence is not obtained in a reasonable number of iterations, a new Jacobian is calculated. If convergence is still not obtained, the time step is reduced. When convergence is obtained within a specified number of iterations, the time step is increased.

To be able to consider many different precipitates, the precipitation of a solid is only included in the set of equations when it actually occurs. One type of precipitate may form at one node point while another type could form at a different point. After each time step, the solubility constraint for every precipitate that is being considered is tested at all the node points. If any of the solubility constraints is exceeded at a node point, the total amount of each basis species is computed and a new distribution of species is calculated at that node point. All the solubility constraints are considered when the new equilibrium is calculated. From that point on, the solubility constraint

is satisfied for any precipitate which has formed at the node point and is included in the system of differential/algebraic equations which are solved simultaneously, i.e., the two-step procedure is only used for the time step when the precipitate first forms. The transport equation at that node point will now include an additional term which is the change in the amount of precipitate at that point. For dissolution, the opposite occurs: if $[A][B] < K_k$, a new equilibrium distribution of species is calculated. If the precipitate has redissolved, the solubility constraint equation will no longer be satisfied at that node point.

Because the matrix G is never inverted, it can be singular. New chemical reactions are handled by calculating the residues of the new equations describing the reactions. The calculation of the Jacobian is done numerically and therefore is independent of the types of chemical reactions considered. Nonequilibrium chemistry can be considered by replacing the calculation of the residues of the mass action equations with those of the residues of kinetic rate equations, and radioactive decay can be included by adding a decay term to the transport equation.

The matrix G is never stored itself, just the residues for each guess. However, the Jacobian requires the calculation and the storage of the changes in residue of each equation with respect to the changes in all the unknowns at a node point and at the two neighboring node points. Although only the nonzero block matrices are stored, this storage requirement can be excessive for some computers. It is possible to break up the Jacobian matrix into several different blocks and then store these blocks separately. For example, this procedure helps to overcome some of the storage limitations of the CDC 7600 computer which was used for these calculations.

Different boundary conditions are possible with CHEMTRN. The flexibility is obtained by expressing the boundary conditions in the form of (19) as stated by Kee and Miller [1980]. Both time-dependent and steady-state boundary conditions can be studied. For the cases considered below, a concentration boundary condition was used at the inner boundary where the magnitude of the concentration was determined by a solubility constraint,

$$K_{12} = [A_1][A_2] \quad (23)$$

where K_{12} is an equilibrium solubility product. A semi-infinite system was modeled by imposing a no-flux condition at the outermost nodes of a finite grid. Depending on the grid size chosen and the simulated time, this boundary condition could be imposed far enough away from the inner nodes so it would not affect the solution at these points.

An additional aspect of CHEMTRN is the treatment of the hydrogen ion activity. In most chemical systems, the hydrogen ion can be considered a master variable since many chemical reactions depend on its activity. In an aqueous solution, the dissociation of water is an important source of hydrogen ions, i.e.,

Most available chemical transport models do not incorporate this reaction. Since calculations involving solubility, sorption, and complexation often depend on pH, failure to account for the dissociation of water can result in incorrect estimates of chemical migration. Therefore, we have included this chemical phenomenon in CHEMTRN.

To avoid convergence problems, CHEMTRN solves for a dummy concentration, y , defined by

$$y = m_{H^+} - m_{OH^-}. \quad (24)$$

This method is employed because a mass balance equation for either H^+ or OH^- must include the concentration of water. Relatively large changes in the former produce extremely small changes relative to the concentration of the latter. To solve for y , a slight modification must be made to the mass balance equations for H^+ and OH^- . The mass balance equation for hydrogen ion is

$$L\left(m_{H^+} + \sum_i a_{i,H} m_{c_i}\right) + \frac{\partial}{\partial t} \bar{W}_{H^+} = -L(m_{H_2O}), \quad (25)$$

and for the hydroxyl ion

$$L\left(m_{OH^-} + \sum_i a_{i,OH} m_{c_i}\right) = -L(m_{H_2O}). \quad (26)$$

If (26) is subtracted from (25), the result is

$$L \left[y + \sum_i (a_{i,H+} - a_{i,OH-}) m_{c,i} \right] + \frac{\partial}{\partial t} \bar{W}_{H+} = 0. \quad (27)$$

An additional relationship is obtained from the mass action equation for the dissociation of water:

$$[H^+][OH^-] = K_w \quad (28)$$

where K_w has the value of $10^{-13.99}$ at 25 C.

EXAMPLES

Four different cases are presented here. The first case tests the accuracy of the numerical model CHEMTRN by solving a problem with a known analytical solution and comparing the numerical simulation with the analytical solution. The second case uses CHEMTRN to model a field test where the primary chemical mechanism is sorption. Parameters which have some uncertainty associated with them are varied to show their effects in matching the numerical solution to the measured values. The next case looks at the validity of using a kD type of model to simulate chemical transport away from a repository and makes recommendations as to when such a model is valid. It includes an example where surface complexation is used to model sorption of ions. The last case illustrates the ability of the model to take into account precipitation or dissolution of solids.

To illustrate that CHEMTRN gives reasonable results, it has been used to simulate the transport of a chemical species in a semi-infinite medium where the initial concentration of the species is m_i for $0 < x < \infty$ and where at time $t > 0$, the concentration at $x = 0$ is maintained at m_b . Far from this boundary, the concentration of the species remains at the initial concentration. For this example, the sorption of the species was

not considered. The equation governing the transport of the chemical species is

$$\frac{\partial m}{\partial t} + v \frac{\partial m}{\partial x} = D \frac{\partial^2 m}{\partial x^2} \quad (29)$$

The analytical solution for the concentration of the species as a function of time and position is known and given by (Ogata and Banks, 1961):

$$\frac{(m - m_i)}{(m_b - m_i)} = \frac{1}{2} \operatorname{erfc} \left(\frac{x - vt}{2\sqrt{Dt}} \right) + \frac{1}{2} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{2\sqrt{Dt}} \right). \quad (30)$$

Figure 4.1 is a comparison between this analytical solution and the numerical solution of the same problem using CHEMTRN. The velocity used was 0.1 m/hr and the dispersion coefficient was 1.0 v . The comparison was made at 10 and 20 hrs. However, in the numerical solution a boundary condition of $\partial m / \partial x = 0$ was imposed only 4.75 m downstream. The deviation of the numerical model from the analytical solution occurs because the influence of this boundary is being felt.

In addition to being transported downstream, a species can be sorbed onto the solid matrix. A common method of handling sorption is to assume that the amount of sorbed material is proportional to the concentration of that species in the aqueous phase, $\bar{m} = k_D m$ where k_D is the distribution coefficient. When this k_D type of model is appropriate, one can consider the same problem as above but with the species sorbing as well as being transported. The governing equation now includes a term for the sorption of the ion,

$$\frac{\partial m}{\partial t} + \frac{\partial \bar{m}}{\partial t} + v \frac{\partial m}{\partial x} = D \frac{\partial^2 m}{\partial x^2} \quad (31)$$

The analytical solution is obtained by assuming that k_D is constant and replacing both v and D in (30) by an effective velocity and dispersion coefficient, v' and D' , where $v' = v/(1 + k_D)$ and $D' = D/(1 + k_D)$. Figure 4.2 is a comparison between the analytical solution and the numerical simulation when Sr^{2+} is being transported downstream in a groundwater consisting of 10^{-3} Na^+ , 10^{-4} Ca^{2+} , 10^{-8} Sr^{2+} , $4.5 \times 10^{-5} \text{ CO}_3^{2-}$, $1.11 \times 10^{-3} \text{ Cl}^-$ (all concentration units are in moles/l solution).

Equilibrium constants of 0.66 for Sr^{2+} replacing Na^{+} and 0.66 for Ca^{2+} replacing Na^{+} were used. At $z = 0$, a solubility product for strontium carbonate was used to calculate the amount of Sr^{2+} and CO_3^{2-} entering the groundwater. For both the initial conditions and the boundary conditions, the k_D as defined above is 450. Note that k_D is unitless as defined here because both m and $\bar{m}$ have been expressed in the same units of moles/l solution. The comparison in Figure 4.2 is done on semi-log paper where differences between the exact solution and the numerical calculations are more evident. Again, the numerical model agrees well with the exact solution. The slight deviation of the numerical calculation from the analytical solution is because of the size of the finite grid spacing used.

CHEMTRN has also been used to simulate the field test described in the paper by Valocchi *et al.* [1981] where treated municipal wastewater effluent was injected into a shallow aquifer in the Palo Alto (California) Baylands region. The principal chemical mechanism thought to govern transport here is ion exchange between Na^{+} , Ca^{2+} , and Mg^{2+} . Field data used for this simulation were obtained from Valocchi *et al.* [1981]. More data are available in Roberts *et al.* [1978] and Charbeneau and Street [1978], referenced by Valocchi *et al.* [1981].

A simulation was done for the fluid arriving at well S23, 16 m from the injection site. The initial composition of groundwater in this region consisted of 5700 mg/l Cl^{-} , 1990 mg/l Na^{+} , 436 mg/l Mg^{2+} , and 444 mg/l Ca^{2+} . The effluent water was injected at an average rate of 21 m^3/hr and had an average composition of 320 mg/l Cl^{-} , 216 mg/l Na^{+} , 12 mg/l Mg^{2+} , and 85 mg/l Ca^{2+} . As given by Valocchi *et al.* [1981], the aquifer thickness was taken to be 2 m, the solid matrix density was 2500 g/l, the CFC was 0.1 meq/g, and the porosity was 25%.

Figures 4.3a and 4.3b are comparisons of the field measurements of the exchanging ions, Ca^{2+} and Mg^{2+} , at well S23 and the simulations of these measurements using CHEMTRN. For this simulation, radial flow was assumed with the fluid velocity proportional to $Q/(2\pi b\phi r)$; Q is the injection rate, and b is the aquifer thickness. The dispersion coefficient used, including the numerical dispersion, was about 1.3v for this

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example. The numerical dispersion accounts for approximately 20%. The selectivity coefficient used for the exchange reaction of Mg^{2+} replacing Na^{+} was 0.65 and that for Ca^{2+} replacing Na^{+} was 1.0. Note that the selectivity coefficients in CHEMTRN are defined using a mole fraction convention instead of an equivalent fraction convention as used by Valocchi *et al.* [1981]. The selectivity coefficients used here should be multiplied by about 2 for comparison with those of Valocchi *et al.* [1981]. The results of the simulation are encouraging given the fact that one-dimensional flow with only longitudinal dispersion was assumed. Additional data on the SO_4^{2-} , HCO_3^{-} , CO_3^{2-} , and H^{+} ion concentrations are necessary to assess the importance of complexation effects on the transport of Ca^{2+} and Mg^{2+} .

The parameters which have some uncertainty associated with them and upon which the simulation is primarily dependent include the fluid velocity, the number of sorption sites, and the equilibrium exchange coefficients. The number of sorption sites per ℓ solution is related to the cation exchange capacity as given in (12) and depends on the porosity and solid and liquid densities. The fluid velocity, concentration of sorption sites, and the equilibrium constants for sorption were varied to show the sensitivity of the match. Figure 4.4a shows the concentration of Ca^{2+} at the well 16 m from the injection point just as in Figure 4.3a. However, included on the plot is the concentration when the fluid velocity in the porous medium is varied. In one case, the velocity is calculated as $1.3Q/(2\pi b\phi r)$ while in the second case it is $0.7Q/(2\pi b\phi r)$. We see that changing the velocity does not really change the shape of the curve, but just moves it in space. Given that there is some uncertainty associated with the measured values of b and ϕ , one could obtain the actual velocity by fitting the concentration profile for a nonsorbing species. From such a fit, both the dispersion coefficient and velocity could be obtained.

The concentration of sorption sites was also varied from 0.5 to 1.0. The cation exchange capacity measured from core data was 0.1 meq/gm. Using values of porosity and densities as given above, this converts to a N_s of 0.75 sites/ ℓ solution. Figure 4.4b shows the comparison of the numerical simulation with the measured field values

when N_s was varied. When three species are competing for the sorption sites on the solid surface, and when the concentration of the species in the feed solution varies from the concentration of the groundwater in place, plateau zones can develop in the concentration profiles [Helfferich and Klein, 1970 and Valocchi et al., 1981]. When N_s is varied, the width of this plateau changes as shown in the figure. One can also vary the equilibrium exchange constants for Ca^{2+} and Mg^{2+} exchanging with Na^+ . In Figures 4.4c and 4.4d, the equilibrium exchange constants have been varied over the range of measured values as given in the appendix of Valocchi [1981]. In Figure 4.4c, the calculated concentration of Ca^{2+} at the well is plotted and in Figure 4.4d, the concentration of Mg^{2+} is plotted. Again there is a change in the width of the plateau region developed in the measured concentrations. This change is approximately the same amount that is obtained when N_s was varied because the activity of the sorbed phase has been expressed as the ratio of the molar concentration of the sorbed species to the total molar concentration of sorbed species. The equilibrium constants are then proportional to the value of N_s , so a change in the equilibrium constants is very similar to a change in N_s and the two parameters cannot actually be varied independently. We see from the comparisons that the match of the numerical simulation is fairly sensitive to changes in fluid velocity and the values of equilibrium constants. Although the equilibrium constants were varied slightly for the best fit, the actual values used were all within the range of variation of the measured values.

The above cases show that CHEMTRN can be used with confidence to model chemical transport in porous media. It was then used to consider the validity of using a k_D type of model to simulate chemical transport of radionuclides away from nuclear waste repositories. Many workers in the area of contaminant transport have assumed that the transport of toxic wastes in a groundwater can be calculated using the constant retardation factor. Elementary ion exchange theory predicts that the distribution coefficient is approximately independent of the concentration of the ion of interest when the latter is extremely low relative both to the concentration of the supporting electrolyte and the cation exchange capacity. Under these conditions, the ionic strength of the solution is determined mainly by the supporting electrolyte and

is approximately constant; therefore, activity coefficients of both sorbed and dissolved species remain constant. In addition, since the anionic composition of the solution remains approximately constant, the degree and effects of complexation are invariant. When the aqueous phase concentrations of sorbable ions are comparable, then site competition, complexation, and ionic strength effects are expected to result in variable distribution coefficients.

Figure 4.5 shows calculations done using CHEMTRN when competition for sites on the solid matrix affects the sorption of the radionuclides. In this case the groundwater consisted of 10^{-4} Na^+ , 10^{-5} Ca^{2+} , 10^{-8} Sr^{2+} , 4.5×10^{-5} CO_3^{2-} , and 3×10^{-3} Cl^- (concentration units of moles/l solution) where the calculated value of k_D varies from 5000 for the initial conditions to 2000 for the inner boundary condition. Plotted in the figure is the solution assuming that the sorption of Sr^{2+} follows a constant k_D model with k_D equal to 2000. The constant k_D model is inaccurate when compared to the numerical solution which includes site competition. The bulk of the Sr^{2+} is transported at a slightly faster rate than predicted by a constant k_D model with a k_D of 2000. As Sr^{2+} is sorbed, Ca^{2+} and Na^+ are displaced from the solid matrix. Simplifying the equations by assuming only sorption, the mass conservation equation for Sr is

$$\frac{\partial m_{\text{Sr}}}{\partial t} + \frac{\partial \bar{m}_{\text{Sr}}}{\partial t} = D \frac{\partial^2 m_{\text{Sr}}}{\partial x^2} - v \frac{\partial m_{\text{Sr}}}{\partial x}.$$

However, $\partial \bar{m}_{\text{Sr}} / \partial t$ can be written in terms of the changes in the basis species Na^+ , Sr^{2+} , and Ca^{2+} . Therefore,

$$\frac{\partial m_{\text{Sr}}}{\partial t} + \frac{\partial \bar{m}_{\text{Sr}}}{\partial m_{\text{Sr}}} \frac{\partial m_{\text{Sr}}}{\partial t} + \frac{\partial \bar{m}_{\text{Sr}}}{\partial m_{\text{Ca}}} \frac{\partial m_{\text{Ca}}}{\partial t} + \frac{\partial \bar{m}_{\text{Sr}}}{\partial m_{\text{Na}}} \frac{\partial m_{\text{Na}}}{\partial t} = D \frac{\partial^2 m_{\text{Sr}}}{\partial x^2} - v \frac{\partial m_{\text{Sr}}}{\partial x}.$$

As seen from these equations, the sorption of Sr^{2+} depends on the changes of Na^+ and Ca^{2+} as well as Sr^{2+} concentrations in the aqueous phase. When the changes in concentration of the background ions become important, the constant k_D model overpredicts the sorption of Sr^{2+} . It is also noted that low levels of Sr^{2+} are transported for much longer distances at a level just slightly greater than the background level.

However, the Sr^{2+} concentration plotted consists of both the strontium from the waste form and that which was initially sorbed on the rock matrix.

A k_D model can be reasonable in many cases, even when the value of the k_D is varying throughout the groundwater. Figure 4.6 is a plot of the concentration of Sr^{2+} when the concentration of Ca^{2+} is not important and Sr^{2+} is primarily exchanging with Na^+ . The computed value of the k_D varies from an initial value of 5000 to a value of 2000 at the boundary. Although the computed value of k_D is varying, the amount of Na^+ that is being displaced from the solid surface does not change the background concentration significantly. We get reasonable results for the sorption of Sr^{2+} using a simple constant retardation of 2000 as shown in the figure.

Many solids common to natural systems (e.g., silica) exhibit surface amphotericism, i.e., they possess ionizable surface sites, the amounts and types of which are determined by the pH of the surrounding aqueous solution. For these materials, sorption can be thought of as taking place by surface ionization and complexation [Davis et al., 1978] instead of by simple ion exchange. Distribution coefficients in such systems may be strong functions of pH and solution composition even when contaminant species are present in trace amounts. In addition a charged layer can develop at the surface so that both cations and anions can be sorbed. As stated above, a cation with a charge greater than unity can be sorbed at a single surface site in the surface complexation model; this contrasts strongly with the ion exchange model wherein a cation must displace an equal amount of charge. A cation with a +2 charge might be sorbed more easily if it had to form a bond with only one surface site instead of two adjacent ones.

Figure 4.7 is an example where surface complexation has been used to model the sorption of lead in the form of Pb^{2+} and PbOH^+ on $\gamma\text{-Al}_2\text{O}_3$. The data for the reactions and the needed constants are taken from Davis and Leckie [1978]. For the dissociation of a site (reaction R4) a pK of 11.5 was used and for the formation of a site with a positive charge (reaction R5) a pK of 5.7 was used. The background electrolyte was NaClO_4 and the pK's for the sorption of the background cation and anion were 9.2 and 7.9 respectively. Following the discussion of Davis and Leckie [1978], Pb^{2+}

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primarily forms a complex with only one surface site instead of two. A surface site density of 8 sites/nm² and a surface area of 117 m²/g were used. For this example, the total concentration of Pb in the aqueous phase was assumed to be 2.9×10^{-4} moles/l solution and the pH of the solution was 7. Then a feed solution equivalent to the initial solution but with a pH of 4.5 was introduced at $x = 0$ at a velocity of 0.1 m/hr. Plotted in Figure 4.7 are the concentrations of aqueous Pb²⁺, PbOH⁺, H⁺ and sorbed Pb in the form (SO⁻Pb²⁺) and (SO⁻PbOH⁺) and sorbed H⁺ in the form of SOH after 5 hours. As seen in the figure, the concentration of the Pb²⁺ ion in the aqueous phase is approximately constant. The ratio of the total amount of sorbed Pb to the total aqueous phase concentration varies from 18 initially to almost 0 at the boundary. This surface complexation model clearly gives a vastly different extent of sorption than the simple k_D model.

The surface complexation model has not been directly compared to the ion exchange model because of the fundamentally different types of reactions which are considered in the two cases, i.e., Pb²⁺ is forming a bond with only one surface site in the surface complexation case while it must form a bond with two sites in the ion exchange case. However, the equations describing ion exchange would produce a change in sorption proportional to $[PbOH^+][SOH]/[H^+]$ which is not the case here. This quantity changes from a value of 2 initially to a value of 4.8×10^{-5} at the boundary. The variation results from the change in the number of available sites for sorption because of the change in the surface charge for different pH values.

Precipitation/dissolution of solids is also included in the model. To illustrate the capability of CHEMTRN in this respect, it was used to simulate precipitation when a Na⁺-rich solution flows into a one-dimensional column of porous medium which has Ca²⁺ sorbed on the solid. Initially, the fluid in the column consists of 1.5×10^{-3} Ca²⁺, 10^{-5} Na⁺, 6.6×10^{-4} CO₃²⁻, a pH of 8 and enough Cl⁻ to balance the solution electrically. Then a solution that has a higher level of Na⁺ (1.1×10^{-2}) is fed into the column. The Ca²⁺ ion is displaced from the solid matrix. The conditions of the fluid were set so that the solubility product of CaCO_{3(s)} would be exceeded

downstream from the boundary. The boundary condition maintained at $x = 0$ is a constant concentration condition although a flux boundary condition could also be imposed. The dissociation of water and the formation of the complexes NaCO_3^- , NaHCO_3^0 , NaOH^0 , HCO_3^- , H_2CO_3^0 , CaCO_3^0 , CaHCO_3^+ , and CaOH^+ were included in the calculation. Plotted in Figure 4.8 is the amount of precipitate $\text{CaCO}_{3(s)}$ that forms as the Na^+ -rich solution flows into the column at a velocity of 0.1 m/hr. As the time increases from 0.1 hr to 10 hours, more precipitate forms downstream. After 5 hours, the level of Ca^{2+} near the boundary starts to decrease and some of the precipitate begins to redissolve. We see that after 10 hours, all the solid precipitate has redissolved at the first node point.

To illustrate the effect of including precipitation of $\text{CaCO}_{3(s)}$ in the calculations of the above example, Figure 4.9a is a plot of the ions Ca^{2+} , Na^+ , CO_3^{2-} , and OH^- as a function of distance after 5 hours when the precipitation of $\text{CaCO}_{3(s)}$ is ignored and Figure 4.9b is the case when precipitation is included. The initial pH in both of these cases is 8 and the pH of the feed solution is 12. In Figure 4.9a, two distinct chemical mechanisms can be seen. First Na^+ displaces Ca^{2+} from the solid matrix and we see a substantial increase in the aqueous concentration of Ca^{2+} . Secondly, as the solution with the higher pH is feed into the column, the concentration of CO_3^{2-} increases. As the concentration of H^+ is decreased, the concentration of H_2CO_3 decreases proportional to $[\text{H}^+]^2$ shifting the equilibrium concentration toward CO_3^{2-} . The change in the concentration of the other complexes competing for CO_3^{2-} does not compensate for the shift resulting in a significantly increased level of CO_3^{2-} . However, when the precipitation of $\text{CaCO}_{3(s)}$ is included, the level of the carbonate ion is reduced. Although the Ca^{2+} ion is being depleted as well, the change in CO_3^{2-} is proportionally greater because it is already a magnitude lower in concentration. The change in the concentration of OH^- is also seen to be much steeper in Figure 4.9b than in Figure 4.9a. The concentration of Na^+ is not affected strongly by the inclusion of $\text{CaCO}_{3(s)}$ because the concentration of the complexes NaOH^0 , NaHCO_3^0 , and NaCO_3^- which would provide this interaction are significantly lower than the concentration of Na^+ .

For the case where the transport of Sr^{2+} is considered, the inclusion of the precipitate $\text{CaCO}_3(s)$ was not found to be important. Figure 4.10 is a plot of the concentration of Sr^{2+} when precipitation of $\text{CaCO}_3(s)$ is included in the calculations. For this example, the initial conditions are $1.6 \times 10^{-3} \text{ Na}^+$, 10^{-10} Sr^{2+} , $2 \times 10^{-4} \text{ Ca}^{2+}$, a pH of 7 and a total concentration of 1.8×10^{-3} of CO_3^{2-} in the aqueous phase. At the inner boundary solid SrCO_3 is assumed to be in equilibrium with the initial groundwater. As Sr^{2+} and CO_3^{2-} is leached into the groundwater, $\text{CaCO}_3(s)$ forms at the boundary. The principal effect of including the formation of this solid, is the increased equilibrium concentration of Sr^{2+} in the groundwater at the waste canister. Because strontium is not strongly complexed, there is little interaction between the changes downstream and the transport of Sr. Figure 4.10b is a plot of the amount of precipitate for this case and the concentration of the ions CO_3^{2-} and Ca^{2+} . The fluid velocity used for this example was 0.1 m/yr.

SUMMARY AND CONCLUSIONS

CHEMTRN, a transport model which accounts for many equilibrium chemical processes common to hydrochemical systems, has been developed. CHEMTRN provides for complexation in the aqueous phase and treats sorption as either an equilibrium ion exchange or a surface complexation process. The sorption algorithm specifies a constant finite surficial density of exchange sites for cations in the case of ion exchange or a variable density of sorption sites in the case of surface complexation and accounts for competition among different species for occupancy of those sites. CHEMTRN also includes algorithms describing the dissociation of water, the non-ideality of both sorbed and solute species and the precipitation/dissolution of solids.

Several calculations have been made with CHEMTRN to determine the accuracy of the model and the necessity for inclusion of specific chemical processes in this and other models used to predict contaminant transport.

From the results of the calculations given here and those presented in Miller and Benson [1982], several conclusions can be drawn:

1. CHEMTRN has been used to simulate a problem with a known analytical solution and excellent results were obtained.
2. Good results were obtained when CHEMTRN was used to simulate a field test where ion exchange was the principal chemical mechanism.
3. When the concentration of a positively charged contaminant is extremely small relative to the concentration of the supporting electrolyte (e.g., NaCl) and the CEC of the sorbing material, the distribution coefficient (k_D) of the trace ion is constant. If dissolution of the wasteform does not alter the groundwater composition, a k_D model could be used to simulate the transport of this trace ion. However, the distribution coefficient would have to be measured or calculated in a manner designed to duplicate exactly the situation expected to exist in the near-wasteform region at all times after loss of wasteform integrity. In addition, it should be noted that the definition of *trace* for each cation of interest must be determined experimentally.
4. When the number of sorbing sites is not a strong function of pH but when the concentration of the contaminant is comparable to the concentration of the principal exchanging ions, a constant distribution coefficient model is inadequate to simulate the mass transport process.
5. When the number of sorption sites is a strong function of pH, a constant distribution model is inadequate.
6. Migration of a non-trace contaminant far ahead of where it is initially strongly sorbed was found to occur when surface site constraints were included in the model. This phenomenon is not adequately accounted for in models which employ constant distribution coefficients.
7. Incorporation of aqueous complexation in the model does not significantly

enhance the mobility of a weakly complexed species such as strontium. However, other radionuclides such as the actinides may be strongly complexed in groundwater to the point that only a minimal fraction of the element may exist as positively charged species [Langmuir, 1978]. Therefore, the incorporation of complexation phenomena in models of nuclear waste transport appears a necessity for these radionuclides.

8. Allowing water to dissociate resulted in profound effects on the chemistry of the system. The dissolution of the wasteform at the inner boundary can buffer the pH of the groundwater. In addition, the inclusion of the dissociation of water allows pH to vary along the transport path. This, in turn, causes changes in the the amount and type of complexes formed and the amount of sorption possible.
9. Precipitation/dissolution of solids will effect the transport of radionuclides only if the radionuclide precipitates out itself, or if it is strongly complexed such that changes in other species in the groundwater is linked to the changes in the radionuclide. Effect of changes in porosity were not considered here.

In general, the results of simulations with several chemical algorithms in the model CHEMTRN indicate that the assumption of a constant distribution coefficient (k_D) for interphase mass transfer cannot adequately account for changes of chemical composition of either bulk or trace chemical constituents in groundwater. A higher level of chemical complexity is needed using thermodynamic equilibrium constants for all chemical reactions, using activity corrections via activity coefficients, accounting for changes in ionic strength, accounting for finite exchange or sorption capacity of the solid phase and competition for sorption sites among aqueous species, accounting for complexation of aqueous species, the ability to compute variations of pH, and the ability to account for precipitation/dissolution equilibria of secondary solid phases. In addition, system with variable Eh will require algorithms for oxidation-reduction reactions and significant precipitation or dissolution may require the ability to simulate

changes of flow velocity caused by increases or decreases of porosity. These effects have not been simulated by CHEMTRN, but are regarded as necessary components of an adequate transport model.

These requirements for adequacy in geochemical transport modeling imply corresponding needs for thermodynamic, chemical, and mineralogical data to be used as input to chemical algorithms. These data include thermodynamic equilibrium constants for aqueous complexation, ion exchange, and surface complexation reactions, specific sorptive capacities of solid phases (as functions of pH if appropriate), and free energies of formation of solid phases and the aqueous species in equilibrium with them. Many of these data exist within various geochemical data bases and can be integrated into a single data base to be used selectively in applications to specific geochemical transport systems. Other data do not exist and would have to be measured experimentally in order to implement algorithms in specific systems. For example, equilibrium constants appropriate to surface complexation reactions have been determined for only a very limited number of chemical systems, and many of those that have been measured have little relevance to the transport of nuclear waste. As another example, the mechanism of sorption of actinide element species by surfaces of silica and smectites has not been defined; experiments would have to be done to determine if the mechanism is ion exchange, surface complexation or another process such as Langmuir sorption. Unfortunately, practically all of the measurements of k_D values made over the past fifteen to twenty years are useless as input to thermodynamically based chemical algorithms.

RECOMMENDATIONS FOR CONFIRMATORY TESTS

A need exists for data which could not only assist in validation of chemical algorithms used in CHEMTRN and other transport models, but also extend a model's applicability to a wide variety of chemical systems. Such data might be obtained from field and laboratory experiments, from study of existing occurrences of waste transport, and from examination of natural analogs of waste disposal sites and their environs.

At present it is not possible to define a large-scale, field experimental plan for verifying chemical algorithms because of current lack of an adequate description of hydrodynamic dispersion on a large-scale. Hydrodynamic dispersion coefficients estimated from large-scale field experiments reported in the literature exhibit generally non-predictable dependence on the spatial scales of the experiments caused by non-quantifiable heterogeneities in the geologic media. Thus, until a better means for modelling hydrodynamic dispersion on a large scale is found, uncertainties in this transport parameter could overwhelm variations due to purely chemical effects. On the other hand, current descriptions of hydrodynamic dispersion appear to be adequate for modelling small-scale transport systems in which the porous medium is known, or can be assumed, to be homogeneous.

Thus, results of laboratory experiments on chemical transport through engineered barrier materials could be used to predict the behavior of large scale, homogeneous, engineered barriers with a high level of confidence. Similarly, small-scale field experiments such as that described earlier in this report can be used to provide validation of a model's ability to predict chemical behavior during transport through natural materials in the near field. It is recommended that small-scale laboratory and field experiments of these types be conducted with chemical systems including the most significant fission products and actinide elements. For example, the transport of wastes from the N-Reactor disposal area at the Hanford site would fall in this category.

On the other hand, comparisons of natural analogs with transport model predictions would furnish tests of the predictions over time periods comparable to or longer than those applicable to a waste repository. It is recommended that natural occurrences containing long-lived radio-elements be studied to determine how these elements migrate from sites of origin in response to long-term natural processes, and that the data developed be used as reference standards for model predictions. Two natural occurrences of particular interest which are now under investigation are the Ranger No. 1 and the Jabiluka No. 1 uranium deposits of the East Alligator Rivers uranium fields in the Northern Territory of Australia (Birchard, 1982).

This experimental program would not only help define the level of sophistication needed in geochemical models, but would also assist the NRC toward resolution of several other key issues in their review of the national geochemistry program. These issues are definition of the proper laboratory procedures required to assess the retardation properties of a site, the extent to which laboratory results can be utilized in lieu of field tests, definition of the levels of accuracy and confidence required in site determinations of radionuclide migration, and comparison between natural analogues and the results of modelling.

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XBL 8210-3128

4.1 Comparison of analytical solution and numerical simulation using CHEMTRN

4.2 Comparison of analytical solution and numerical simulation using CPMTRN for transport of a sorbing species. Analytical solution assumes a k_D type of model for sorption.

4.3a Comparison of field test [Valocchi et al., 1981] with numerical simulation using CHEMTRN for the exchanging ion Ca²⁺.

XBL 829-2434

XDL 029-2435

4.3b Comparison of field test [Valocchi et al., 1981] with numerical simulation using CHEMTRN for the exchanging ion Mg^{2+} .

4.4a Sensitivity of the fluid velocity in obtaining the best fit of the numerical simulation to the field data [Valocchi et al., 1981].

XBL 029-24346

4.4b Sensitivity of the cation exchange capacity in obtaining the best fit of the numerical simulation to the field data [Valocchi et al., 1981].

XBL 829-2434C

4.4c Sensitivity of the equilibrium exchange constants in obtaining the best fit of the numerical simulation to the field data [Valocchi et al, 1981] for the exchanging species Ca^{2+} .

XBL 829-2434A

XBL 829-2435A

4.4d Sensitivity of the equilibrium exchange constants in obtaining the best fit of the numerical simulation to the field data [Valocchi et al., 1981] for the exchanging species Mg^{2+} .

4.5 Comparison of ion exchange model with a k_D type of sorption model when changes in the background electrolyte concentrations are important

XBL 6210-2592

4.6 Comparison of ion exchange model with a k_D type of sorption model when changes in the background electrolyte concentrations are not important.

4.7 Sorption of lead using a surface complexation model.

XBL B210-3131
4.8 Precipitation of $\text{CaCO}_3(s)$ as a function of distance and time.

XBL 8212-4976

4.9a Concentration of Ca^{2+} , OH^- , CO_3^{2-} , and Na^+ as a function of distance after 5 hours when $\text{CaCO}_{3(s)}$ is allowed to precipitate.

XBL 8212-4975

4.9b Concentration of Ca^{2+} , OH^- , CO_3^{2-} , and Na^+ as a function of distance after 5 hours when $\text{CaCO}_3(s)$ is not allowed to precipitate.

XBL 8210-2593

4.10 Concentration of Sr^{2+} as a function of distance after 15 yrs when the precipitation of $\text{CaCO}_3(\text{s})$ is included and when it is not included.

XBL 8210-2594

4.11 Concentration of Ca^{2+} , CO_3^{2-} , and $\text{CaCO}_3(\text{s})$ for the examples plotted in Figure 10.

5. TASK 5. GEOLOGIC SYSTEMS AS ANALOGUES FOR LONG-TERM RADIOACTIVE WASTE ISOLATION (H. A. Wollenberg and S. Flexser, Lawrence Berkeley Laboratory D. G. Brookins and M. Abashian, University of New Mexico L. H. Cohen and A. E. Williams, University of California, Riverside)

INTRODUCTION

The ability of host rocks in the near-field repository environment to retain radionuclides and to inhibit their transport into and through the groundwater system, is an important consideration of nuclear waste isolation. During Fiscal Year 1982, three natural occurrences in rock types considered likely candidates for repository hosts in the United States--tuff, basalt, and bedded salt--were investigated as to their abilities to retain radionuclides and inhibit their transport. The three occurrences were all "fossil", in that the intrusive events that introduced radioelements occurred several million to hundreds of millions of years ago. Therefore, the distribution of radioelements in and around these occurrences, observed today, has resulted not only from the initial intrusive event, but also from events subsequent to the intrusion. By examining chemical contents of the intrusive and host rocks, chemical gradients at or away from the contacts between them, and (in the cases of basalt and tuff) the loci of radioelements in the rock matrix and fracture filling material, one obtains indications both of the gross retentivity of the rocks over time, and more importantly, of the movement of radioelements in the fracture-controlled hydrologic system. The chemical distributions observed at these natural occurrences

furnish the initial data for entry into models that predict the transport of radionuclides, and will be compared with distributions predicted and subsequently observed at candidate repository sites. This will furnish valuable input to the assessment of site characterization reports and, ultimately, to the evaluation of license applications.

Activities in the first project year emphasized occurrences in granitic rock: the contact between a Tertiary quartz monzonitic stock and Precambrian country rock, and discrete uranium-rich veins in granite and quartz monzonite. Investigation of samples from the former locality were described by Flexser and Wollenberg (1982) and Brookins et al. (1981), and from the latter occurrence by Shea (1982), and indicated that no significant migration of radioelements or fission-product analog elements occurred from the intrusive or the veins into the country rock.

Activities in Fiscal Year 1982 emphasized investigation of the effects of a monzonitic intrusive into tuffaceous terrane. Samples were also collected and preliminary analyses made of contact zones between a dike in bedded salt and intrusive rocks in contact with basalt of the Columbia River plateau.

TUFF

At the occurrence at Eldora, Colorado there was apparently no circulating hydrothermal system accompanying or subsequent to the intrusion of quartz monzonitic magma into a Precambrian crystalline terrane (Brookins et al., 1981). In contrast, the presence of strong hydrothermal circulation in tuffaceous rock in response to the intrusion of the Alamosa River stock

near Platoro, Colorado was evident from oxygen isotope ratios measured by Williams (1980) on samples collected over a broad region. Based on this evidence, we have investigated the contact zone and areas away from the contact between the stock and the intruded La Jara member of the Treasure Mountain tuff, primarily to determine if there was any movement of radioelements and fission-product-analog trace elements from the monzonite into the tuff, or within the tuff, in response to the circulating hydrothermal system.

The Platoro caldera complex which encompasses the Summitville and Platoro calderas and the Alamosa River stock, has been described by Lipman (1975). The stock, of monzonitic composition, was emplaced at 29.1 ± 1.2 MYBP into predominantly andesitic volcanics forming and filling caldera structures. The La Jara is predominantly a welded ash flow tuff, ejected by an explosive event at 29.8 ± 1.2 MYBP (Lipman, 1975). Lipman describes the La Jara as a multiple ash flow cooling unit, predominantly of phenocryst-rich quartz latite. The tuff is primarily densely welded and devitrified, the rock dark gray and propylitized; silica contents average 65%.

The Alamosa River stock in the area sampled consists of fine to medium grained equigranular monzonite, ranging in silica content from 57 to 62%.

Based on analyses of oxygen isotope ratios in 260 minerals and whole-rock samples from the Alamosa River stock region, Williams (1980) suggested that the heat from the stock and other small intrusions initiated extensive hydrothermal circulation. A roughly concentric aureole of $\delta^{18}O$ depletion was noted by Williams around the south and east margins of the stock, with depletion enhanced along two major faults, attesting to the importance of

fracture permeability in the circulation of this system. Temperatures of the hydrothermal system were estimated to be in the range 250-370°C.

For our studies, samples from the Alamosa River stock area were collected at several locations as shown in Figure 5.1. A detail traverse was made across the intrusive - tuff contact, as well as regional traverses in the tuff and in the andesite away from the stock, for subsequent examination of the distribution of radio- and trace elements. The results of these analyses will allow us to evaluate the extent and magnitude of migration and transport of these elements in a convective setting in the tuffaceous rocks.

Petrographic examination of thin sections shows that the monzonite intrusive is composed, in order of abundance, of interlocking laths of plagioclase feldspar, finer interstitial K-feldspar and quartz, and biotite and pyroxene. Accessory minerals include apatite, zircon, and sphene. Alteration of primary minerals is common, and increases in intensity closer to the contact with the tuff. Pyroxene is altered to opaque minerals, chlorite, fine biotite and sphene; primary biotite is partly altered to chlorite. Monzonite within 10 m of the contact has fine biotite-chlorite stringers emanating from altered mafic grains, and within 4 m of the contact, plagioclase is significantly altered to sericite.

The tuff is seen in thin section to be rich in phenocrysts, mostly plagioclase, with lesser K-feldspar, biotite and pyroxene. The matrix interstitial to the phenocryst grains is composed of a very fine mosaic of feldspars and quartz, which probably formed by crystallization of a primary glass phase. The matrix shows occasional evidence of primary

Figure 5.1. Simplified geologic map, showing location of samples and traverses near Platoro, Colorado.

XBL 621-1622

welding textures, but in most samples those textures have been destroyed by crystallization and alteration.

Alteration of the tuff related to the monzonite contact has affected both the phenocrysts and the interstitial matrix. The matrix shows a progression of alteration beginning with the development of calcite, intergrown in the fine quartz-feldspar mosaic, within 60 m of the contact. This is followed within 40 m of the contact by the appearance of chlorite and sericite, and by stringers and overgrowths of quartz which increase in abundance and coarseness toward the contact. Epidote also becomes a common matrix alteration within 12 m of the contact. Phenocryst alteration in the tuff more than 60 m from the contact is mainly confined to biotite, which is partly altered to fine opaque grains and sphene. Closer to the contact, pyroxene grains are altered to an opaque mineral, probably magnetite, and within 30 m of the contact biotite grains have been reduced to mere streaks of fine opaque grains, with associated epidote and sphene.

The distribution of uranium in rocks of the Platoro contact zone, represented by a traverse at Telluride Mountain (Figure 5.1), was examined by fission-track radiography. Uranium in the monzonite is mainly confined to minute accessory grains (probably zircon) which occur most typically in grains of potassium feldspar. Uranium also occurs, though more rarely, with altered mafic grains in monzonite close to the contact, and is probably associated there with very fine sphene. In contrast to the monzonite, the tuff rarely contains uranium-bearing accessory grains. Instead, U in the tuff usually occurs in low concentrations in the fine feldspar-quartz intergrowth comprising the matrix between phenocryst grains. The actual

monzonite and tuff, identifiable in thin sections, is marked by a dense intergrowth of epidote and lesser sphene. Uranium is often associated there with sphene, but is otherwise absent from the contact. The contact is also cut by fine hematite-filled fractures extending into adjacent tuff and monzonite. Uranium does not appear to be associated with these fractures within the immediate contact zone or on either side of the contact.

Results of neutron activation analyses of some trace elements in samples of monzonite and tuff from the meter-scale traverse across the contact at Telluride Mountain have been plotted, and comprise Figure 5.2. (Detailed discussion of the results is covered in a recent paper by Brookins et al. (1982)). Strong contrasts between monzonite and tuff are evident, with higher contents of Cs, Rb, Sc, V, Fe, Th, U and Co in the monzonite. On the 10-meter scale of sampling, there are suggestions of gradients in Cs, Th and Co in the tuff, with abundances of these elements increasing towards the contact. In general, the elements studied except for Cs, Th and Co, show no evidence for migration between stock and intruded rocks. Elemental distribution in the rocks appears to be mineralogically controlled, and local whole-rock chemical variations reflect mineralogical variations. On a broader scale, analyses of samples from the Conejos River traverse (Figure 5.3), extending several kilometers from the contact, indicate that there are no apparent chemical gradients to match the regional gradients in whole-rock $\delta^{18}\text{O}$ in the La Jara tuff.

The rare earth distribution for samples of La Jara tuff taken 10, 25, and 45 meters from the contact with the Alamosa River monzonite are shown in Figure 5.4. The curves are virtually identical for the light rare

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Figure 5.2. Variation in element contents between monzonite and tuff, Telluride Mountain traverse.

Figure 5.3. Variation of element contents between monzonite and tuff over several kilometers.

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Figure 5.4. REE distribution in tuff near monzonite contact.

earths and show some scatter, part of which may be experimental, for the mid- to heavy-rare earths. Five other tuff samples would plot within the limits of the curves shown here.

At about 6 km from the contact several basic volcanic inclusions are found in the tuff. Figure 5.5 shows the rare earth distribution for one such inclusion (A26b), the tuffaceous host rock in contact with the inclusion (A26a), and tuff several km from this site (A20). The curves for the two tuffaceous samples show good agreement with each other and with the curves shown in the other figures. The inclusion shows a slightly different pattern which may or may not be real; gamma spectrometry of the sample did not reveal any anomalous U, Th or K distribution in the vicinity of the inclusions.

An epidotized breccia zone at the contact between the monzonite and La Jara tuff has been sampled in detail. The breccia samples were divided into a dark green, epidote-rich sample (14a) and an epidote poor sample (14b). The stock sample, 15, was collected two meters from the contact. The epidote-rich sample possesses a low total REE content (Figure 5.6). The epidote-poor sample shows a pattern very similar to that of from the monzonite. When compared to all other data, the tuffaceous, epidote-rich sample is depleted in the REE, and this may be due to the effect of the intrusion, hydrothermal activity or other factors.

Oxygen isotope data have been obtained for samples from the Telluride Mountain traverse. $\delta^{18}\text{O}$ values of the tuff show a wide variation, ranging from +0.8 ‰ to +3.6 ‰ in the zone within 60 m of the contact. Values in the monzonite within 10 m of the contact are +2 ‰. The general degree

Figure 5.5. REE distribution in tuff and basic inclusion.

Figure 5.6. REE distribution in monzonite and tuff.
 Monzonite (A-15), contact breccia zone (14a),
 monzonite - tuff (14b).

of depletion in the monzonite and in the tuff is consistent with previous data (Williams, 1980). However, the ^{18}O depletion does not, on the scale examined in the Telluride Mountain traverse, show any consistent gradient away from the intrusive in the tuff. Local fracture permeability variations appear to control the variations observed in the ^{18}O depletion of any specific sample. Although rock samples from the Telluride Mountain traverse are quite variable in $\delta^{18}\text{O}$, they are all significantly depleted relative to normal igneous rock. Water-rock mass ratios greater than 0.1 are implied for even the least ^{18}O - depleted samples. The samples lowest in $\delta^{18}\text{O}$ indicate water/rock values greater than 0.3.

With regard to the Platoro occurrence, the following conclusions are stated:

1. The oxygen isotopic studies show the effect of extensive hydrothermal activity on the intruded rocks, as well as the host tuffaceous and flow rocks.
2. Convective cooling has been demonstrated by Williams (1980) for the Alamosa River Stock.
3. The distribution of U, Th, REE, V, K, Ti, in each rock is apparently unaffected by the intrusion or is the result of complete homogenization by the hydrothermal circulation. This is true also for Rb, Sr, and others, although for some of these elements there is no strong chemical gradient between the rocks.
4. Within ten meters of the contact, some elements show evidence for contact zone mobility.
5. Both monzonite and tuff have essentially retained their bulk chemistry during and after intrusion.

6. The absence of discernable large-scale elemental migration between the tuff and monzonite, even in a convective system, supports continued assessment of such rocks for nuclear waste repository consideration.

BASALT

Sites were identified in the Pacific Northwest (Figure 5.7) where intrusive rocks cut basalt of the Columbia River plateau. A quarry near Wind Mountain in the Columbia River Gorge, Washington, provided samples of large (meter-scale) xenoliths of basalt in diorite - quartz diorite, and samples were obtained of fractured and unfractured rock, centimeters and decimeters away from contacts between these rock types. At a second site, a quarry on the East fork of the Hood River, Oregon, a rhyodacite dike cuts basalt of the Frenchman Springs member of the Wanapum Formation. Typical major-element analyses of the intrusives and basalt are listed in Table 5.1.

Sites in the western Cascade Range, Oregon, were also examined where intermediate or felsic dikes and stocks intrude andesitic and basaltic flows and volcanoclastic rocks (Peck et al., 1964). At one of these locations, a mineralized, hydrothermally altered granodioritic pluton intruding andesitic flows near Nimrod in the canyon of the McKenize River, field gamma spectrometry indicated relatively high radioelement contents in the pluton in contrast to lower contents in the andesite. However, where road access is available, the contact is concealed by slope debris. Also, this location is less definitive an analog than the quarries in basalt on the Hood River or at Wind Mountain, because the andesite flows at Nimrod are variable in thickness and are intercalated with numerous volcanoclastic horizons.

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Figure 5.7. Location map, sampling sites in the Columbia River - Hood River area.

Table 5.1. Published Chemical Analyses of Basalt and Intrusive Rocks in the Columbia River-Hood River Region.

(Percent)				
	(1)	(2)	(3)	(4)
SiO ₂	53.8	50.3	65.7	71.7
Al ₂ O ₃	13.9	13.1	17.4	13.6
Fe ₂ O ₃	2.6	13.2	1.9	1.8
FeO	9.2		2.0	
MgO	4.1	4.0	2.1	0.3
CaO	7.9	7.1	3.4	1.4
Na ₂ O	3.0	2.2	4.5	4.0
K ₂ O	1.5	1.2	1.1	3.7
TiO ₂	2.0	7.1	0.8	1.4
P ₂ O ₅	0.4		0.3	
MnO	0.2	0.2	0.03	0.04
H ₂ O	1.2		0.4	

(ppm)		
	(4)	(2)
Rb	120	190
Cs	2	5
Ba	600	640
Hf	5.4	5.0
Cr	2	40
Co	3	37
Ni	<10	<30
Sc	2.3	37.7
Zn	15	4.5
Ta	1.3	0.84
La	25	23
Ce	56	52
Nd	15	27
Sm	2.6	6.3
Eu	0.66	2.2
Tb	0.41	1.0
Dy	2.5	7.9
Yb	1.7	3.7
Lu	0.22	0.54
U	4.5	1.3

KEY TO COLUMN NUMBERS

- 1) Average Yakima Basalt (Waters, 1961)
- 2) Frenchman Springs Member, Wanapum Formation Basalt, quarry on Hood River (Wollenberg, et al., 1979)
- 3) Quartz Diorite, Wind Mountain, Washington (Wise, 1970)
- 4) Felsic Dike, quarry on Hood River, Oregon (Wollenberg, et al., 1979)

The samples of flood basalt and intruding rocks from the Columbia Gorge and Hood River sites were analyzed for radioelement contents by laboratory gamma spectrometry. At the Wind Mountain quarry, a basalt xenolith in contact with quartz diorite was sampled on a centimeter scale, near and away from the contact, and two samples were obtained of the quartz diorite. Variations in radioelement contents are plotted in Figure 5.8. The apparent depletion of U and Th in basalt at the contact supports Free's (1976) thesis that assimilation of basaltic material occurred with intrusion of the quartz diorite. The U, Th, and K contents of the basalt xenolith at Wind Mountain are considerably lower than those of basalt farther from the quartz diorite contact at Shellrock Mountain on the opposite side of the Columbia River. There is greater contrast in radioelement contents of basalt and quartz diorite at Shellrock Mountain than at the basalt xenolith/quartz diorite contact zone at the Wind Mountain quarry, also supporting the assumption of assimilation of components of the basalt by the quartz diorite at Wind Mountain.

Results of laboratory gamma spectrometric analyses of the sample set from the Robin Hood quarry on the East fork of the Hood River are listed on Table 5.2, and the distribution of U and Th contents plotted on Figure 5.9. This occurrence is considered to be more analogous to waste repository conditions than the sites in the Columbia Gorge, because of the sharp contrast in radioelements between the rhyodacite dike and the basalt. More detailed examination of fracture orientation, and analyses of fracture-surface and fracture-filling material by neutron activation and radiographic

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Figure 5.8. Variation of uranium and thorium in a basalt xenolith and quartz diorite at the Wind Mountain Quarry, Washington.

Table 5.2. Radioelement Contents of Dike in Contact with Basalt; Quarry, Hood River, Oregon.

Sample	U(ppm)	Th(ppm)	K(%)	Distance from contact (m)
DIKE				
RQ 1	3.68	12.3	2.59	2.23
RQ 2	3.90	14.4	3.18	1.64
RQ 3-1	4.43	13.1	3.11	0.82
RQ 3-2	5.48	14.5	3.72	0.82
RQ 4	3.89	11.5	3.09	at contact
BASALT				
RQ 5	1.15	4.34	1.25	at contact
RQ 5 (sample inverted)	1.06	4.02	1.06	at contact
RQ 6	1.21	4.27	0.84	0.3
RQ 7	1.31	4.41	0.88	0.87
RQ 8	0.53	3.64	0.47	1.38
RQ 9	0.89	3.23	0.75	1.59
RQ 10	1.19	4.11	0.92	2.69
RQ 11	1.03	3.58	0.90	5.23

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Figure 5.9. Variation of uranium and thorium in a rhyodacite dike and basalt at a quarry on the East Fork of the Hood River, Oregon. Error bars on ordinates indicate standard deviations for samples of the two rock types.

methods may indicate whether radionuclides moved preferentially through the basalt's fracture system at the time of, or subsequent, to intrusion of the dike.

SALT

A condition analogous to a repository in bedded salt might be provided by the occurrence of a dike intruding salt beds. Such occurrences are located in the Delaware Basin salt beds of southeastern New Mexico, in salt beds of the Salina Basin in northwestern New York, and in salt beds of the Zechstein in West Germany. From the latter deposit we were fortunate to receive, through the good offices of William T. Holser and Robert Kuhn, a set of samples of basaltic dike rock and adjacent bedded salt from the Kalibergwerke Mine, Hattorf, Philipstahl, West Germany (written communications, 1981). Samples were also obtained of a kimberlitic dike and adjacent salt from the Cayuga Mine of the Cargill Company, near Ithaca, New York. These latter settings, samples, and preliminary laboratory gamma spectrometric analyses of uranium, thorium, and potassium are briefly described.

Kalibergwerke Mine, West Germany

The dike rock is indicated by Robert Kuhn to be basaltic, of Miocene age. It intruded potash and salt horizons of the Werra Series of the Zechstein. Samples were collected of the dike and of as pure salt as was obtainable; one sample, judging by its 13.5% potassium content is of polyhalite. As indicated in Table 5.3, the results of preliminary gamma

Table 5.3. Whole-rock Laboratory Gamma Spectrometric Analyses
Kalibergwerke Mine, Germany.

Sample	U (ppm)	Th (ppm)	K (%)
1. Mafic dike rock.	2.1	7.6	2.4
2. Salt, faint dark layers at dike contact.	-	-	0.22
3. Salt, ~15 cm from dike.	-	-	0.09
4. Salt, ~45 cm from dike; some organic material.	0.002	-	0.40
5. Salt, ~1.2 m from dike.	-	-	0.21
6. Salt, most likely polyhalite.	0.13	-	13.5

spectrometric measurements, the salt samples were spaced from the dike contact to a distance of 1.2 m. Table 5.3 indicates that the dike has appreciable radioelement contents, while, with the exception of the salt sample at 45 cm from the dike containing some organic material, the radioelement content of the salt is below the sensitivity of the gamma measurements. The K contents of the salt, 0.09 to 0.40%, probably are the result of some potassium-mineral contamination and are probably not related to the dike, in that there does not appear to be a systematic decrease in K from the contact into the salt.

Cayuga Mine, New York

The occurrence of the dike intruding the salt at the Cayuga Mine was described by Broughton (1950). The salt bed, ranging from 5 feet or less to more than 60 feet in thickness belongs to the Syracuse Salt Formation of the Upper Silurian Salina Group. The dike rock is a greenish gray kimberlite with prominent olivine phenocrysts, altered almost completely to serpentine. The phenocrysts contain a brown, fresh mica, and the groundmass consists of a faulted aggregate of calcite, serpentine and chlorite. The dike is extremely brecciated in places and varies in width from a few inches to several feet over short distances. The dike breccia is intimately intruded by the salt, and where this has occurred the salt is reddish in color in contrast to its normal whitish-gray. There are no macroscopic effects apparent in the salt at its contact with the dike. Broughton (1950) envisioned the following sequence of events: (1) intrusion of a very fluid kimberlitic magma in a tension joint cutting the underlying limy shale, the salt, and the overlying Devonian limestone and shale, (2) the formation of an

intricately frozen contact between the dike and salt as the dike rapidly lost heat through salt, (3) extension of the dike, its brecciation, and intrusion of the salt between the breccia pieces, (4) recrystallization of the salt at the dike fragment contacts. According to a report by Stone and Webster Corporation (1978) geologic evidence suggests that the peridotitic-kimberlitic dikes in the Cayuga area are of Permian age, intruded at the time of horizontal faulting. Radiometric age determination attempts have been inconclusive; dating of the micas, reported by Zartman et al (1967), gave an age older than the country rock, while a Rb - Sr date on the mica was 136 million years, probably too young an age given geologic evidence.

Preliminary laboratory whole-rock gamma spectrometric analyses of radioelements in Cayuga Mine samples, obtained from dike and salt exposed in workings on the 2300-foot level, are listed in Table 5.4. As with the Kalibergwerke samples, uranium and thorium in the salt are below detection limits of this method. Potassium contents of the salt are significantly lower than at Kalibergwerke, attesting to the relative purity of the Cayuga salt which has no adjacent potash beds.

It was hoped that a horizontal hole could be drilled through a salt pillar and into and through the kimberlitic dike, to obtain an continuous core of salt and dike from a depth of ~2300 feet in the Cayuga Mine. However, attempts to core were unsuccessful because of inadequacies of the mine's core drilling equipment, coupled with unfavorable stress conditions at the edge of the pillar. It was therefore necessary to obtain chip samples from a pillar face, containing good exposures of the dike and a continuous exposure of salt. The locations of the first set of samples

Table 5.4. Whole-rock Laboratory Gamma Spectrometric Analyses,
Initial Sampling, Cayuga Mine, New York.

Samples	U (ppm)	Th (ppm)	K (%)
Kimberlite dike, center material.	1.69	12.57	1.49
Kimberlite dike at contact w/salt.	1.51	11.70	1.07
Salt, at contact with dike.	-	-	0.011
Salt, ~1 ft E of contact.	-	-	0.011
Salt, ~5 ft E of contact.	-	-	0.013
Dike, containing salt vein.	1.54	9.52	1.09

(labeled CARG) and the more recent set (labeled CAY), as well as the site of the unsuccessful drilling are shown in Figure 5.10, and a vertical profile of the recently sampled face and sample location is shown in Figure 5.11. As indicated in Figure 5.11, the set of samples covers the area from the center of the dike, to directly on the dike/salt contact, to ~4.1 m west of the contact in the salt.

The samples will be initially examined petrographically, and analyzed for radioelement contents by gamma spectrometry. Selected samples will be analyzed for trace elements by neutron activation and will be prepared for identification of fluid inclusions and analyses of their contents.

In summary, detailed examinations of intrusive contacts in crystalline and tuffaceous rock indicate that radioelements and fission-product analogue elements have apparently not migrated from the intrusives into or through the country rock, nor is there appreciable evidence for redistribution of these elements in the country rock in response to convective or conductive thermal events associated with the intrusives. Preliminary gamma spectral analyses of samples from contact zones between dikes and Columbia River plateau basalt and bedded salt also suggest the absence of radioelement migration or redistribution.

The emphasis of the project in Fiscal Year 1983 will switch from examination of "fossil" occurrences to investigation of active hydrothermal systems. Sites will be selected that are well documented, i.e., where rock types are well described, hydrologic and thermal conditions are well known, there is a good base of water chemistry data, and where samples of material

Figure 5.10. Portion of the Cayuga Mine, New York, showing kinberlite dike and sampling locations.

Figure 5.11. Sketch profile (from photographs) of the south face of a pillar in the Cayuga Salt Mine, New York, showing the locations of samples of the salt and the intruding kimberlite dike.

from zones of circulation as well as from relatively impermeable zones also available. Investigation of the differences in mineralogy and in the concentration of key elements between these zones will be definitive in disclosing the geochemical behavior of candidate rock types in the near field of a repository.

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FIGURES

- 5.1. Simplified geologic map, showing location of samples and traverses near Platoro, Colorado.
- 5.2. Variation in element contents between monzonite and tuff, Telluride Mountain traverse.
- 5.3. Variation in element contents between monzonite and tuff over several kilometers.
- 5.4. REE distribution in tuff near monzonite contact.
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- 5.2. Radioelement contents of dike in contact with basalt; quarry, East Fork of the Hood River, Oregon.
- 5.3. Whole-rock laboratory gamma spectrometric analyses, Kalibergwerke Mine, West Germany.
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