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*Research and Development Related to the
Nevada Nuclear Waste Storage Investigations*

October 1-December 31, 1984

Compiled by K. W. Thomas

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ABSTRACT

This report summarizes some of the technical contributions by the Los Alamos National Laboratory to the Nevada Nuclear Waste Storage Investigations (NNWSI) Project from October 1 through December 31, 1984. The report is not a detailed technical document but does indicate the status of the investigations being performed at Los Alamos.

EXECUTIVE SUMMARY

GEOCHEMISTRY

Groundwater Chemistry

Groundwater properties that are insufficiently known are the amount and identification of particulates and colloids moving with the groundwater. Small mineral particulates from tuff and natural colloids such as iron hydroxides are potential transporters of sorbed and coprecipitated waste elements if the solids move through the fractures or open porosity of the tuff with the natural water flow. We have positioned the Los Alamos mobile geochemistry laboratory adjacent to well J-13 so that a portion of all the water pumped from this well over a period of time can be filtered for particulates. This well was chosen because it is the production well closest to the candidate Yucca Mountain repository site and because the main water-producing zone is in the Topopah Spring Member. Water is diverted from the well at approximately 3.5 ℓ/m into the mobile laboratory and through a large (293-mm) stainless steel, One-Sevener Nuclepore membrane filter holder. This filter housing is loaded with seven polycarbonate filter membranes with 0.45- μm -diameter pores to filter large particles. The first filtrations are for checking the operation of the equipment over unattended periods of approximately 1 month. Subsequent filtrations will use filters with a smaller pore size of 0.05- μm diameter. In addition, an Amicon Hollow Fiber System is on order. This unit, when installed in-line in the mobile laboratory, will be used to concentrate the filterable solids between 1 and 50 nm in diameter, the size fraction considered to be essentially colloidal. From the quantities of particulates and colloids collected and from the volume of water passed through the filters, estimates will be made of the quantity of solid materials that can be transported in these tuffs along with the moving water. Because this well is being pumped, the artificially fast-moving water can be considered as carrying a maximum amount of solids with it. If sufficient quantities of solids are obtained, sorption experiments will be carried out on the particulates.

Natural Isotope Chemistry

An exploratory shaft experiment is planned to measure the decrease of naturally occurring ^{36}Cl as a function of the depth of the shaft. The ^{36}Cl should be carried with any water moving through the unsaturated zone. The ^{36}Cl decrease would result from

radioactive decay, which would serve to time the water movement. The ^{36}Cl is measured as the ratio of ^{36}Cl to total chlorine. The introduction of inactive chlorine, for example from well J-13 water used during the mining of the exploratory shaft, would compromise the results of this experiment, unless appropriate corrections are made. The quantity of well J-13 water in each sample taken for ^{36}Cl analysis can be determined if a suitable tracer is introduced into the well J-13 water. Experiments this quarter were directed toward finding a tracer for the well J-13 water. Bromide anions from a NaBr solution in well J-13 water were eluted from a column of crushed Topopah Spring Member tuff as rapidly as was tritium, which demonstrates the nonsorbing characteristics of bromide anions on this tuff. The bromide analysis techniques developed for this work are sensitive to bromide concentrations greater than 0.4 ppm in well J-13 water. Thus, bromide in the form of a NaBr solution appears to be a suitable tracer for the well J-13 water to be used during construction of the exploratory shaft.

Hydrothermal Geochemistry

Much of the effort on this task this quarter has gone into revising the program plan. The primary objective of this task is to develop a model that will describe the natural evolution of the mineralogy and water chemistry in Yucca Mountain and the effect of emplacement of a repository upon that evolution. Because the highly glassy state in which many of the rocks of Yucca Mountain were originally laid down is highly unstable, it can not be assumed that the present mineral assemblages are stable. Such silica polymorphs as cristobalite and tridymite are certainly unstable, and clinoptilolite is unlikely to form part of a stable assemblage. One of the factors that may control the metastability of clinoptilolite is the activity of aqueous silica. If Yucca Mountain were to reach its equilibrium state, the silica activity would be fixed by the solubility of quartz. Such, however, is not the case in Yucca Mountain at the present time. Elevated silica activities are to be expected from the presence of glass and silica polymorphs other than quartz and are observed in the waters of Yucca Mountain. Increased silica activity should increase the stability of clinoptilolite relative to feldspars. The higher the silica activity, the higher should be the temperature at which clinoptilolite transforms to feldspar.

At present, the temperature at which clinoptilolite transforms to feldspar at any particular silica activity is not known. However, recently published data on the entropy of clinoptilolite allow us to make preliminary estimates of the relative effects of the silica activity and temperature on the stability of clinoptilolite. These estimates indicate that if clinoptilolite is in equilibrium with feldspar at 25°C, with a silica activity in equilibrium with quartz, it would be in equilibrium with feldspar at about 100°C if the silica activity were controlled by amorphous silica. The entropy used for clinoptilolite was determined by calorimetry and, therefore, somewhat underestimates the entropy because it does not measure configurational entropy that is almost certainly present in clinoptilolite. Also, the heat capacity of clinoptilolite above 25°C was estimated using a heat capacity for zeolitic water in analcime. Low-temperature heat capacity measurements suggest that this will result in an underestimation of the heat capacity of clinoptilolite. Both of these factors tend to increase the temperature increase in the stability of clinoptilolite that would be predicted because of an increase in silica activity.

Solubility Determinations

An assessment of the relative importance of different radionuclides found in various types of nuclear waste has been started. This assessment will attempt to highlight those radionuclides that are present in large quantities in the waste, that must be well contained, or that present special problems. Work is continuing on determination of the solubility product of hydrous plutonium oxide, the formation constants of Pu(IV) with carbonate, and the formation constants of Am(III) with carbonate. The effects of radiolysis on reactions in the Pu(VI)-Pu(V)-Pu(IV)-colloid system are being investigated. Under certain conditions, alpha radiolysis may control plutonium concentrations in solution. Complexes of Am(III) with carbonate are being studied by examining the competition between carbonate and citrate for Am^{3+} . Data obtained so far indicate that a mixed complex is formed in this system.

Sorption And Precipitation

Sorption experiments examining the effects of variations in groundwater composition have continued this quarter. We are using water from well UE-25p#1, well H-3, well J-13,

and deionized water. The UE-25p#1 water has a much higher salt content than J-13, water, whereas water from well H-3 has a somewhat lower salt content. Well H-3 water has been measured to be slightly reducing in the field and exhibits the highest pH (~9) of waters examined to date from Yucca Mountain. As expected, elements that sorb by ion exchange, such as strontium, barium, or cesium, have lower sorption coefficients in the more concentrated UE-25p#1 water than in J-13 water. Sorption coefficients for these elements are about the same or slightly higher in H-3 water. Uranium and selenium sorption coefficients in UE-25p#1 and H-3 water are not very different from those in J-13 water except for a slightly lower uranium value in the UE-25p#1 water for a zeolitized tuff. Neptunium measurements were made with UE-25p#1 water under ambient atmospheric conditions and in the CO₂-controlled atmosphere box. Sorption coefficients in the CO₂ atmosphere were significantly lower than under the ambient measurements. However, the coefficient for this water measured in air was the same as that for J-13 in air, whereas the coefficient for UE-25p#1 water in the CO₂ box was much lower than the J-13 CO₂ box measurement.

Batch sorption measurements have been made for thorium on a variety of tuff samples at pH values near 5. The coefficients range from ~2000 to ~24,000 mL/g and do not exhibit a correlation with tuff mineralogy. Studies of uranium made at pH values close to 7 in the CO₂-controlled atmosphere box continue to yield sorption coefficients higher than those achieved under ambient conditions where the pH is ~8 to 9.

The long-term sorption experiments on technetium and neptunium have been completed. Over a period of 15 months there were no changes in the technetium sorption coefficients that were nearly zero. The neptunium values increased only slightly with time and were on the order of 5 mL/g. Work on neptunium isotherms is continuing. Results to date indicate that the sorption coefficient changes little over concentrations spanning 7 orders of magnitude.

The first serial sorption experiment with plutonium has been completed. The first phase gave a sorption coefficient of 260 mL/g. The second phase gave a value of 185 mL/g. A second experiment is under way that will entail four serial measurements to determine

if the sorption values continue to decline. These first results, however, show no gross difference between the sorption of the plutonium in the first and second phases.

Six-week sorption ratios measured using a plutonium tracer prepared in a bicarbonate buffer solution were compared with those obtained using our standard method of tracer preparation. Sorption ratios were measured at several different times, and the original buffered plutonium solution was periodically monitored for stability. Some changes were observed in the buffered tracer after 3 weeks. The 6-week sorption ratio for the buffered tracer was less than half that measured using the standard tracer preparation. It has been observed in the past that plutonium sorption values can vary widely depending upon the method of plutonium tracer preparation. More experiments will be performed and comparisons will be made at times less than 6 weeks.

A comparison was made of sorption ratios measured using an americium tracer prepared in a bicarbonate buffer solution and those obtained using our standard method of tracer preparation. There was very little difference in sorption ratios for these two preparations. However, it was discovered that an aliquot of the buffered solution did not remain stable for the duration of the sorption experiment; thus, the form of the americium during the buffered experiment is uncertain. The experiment will be repeated for shorter times. Of note, however, is the result that the buffer itself does not seem to affect the sorption measurements.

Experiments with microbes isolated from the surface of Yucca Mountain illustrate the role microorganisms may play in the sorption of radioactive waste elements on tuff. In the presence of microorganisms, the amount of plutonium in the solid phase of batch sorption experiments is higher than in their absence. Follow-up experiments performed in the absence of crushed tuff show that plutonium can be sorbed by the bacteria. Additional experiments are under way to determine if this sorption is dependent upon bacterial concentration and if it is species dependent.

Dynamic Transport Processes

The technetium is believed to be present as an anion, the pertechnetate ion in oxidizing water. If this is in fact the case, very little retardation can be expected for technetium under the geochemical conditions expected at Yucca Mountain. Several well-understood

anions were eluted through a large crushed tuff column containing G-2-2017 tuff and, as reported in the previous progress report, these anions, with the exception of fluoride, exhibited the anion exclusion effect. G-2-1027 tuff contains the zeolites mordenite and clinoptilolite, and anion exclusion observed was in qualitative agreement with the intracrystalline volume of these zeolites. Technetium was eluted through the same column, and 76% of the technetium eluted with the same volume as expected for anions; the remaining activity was retained by the column. This important phenomenon needs to be understood because it may indicate an unexpected natural barrier to technetium migration at Yucca Mountain.

A small fraction of plutonium and americium tracer has been found to elute from small crushed tuff columns in advance of tritiated water. As much as 14% of an americium carbonate spike eluted about 30% earlier than did tritiated water. Approximately 1.5% of a plutonium colloid spike prepared in sodium bicarbonate water eluted 30 to 40% earlier than did tritiated water. The difference in retention volume is significantly larger than would be expected for an anion exclusion effect based on the mineralogic compositions of the tuff used, GU-3-1301. This suggests the hydrodynamic chromatography effect on particulates in both cases. These results also suggest that even crushed tuff columns act as filters because most of the activity is retained and that intact tuff should be even more efficient.

The particle size distribution of plutonium colloid has been determined for the first time using the Los Alamos autocorrelator photon spectroscopy (APS) system. The system is laser based and uses a phenomenon called dynamic light scattering or quasielastic light scattering. The scattered light is detected by a photomultiplier and the signal is processed by an autocorrelator. The resulting correlation function is of the form of a Fredholm integral of the first kind, containing the particle size distribution. The integral equation is being inverted by the code INVPOS using optimal smoothing and a positivity constraint as prescribed by the method of Butler et al. (1981). The peak of the size distribution, determined by INVPOS, for the plutonium colloid prepared in 10^{-3}M bicarbonate solution was 120 nm. The size distribution also agreed with the observation that nearly all of the colloid passed through a $0.4\text{-}\mu\text{m}$ Nuclepore filter and 96% was removed by a $0.05\text{-}\mu\text{m}$ filter.

Future experiments will determine if the size distribution varies with method of preparation or age of the suspension.

Monodisperse polystyrene particles with diameters from 60 nm to 1.0 micron have been acquired for testing the APS system. The particle size distribution for these suspensions has been redetermined by electron microscopy in order to determine the actual shape of the distribution for testing the INVPOS code.

A new containment vessel has been designed and is now in use for fracture flow experiments. The new design will provide protection from leaks that have developed in the past during long-term experiments with sorbing tracers. This design will not, however, interfere with the diffusion of tracers and provides a reservoir of water around the fractured core that can be sampled periodically for tracers. A second jacket will be installed in the future to provide a means of temperature control that will become more critical when unsaturated flow experiments are performed.

Retardation Sensitivity Analysis

Geochemical transport modeling plays a significant role in characterizing the macroscopic far-field environment and performance assessment of potential nuclear waste storage sites. Until the development of multicomponent transport models such as TRANQL, hydrogeologists have traditionally relied upon distribution coefficients (commonly referred to as K_d) to describe the rate of migration and retardation of a radionuclide within the porous medium. Once a K_d has been determined by laboratory field methods, it is used to define the retardation factor that in turn describes the velocity of the reactive solute relative to the average linear groundwater velocity (Freeze and Cherry 1979). Because this approach is conceptually and computationally simple, the use of distribution coefficients has been liberally applied to explain observed contaminant transport in soils and aquifers (Grove and Wood 1979; Krishnaswame et al. 1982; Schwartz et al. 1982; Jackson and Inch 1983). However, recent investigations (Reardon 1981; Miller and Benson 1983; Valocchi 1984) have shown that the use of distribution coefficients in predicting, rather than describing, observed contaminant migration may be inadequate and may not always be appropriate. Recently, more sophisticated multicomponent geochemical transport models (for example, TRANQL) have been developed. These models are able to incorporate

all equilibrium chemical reactions that may be significant in describing and predicting transport such as aqueous-phase complexation, ion exchange, simultaneous adsorption, precipitation/dissolution, and dissociation of water. In this report TRANQL and the K_d approach to transport modeling are compared. First, a review of multicomponent transport models and TRANQL are discussed. Second, the development and limitations of the K_d approach are discussed. Third, TRANQL and the K_d model are compared in terms of their predictive capability.

Applied Diffusion

In situ measurements of diffusivity will require analyses of tracers that have diffused through Topopah Spring Member and Calico Hills tuffs. Bromide anions have been identified as nonsorbing tracers for aqueous solutions in Topopah Spring Member tuff that may be used in these diffusion experiments. This quarter, work continued to develop a more sensitive and more convenient bromine analysis procedure than the ion chromatography technique that is used currently. A neutron activation method was developed in which a 250- μl solution containing bromine was evaporated onto filter paper. The dry filter paper was irradiated in a flux of $\sim 3 \times 10^{12}$ neutrons $\text{cm}^{-2}/\text{s}^{-1}$ for 2 h and then permitted to decay for ~ 30 h before the decay of ^{82}Br was measured. The sensitivity of this method appears to be limited to $\sim 0.02 \mu\text{g Br}/\text{mL}$ solution because of the bromine in the filter paper. However, this sensitivity permits the detection of bromine in concentrations an order of magnitude smaller than that routinely achieved for bromine in well J-13 water by our ion chromatography technique ($0.4 \mu\text{g Br}/\text{mL}$). In addition, this new neutron activation technique permits the analysis of samples with less labor than that currently used in the chromatography method. The bromine content of well J-13 water was determined by the new neutron activation analysis technique to be $\sim 0.05 \mu\text{g}/\text{mL}$.

MINERALOGY-PETROLOGY OF TUFF (D. Bish, D. Broxton, F. Byers, B. Carlos, S. Levy, and D. Vaniman)

During this quarter, studies began on samples from trench-exposed faults in the vicinity of Yucca Mountain. These studies address four possible origins of fault-related mineralogy of interest to NNWSI:

- (1) pedogenic, reflecting only local dissolution and reprecipitation;
- (2) low-temperature spring;
- (3) high-temperature spring; and
- (4) early high-temperature alteration soon after tuff emplacement.

Preliminary petrographic, x-ray diffraction, and fluid inclusion studies indicate that at least two origins are represented by fault-related mineralogy. The first is a high-temperature (145°C) growth of drusy quartz. The second is a low-temperature (sepiolite-assemblage) alteration. Studies of petrographic stratigraphy within the Topopah Spring Member have been extended to include samples from UE-25a#1. These studies confirm the groundmass and phenocryst features previously categorized for determination of internal stratigraphic position within the Topopah Spring Member. As a test of this technique, a sample from Fran Ridge supplied by Lawrence Livermore National Laboratory (LLNL) was placed in relative stratigraphic position. Shard textures were added as a further guide to stratigraphic position within the Topopah Spring Member.

TECTONICS AND VOLCANISM

Volcanic hazard investigations have focused on five topics: the mechanism of emplacement of shallow basalt intrusions, geochemical trends through time of volcanic fields of the Death Valley-Pancake Range (DV-PR) volcanic zone, the possibility of bimodal basalt-rhyolite volcanism, the age and process of enrichment of incompatible elements in young basalts of the Nevada Test Site (NTS) region, and the possibility of hydrovolcanic activity. The stress regime of Yucca Mountain may favor formation of shallow basalt intrusions. However, combined field and drill hole studies suggest that shallow basalt intrusions are rare in the geologic record of the southern Great Basin. The geochemical trends of basaltic volcanism through time in the NTS region provide no evidence of possible future increases in rates of volcanism. Existing data are consistent with declining volcanic activity comparable to the late stages of the southern Death Valley volcanic field. Drill holes USW VH-1 and VH-2 provided no evidence of past bimodal volcanism in the Crater Flat area. The hazards of bimodal volcanism in this area are judged to be low. Several problems remain. First, two magnetic anomalies, one in Crater Flat and the other near the town

of Lathrop Wells, need to be drilled to complete documentation of the volcanic history of the Yucca Mountain region and to further test for buried rhyolite centers. Second, the source of a 6-Myr pumice discovered in alluvial deposits of Crater Flat has not been found. Geochemical studies have shown that the enrichment of trace elements in the younger rift basalts must be related to enrichment of their mantle source rocks. This enrichment predates the basalts of the silicic episode and is, therefore, not a young event. Studies of crater dimensions of hydrovolcanic landforms indicate that the worst-case scenario, exhumation of a repository at Yucca Mountain by hydrovolcanic explosions, is unlikely. Theoretical models of melt-water vapor explosions, particularly the thermal detonation model, suggest hydrovolcanic explosions are possible at Yucca Mountain. Additional calculations may be required on the radiological consequences of basaltic eruptions at Yucca Mountain using an eruption cycle that originates with hydrovolcanic activity.

SEALING MATERIALS EVALUATION

Cementitious materials (grout, mortars, concretes) are being proposed as one major type of potential sealing material for a repository in Yucca Mountain. Introduction of any sealing materials will, in general, cause reactions between the host rock and the sealant because of chemical differences and the reactive nature of fine-grained minerals and glasses in the tuff.

Different concrete-type sealing materials are being evaluated for their potential chemical compatibility with the tuff chemistry. Two approaches to sealant/host rock compatibility were examined. The first concrete used indigenous sands and gravel in the formulation of the sealant; the second used more conventional concrete materials to control the bulk chemical composition of the concrete and thus approached more closely the tuff composition.

The purpose of this project is to evaluate the chemical stability of potential sealing materials. These evaluations will be based upon laboratory studies conducted under a series of conditions that represent a range of credible temperature conditions supplemented by other evaluations based upon thermodynamic considerations and durable analogs from other sources. Experimental thermodynamic studies, stability assessments, development

of a grout dissolution model for fracture seals, thermodynamic properties calculations, and assistance in preparation of the materials recommendation and design requirements report are major activities during FY85. A detailed model that describes the kinetics of dissolution of a heterogeneous, multicomponent assemblage of crystalline phases was developed after the mathematical model presented by Lasaga (1984). Two important properties of the dissolution of crystalline materials were addressed in this paper that make this type of analysis possible: (a) most crystalline materials display a linear dissolution behavior, and (b) a multicomponent system can be described as a weighted linear summation of the component parts. To supplement this dissolution model, predictions for the assemblage of stable phases in cementitious solids were completed that reflect our best interpretation of the phases stable at ambient temperature, 150°C, and 200°C.

A topical report titled "Concrete Studies as Analogs of Cementitious Sealing Materials for a Tuff Repository" was completed by Pennsylvania State University and is being reviewed at Los Alamos. This report presents the results of an investigation of the durability/longevity of concrete in the environs of ancient Rome. Because tuff and volcanic ash were used in the concretes, the results are particularly applicable to a nuclear waste repository in a tuff environment. Evidence from detailed investigations of the analog materials suggests that sealing materials compositionally and microstructurally similar to the ancient pozzolanic cementitious materials will adjust slowly to such an environment, perform well, and remain stable.

I. INTRODUCTION

This report summarizes some of the technical contributions from the Los Alamos National Laboratory to the NNWSI Project, which is managed by the Nevada Operations Office of the US DOE, from October 1 through December 31, 1984. The report is not a detailed technical document but does indicate the status of the investigations being performed at Los Alamos.

II. GEOCHEMISTRY

A. Groundwater Chemistry

Groundwater properties that are insufficiently known are the amount and identification of particulates and colloids moving with the groundwater. Small mineral particulates from tuff and natural colloids such as iron hydroxides are potential transporters of sorbed and coprecipitated waste elements if the solids move through the fractures or open porosity of the tuff with the natural water flow.

We have positioned the Los Alamos mobile geochemistry laboratory adjacent to well J-13 so that a portion of all the water pumped from this well over a period of time can be filtered for particulates. This well was chosen because it is the production well closest to the candidate Yucca Mountain repository site and because the main water-producing zone is in the Topopah Spring Member. Water is diverted from the well at approximately 3.5 ℓ/m into the mobile laboratory and through a large (293-mm) stainless steel, One-Sevener Nuclepore membrane filter holder. This filter housing is loaded with seven polycarbonate filter membranes with 0.45- μm -diameter pores to filter large particles. The first filtrations are for checking the operation of the equipment over unattended periods of approximately 1 month. Subsequent filtrations will use filters with a smaller pore size of 0.05- μm diameter. In addition, an Amicon Hollow Fiber System is on order. This unit, when installed in-line in the mobile laboratory, will be used to concentrate the filterable solids between 1 and 50 nm in diameter, the size fraction considered to be essentially colloidal.

From the quantities of particulates and colloids collected and from the volume of water passed through the filters, estimates will be made of the quantity of solid materials that can be transported in these tuffs along with the moving water. Because this well is

being pumped, the artificially fast-moving water can be considered as carrying a maximum amount of solids with it. If sufficient quantities of solids are obtained, sorption experiments will be carried out on the particulates.

B. Natural Isotope Chemistry (A. E. Norris and P. L. Wanek)

The rate of water flow through the unsaturated zone at Yucca Mountain is an important parameter for calculating the potential discharge of water-borne radioactive waste from a breached nuclear waste repository. One naturally occurring radioactive tracer that can be used to time the rate of water flow through the unsaturated zone is ^{36}Cl . The half-life of this nuclide, 3×10^5 yr, is such that flow times less than 5×10^4 yr cannot be detected. Some hydraulic flux measurements at Yucca Mountain indicate that the water flow through the unsaturated zone may exceed this threshold. Therefore, an experiment is planned to collect samples as the exploratory shaft is mined, which will be used for ^{36}Cl measurements. An accelerator-based mass spectrometer will measure the ratio of ^{36}Cl to total chlorine. The introduction of inactive chlorine into the samples would compromise the results, unless an appropriate correction is made. One source of inactive chlorine is the chloride in well J-13 water, which will be used in mining the exploratory shaft. A well J-13 water tracer would permit the calculation of corrections for this source of inactive chlorine. Experimental work to select a tracer for well J-13 water has been performed this quarter with the following results.

A column of crushed Topopah Spring Member tuff was used to determine the elution of a potential tracer relative to tritiated water. The column material was USW G-4 core retrieved from the 1067-ft depth. This tuff was crushed and sieved. The 75- to 500- μm fraction was used to fill an 8-mm-inside-diameter glass tube to a height of 185 mm. A reservoir of well J-13 water was connected to the column, and 0.5-ml fractions of eluant were collected with a fraction collector. The first potential tracer to be investigated was a NaBr solution. Techniques were developed for the analysis of bromide anions in well J-13 solutions. The nitrate concentration in this water limited the bromide analyses to concentrations greater than 0.4 ppm. Bromide solutions were eluted from the crushed tuff column in three separate experiments, and the bromide peak concentration in each was determined to be split between fractions 9 and 10. The first of a planned series of

experiments was performed in which a solution containing 1 μmol NaBr and 1.3 nCi ^3H was added to the column and then eluted simultaneously with well J-13 water. The results are shown in Table I. The bromide eluted at least as rapidly as the tritium, which demonstrates the nonsorbing characteristics of bromide anions on Topopah Spring Member tuff. If these results are as reproducible as expected, bromide anions in a NaBr solution will have been shown to be an appropriate tracer of well J-13 water in the Topopah Spring Member tuff.

C. Hydrothermal Geochemistry

Much of the effort on this task this quarter has gone into revising the program plan. The primary objective of this task is to develop a model that will describe the natural evolution of the mineralogy and water chemistry in Yucca Mountain and the effect of emplacement of a repository upon that evolution. Because the highly glassy state in which many of the rocks of Yucca Mountain were originally layed down is highly unstable, it can not be assumed that the present mineral assemblages are stable. Such silica polymorphs as cristobalite and tridymite are certainly unstable, and clinoptilolite is unlikely to form part of a stable assemblage. One of the factors that may control the metastability of clinoptilolite is the activity of aqueous silica. If Yucca Mountain were to reach its equilibrium

TABLE I. RESULTS OF ELUTING Br^- AND ^3H SIMULTANEOUSLY FROM A CRUSHED TUFF COLUMN

<u>Column Fraction*</u>	<u>^3H, c/m</u>	<u>Br^-, ppm</u>
7	0.2	0.4
8	6.1	11.1
9	40.4	33.4
10	58.2	76.6
11	56.9	36.6
12	30.6	15.4
13	2.3	0.5
14	0.1	0.4

*The ^3H and Br^- at or below detection limits in the remainder of the 24 fractions collected.

state, the silica activity would be fixed by the solubility of quartz. Such, however, is not the case in Yucca Mountain at the present time. Elevated silica activities are to be expected from the presence of glass and silica polymorphs other than quartz and are observed in the waters of Yucca Mountain. Increased silica activity should increase the stability of clinoptilolite relative to feldspars. The higher the silica activity, the higher should be the temperature at which clinoptilolite transforms to feldspar.

Effect of Silica Activity on the Temperature Stability of Clinoptilolite.

Hemingway and Robie (1984) determined the low-temperature heat capacity of a clinoptilolite with the composition $(\text{Na}_{0.56} \text{K}_{0.98} \text{Ca}_{1.50} \text{Mg}_{1.23}) (\text{Al}_{16.7} \text{Fe}_{0.3}) \text{Si}_{29} \text{O}_{72} \cdot 22\text{H}_2\text{O}$. They also evaluated the entropy at 298.15 K minus the entropy at 0 K and estimated the heat capacity of zeolitic water in clinoptilolite by approximating the heat capacity of anhydrous clinoptilolite as the sum of the heat capacities of 0.56 mol of albite, 0.98 mol of microcline, 1.50 mol of anorthite, 1.08 mol of corundum, 1.23 mol of periclase, 0.15 mol of hematite, and 21.38 mol of quartz. The entropy of zeolitic water at 298.15 K minus the entropy at 0 K can be calculated in a similar manner. For the calculation, entropies for the above minerals were obtained from Robie et al. (1979). The resultant entropy estimate for anhydrous clinoptilolite is 1622.3 J/(mol·K). The 298.15 K entropy for clinoptilolite given by Hemingway and Robie (1984) is 2872.3 J/(mol·K). The average entropy at 298.15 minus the entropy at 0 K for zeolitic water in clinoptilolite is then estimated to be 56.82 J/(mol·K).

For clinoptilolites in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, we can approximate the entropy of clinoptilolite as the appropriate sum of the entropies of albite, microcline, anorthite, quartz, and zeolitic water. To examine the effects of silica activity upon clinoptilolite stability, we can investigate reactions of the type

If we estimate that the activities of the feldspar and H_2O are 1, as they would be for pure phases, then we can write for this reaction at equilibrium that

$$A_{\text{SiO}_2(\text{aq})}^Z = e_R^{-\Delta G/RT}.$$

Because we do not know the free energy of clinoptilolite, we do not know ΔG_R (the change in free energy for the reaction); however, we can make reasonable estimates of the change in ΔG_R with temperature. The free energy of H_2O as a function of temperature can be obtained from Keenan et al. (1969), and the free energy of aqueous silica from Walther and Helgeson (1977). The variation in the free energy of the solid phases with temperature is given by

$$G_T^\circ - G_{T_R}^\circ = -S_{T_R}^\circ (T - T_R) + \int_{T_R}^T C_p dt - T \int_{T_R}^T \frac{C_p}{T^2} dT.$$

In addition to estimating the entropy for clinoptilolite, we must estimate the heat capacity because the measurements of Hemingway and Robie (1984) do not extend above 305 K. This can be done in a manner analogous to that used to estimate the entropy and by using a heat capacity function for zeolitic water obtained from the data on analcime and dehydrated analcime obtained by Johnson et al. (1982). Because the heat capacity and entropy of the feldspar component of the clinoptilolite are approximated by that of feldspar, we need not consider the entropy and heat capacity of feldspar and the feldspar component of clinoptilolite in calculating the variation in ΔG_R with temperature because they cancel out. We can, therefore, do calculations based on the simplified equation

where Y and Z are determined by the composition of the clinoptilolite. If the clinoptilolite is $Na_7 Al_7 Si_{29} O_{72} \cdot 22 H_2 O$, then Z is 8 and Y is 22. For $Na_6 Al_6 Si_{30} O_{72} \cdot 24 H_2 O$, Z is 12 and Y is 24; for $Ca_3 Al_6 Si_{30} O_{72} \cdot 24 H_2 O$, Z is 24 and Y is 24.

Because we do not know the free energy of clinoptilolite, we cannot calculate the activity of aqueous silica in equilibrium with clinoptilolite and feldspar at a given temperature. Instead, to estimate the effects of silica activity on the temperature of clinoptilolite/feldspar equilibrium, ΔG_R has been fixed so that clinoptilolite and feldspar are in equilibrium at 298.15 K at the silica activity fixed by quartz saturation. The silica activity in equilibrium with clinoptilolite and feldspar was then calculated at elevated temperatures.

The resulting calculations are obviously approximate. Two errors are that the configurational contribution to the entropy of clinoptilolite is not included (because it is not

known) and the heat capacity of zeolitic water in analcime is probably less than in clinoptilolite. However, calculations performed with variable entropy and heat capacity indicate that these errors are of only minor consequence. Uncertainty in the water content of clinoptilolite that affects the coefficient Y also has a small effect upon the equilibrium temperature. The only parameter examined that showed important effects was the silicon to aluminum ratio of the clinoptilolite. High-calcium, high-silica clinoptilolites were calculated to be stable up to 125 K higher at amorphous silica saturation than at quartz saturation, whereas the stability of sodium/potassium clinoptilolites with an aluminum:silicon ratio of 1:5 was increased 75 to 100 K. An increase in silica activity from quartz to cristobalite saturation was calculated to cause about a 50 K rise in the temperature stability limit.

This information does not imply that higher silica zeolites are stable at higher temperatures because they may well be less stable at low-temperature, low-silica activity than are lower silica clinoptilolites. It is, however, possible that clinoptilolites are stable relative to feldspars where elevated silica activities are present and will remain stable as long as the silica activity remains elevated and the temperature is not excessively increased, even though they might not be stable if the silica activity were reduced to quartz saturation.

D. Solubility Determinations (D. E. Hobart, T. W. Newton, P. Palmer, and J. F. Kerrisk)

1. Important Radionuclides for Solubility and Sorption. As part of the geochemical site characterization of Yucca Mountain, questions concerning the relative importance of various radionuclides have arisen in the context of studying how solubility and sorption on local minerals affect radionuclide transport. In assessing the suitability of the site, those radionuclides that are present in large quantities, that must be well contained, or that present special problems should be given attention early in the program. An assessment of the relative importance of radionuclides found in various types of nuclear waste has been started. Four factors are being considered in this assessment:

- (1) the quantity of various radionuclides present in the waste,
- (2) the Environmental Protection Agency (EPA) release limits for the radionuclides,

- (3) how different retardation processes such as solubility and sorption might affect radionuclide transport, and
- (4) the physical and chemical forms of the radionuclides.

Three types of waste are being considered: spent fuel, civilian high-level waste, and defense high-level waste. There may be many answers to the question of which radionuclides are most important for a repository at Yucca Mountain. Different answers can arise from consideration of different time scales, different transport mechanisms, different regulations, or different waste types. Three aspects of this question are addressed in this assessment.

- (1) Which radionuclides are present in waste in large quantities relative to their EPA release limits? These are the radionuclides for which the retardation processes of solubility and sorption must be most effective. These are important radionuclides because they must be addressed in performance assessment and, thus, must have the solubility and sorption data base for that kind of analysis.
- (2) Which radionuclides are not retarded by solubility and sorption and are present in large enough quantities to pose release problems? This question can be addressed by simplified performance assessment calculations using estimated solubilities and sorption coefficients. The results of this analysis can be used to highlight radionuclides that may require special consideration because they are not retarded strongly. These radionuclides are important because special design considerations or performance assessments may be required to assure their containment.
- (3) Which radionuclides might require special consideration because of the physical or chemical form of the waste? These are radionuclides that may exhibit unique source-term or transport behavior. They are also important because they may require special data or assessment techniques for performance assessment calculations. As solid waste forms become better defined, other radionuclides may be added to this category.

The work on this assessment is still in progress. Data for radionuclide concentrations in the three types of waste as a function of time after discharge from the reactor have been

collected. Simplified models for the effects of solubility and sorption on radionuclide release are being developed and tested.

2. Actinide Chemistry in Near-Neutral Solutions. The chemistry of actinides in the near-neutral waters found in the vicinity of Yucca Mountain will have a significant impact on actinide solubility and transport in water that interacts with nuclear waste stored there. Three aspects of actinide chemistry are being examined:

- (1) complex formation between Pu(IV) and carbonate,
- (2) solubility product of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ (solid or colloidal sol), and
- (3) complex formation between Am(III) and carbonate.

During the past quarter, we concentrated on the solubility product of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ and complex formation in the Am(III)-carbonate system.

3. Effect of Radiolysis on the Pu(VI)-Pu(V)-Pu(IV)-Colloid System. A knowledge of the equilibrium constant for the reaction

can be used in conjunction with known thermodynamic data to determine the equilibrium constant for the reaction

This equilibrium constant is the solubility product and is fundamental for predicting plutonium solubility as a function of pH and water composition. Concentrations of Pu(VI) and Pu(V) in a series of solutions have been followed in an attempt to understand the effects of radiolysis on this system. These solutions also contain suspensions of colloidal Pu(IV), which is determined by difference between the total plutonium content and the Pu(VI) and Pu(V) contents. The equilibrium quotient for reaction (1),

$$Q_1 = [\text{PuO}_2^{2+}]/[\text{PuO}_2^+]^2 \quad ,$$

has been followed as the reaction proceeds in the forward and reverse directions. The average oxidation state of the plutonium, ox , was calculated from the analytical data and

found to change with time because of the alpha-irradiation from the ^{239}Pu used. For most of the mixtures, ox decreased with time. The decreases in ox in Pu(VI) solutions, which we observe at pH values between 1 and 2, are in quite good agreement with those observed earlier at much higher acid concentrations (Rabideau et al. 1958). Some of the mixtures that are more than 200 days old appear to have reached steady states where the concentrations do not change appreciably with time. Many of the others appear to be approaching steady states. Typical examples are provided by runs starting with pure Pu(V) or pure Pu(IV). Data from these runs are summarized in Table II.

Whether the values for $\log Q'$ observed after long periods represent equilibrium in reaction (1) or merely steady state remains to be determined. Values close to equilibrium might be expected if the rates of reaction (1) are large compared to the rates of the radiolysis reactions. However, this is probably not the case. The forward rate of reaction (1) has been measured at acid concentrations greater than 0.2M (Rabideau 1957), and our data for much lower acid concentrations are consistent with these previous results. For 25°C and unit ionic strength, the rate law was found to be

$$-d[\text{Pu(V)}]/dt = 622[\text{Pu(V)}]^2[\text{H}]^+ \text{Mday}^{-1} \quad (3)$$

TABLE II. EFFECTS OF ALPHA-IRRADIATION ON ^{239}Pu SOLUTIONS

Run Number	Initial		Maximum		Time to Maximum Days	Final		Time (day)	Log Q ^b
	Concentration ^a		Concentration ^a of			Concentration ^a			
	Oxidation State		Initial Product		[V]	[VI]			
1	10	V	0.9	VI	41	0.29	0.49	360	3.8
45	28	V	10	VI	23	1.6	.76	92	3.4
7	30	V	6.7	VI	48	0.32	1.4	343	4.1
43	34	V	9.1	VI	22	0.8	3.1	152	3.7
33	0.044	VI	0.043	V	111	0.02	0.0005	141	3.1
35	9.7	VI	5.5	V	41	1.3	1.1	152	2.8
46	30	VI	12	V	21	2.3	6.8	96	3.1
26	6.2	Colloid	— +V	— +VI	—	0.3	1.4	200	4.2

^aConcentrations are in M x 10⁻³.

^bQ' is the observed concentration quotient: $[\text{Pu(VI)}]/[\text{Pu(V)}]^2$.

Using this rate law, we find the forward rate of (1) for Run 43, where the pH is about 1 and the ionic strength is 1M, to be 9×10^{-4} M/day, and the rate of the alpha-reduction of the Pu(VI) present is expected to be about 5×10^{-4} M/day, based on 0.015 per day. Thus, the observed Q' may be fairly close to the equilibrium value for this mixture. However, for the mixtures with much smaller Pu(V) concentrations, alpha effects will dominate.

4. Complex Formation Between Am(III) and Carbonate. A recent review of thermodynamic data for americium has indicated considerable uncertainty in the identity and formation constants of Am(III) with carbonate (Kerrisk 1984; Bidoglio 1982; Lundqvist 1982). Because americium is an important waste element, this information will be needed to calculate americium solubility in water from Yucca Mountain.

We have found that citrate and carbonate ligands compete effectively in complexing Am(III). We have chosen a spectroscopic method to detect the various species present because the effects of these species can be directly observed spectroscopically rather than merely inferred from distribution or solubility data. Because Am^{3+} is unstable at high pH and CO_3^{2-} is unstable at low pH, these species cannot exist together at measurable concentrations. For this reason we are developing a competitive method using Am(III)-citrate complexes. Previous work (Ohyoshi and Ohyoshi 1971) provides the species and complexation quotients up to a pH of about 6. We are determining the equilibrium in the reaction

Data for these reactions can be combined with data for citrate complexes to give formation quotients for the carbonate species. The current experiments are being done at 23°C, a pH of 11, and an ionic strength of 3M. However, we expect to work at lower pH values and possibly lower ionic strengths.

The data obtained so far indicate that

- (1) spectral changes are large enough that equilibrium can be measured relatively easily,

- (2) the equilibrium quotient for reaction (4) is fairly close to unity, and
- (3) a mixed complex is formed, probably by replacing one citrate with two carbonate ligands.

E. Sorption and Precipitation (K. W. Thomas)

1. Groundwater Composition Effects (B. P. Bayhurst, S. D. Knight, F. O. Lawrence, M. R. Cisneros, and K. W. Thomas). Sorption experiments examining the effects of variations in groundwater composition have continued this quarter. We are studying water from well UE-25p#1, well H-3, and well J-13 and deionized water. The UE-25p#1 water has a much higher salt content than J-13 water, and water from well H-3 has a somewhat lower salt content. Well H-3 water has been measured to be slightly reducing in the field and exhibits the highest pH (~9) of waters examined to date from Yucca Mountain.

Sorption ratios for strontium, cesium, barium, europium, selenium, and uranium in well H-3 water were determined this quarter and are presented in Tables III-V. Results using UE-25p#1 water for strontium, cesium, barium, and europium were reported last quarter but are also included in Tables IV-V along with those determined this quarter for selenium and uranium. Neptunium sorption in UE-25p#1 water was also measured (Table VI). The tuff samples studied were GU-3-1203 and GU-3-1301, vitric tuffs from the Topopah Spring Member; G-1-2901, a devitrified tuff from the Tram unit; and G-1-2233, a zeolitized tuff from the Bullfrog unit. Sorption and desorption times were 6 weeks and the particle size was 75 to 500 μm , wet-sieved. Sorption ratios for strontium, cesium, and barium measured in H-3 water had the expected relationship to tuff mineralogy. Sorption ratios for these elements were highest on the zeolitized tuff, G-1-2233. However, europium had the highest sorption on G-1-2901, a devitrified tuff using H-3 water. Compared to J-13 water sorption ratios, strontium and barium were somewhat higher in H-3 water, perhaps because of the decreased concentration of divalent cations in H-3 water. Cesium values were about the same in both waters. Europium values for G-1-2901, a devitrified tuff, and for G-1-2233, a zeolitized tuff, were significantly lower in H-3 water than in J-13 water. However, the J-13 measurements were taken when the fraction size used was $<500 \mu\text{m}$. Studies made since that time indicate that there may be some particle size effects leading

TABLE III. SORPTION RATIOS USING GROUNDWATER FROM WELL USW H-3 (Cont on next page)

Sample ^a	Traced Feed pH	Element	Traced Feed Concentration (M)	Sorption or Desorption ^b	Sorption Ratios (mℓ/g)		Average Value ^d
					Experimental (pH) ^c		
GU-3-1301	8.81	Sr	1 x 10 ⁻⁶	Sorption	95 (8.95)	97 (8.94)	96(1)
		Cs	5 x 10 ⁻⁹	Sorption	156	157	156(1)
		Ba	6 x 10 ⁻⁸	Sorption	985	755	870(120)
		Eu	1 x 10 ⁻⁷	Sorption	129	132	130(2)
		Sr		Desorption	164 (8.92)	137 (8.93)	150(14)
		Cs		Desorption	190	170	180(10)
		Ba		Desorption	846	700	770(76)
		Eu		Desorption	180	156	170(14)
GU-3-1203	9.01	U	1.1 x 10 ⁻⁶	Sorption	5.8 (9.00)	6.5 (9.04)	6.2(0.3)
		Se	1.9 x 10 ⁻⁹	Sorption	4.1	2.0	3.1(0.8)
G-1-2901	8.77	Sr	1 x 10 ⁻⁶	Sorption	169 (8.87)	199 (8.89)	184(15)
		Cs	5 x 10 ⁻⁹	Sorption	963	1100	1030(70)
		Ba	6 x 10 ⁻⁸	Sorption	1500	1950	1720(230)
		Eu	1 x 10 ⁻⁷	Sorption	2450	3800	3120(680)
		U	1.1 x 10 ⁻⁶	Sorption	0.8 (9.12)	0.5 (9.25)	0.7(0.1)
	9.10	Se	1.9 x 10 ⁻⁹	Sorption	2.0	2.3	2.2(0.1)
		Sr		Desorption	267	265	266(1)
		Cs		Desorption	1330	1510	1420(90)
		Ba		Desorption	1770	2060	1900(160)
		Eu		Desorption	3190	3770	3500(310)

to increased sorption ratios when particles less than $\sim 75 \mu\text{m}$ are included. Results using UE-25p#1 water have been discussed in a previous quarterly (Ogard and Vaniman 1985).

For uranium and selenium, primarily the greatest sorption is observed in deionized water, perhaps because of decreased competition for sorption sites. For selenium, sorption

TABLE III. SORPTION RATIOS USING GROUNDWATER FROM WELL USW H-3 (Cont)

Sample ^a	Traced Feed pH	Element	Traced Feed Concentration (M)	Sorption or Desorption ^b	Sorption Ratios (ml/g)		Average Value ^d
					Experimental (pH) ^c		
G-1-2233	8.81	Sr	8×10^{-7}	Sorption	15 500	17 800	16600(1200)
					(8.91)	(9.87)	
		Cs	4×10^{-9}	Sorption	7100	7200	7150(50)
		Ba	3×10^{-8}	Sorption	30 700	39 600	35 100(4500)
		Eu	8×10^{-8}	Sorption	110	135	120(15)
	9.26	U	1.1×10^{-6}	Sorption	0.5	1.4	1.0(0.4)
					(9.27)	(9.22)	
		Se	1.9×10^{-9}	Sorption	5.7	6.6	6.2(0.4)
		Sr		Desorption	8700	10 400	9500(900)
					(9.01)	(9.01)	
		Cs		Desorption	3760	3970	3860(110)
		Ba		Desorption	14 300	14 000	14 100(200)
		Eu		Desorption	172	176	174(2)

^aParticle size was 75 to 500 μm .^bContact times were 6 weeks.^cSr, Cs, Ba, and Eu were all run in the same experiment and have, therefore, the same pH values. The same applies to U and Se.^dNumbers in parentheses are standard deviations of the mean.

values for the tuffs studied were essentially the same with J-13 and UE-25p#1 waters. However, sorption in H-3 water was greater in J-13 or UE-25p#1 water for tuffs GU-3-1203 and G-1-2233 and was slightly less in these waters for tuff G-1-2901. Uranium results show no trends. For GU-3-1203 the order of decreasing sorption was H-3, UE-25p#1, J-13. For G-1-2233 it was J-13, H-3, UE-25p#1. For G-1-2901, UE-25p#1 showed the greatest sorption with both H-3 and J-13 sorption being a factor of 3 less.

Neptunium sorption ratios were measured for UE-25p#1 water both in air and in the CO_2 -controlled atmosphere box (enriched to ~5% in CO_2) and are given in Table VI. Also listed for comparative purposes are the values for J-13 water presently available. For the UE-25p#1 water, the measurements in air were 1 to 2 orders of magnitude greater than those in the CO_2 atmosphere, yet J-13 results were the same in both atmospheres for

TABLE IV. SORPTION RATIOS FOR URANIUM AND SELENIUM IN SEVERAL WATERS

Core ^a	Element	Water	Feed pH	Concentration (M)	$R_d(\text{ml/g})^b$ (pH)		Average ^c
GU-3-1203	U	J-13	NA	5×10^{-6}	0 (8.40)	0 (8.31)	0
	U	UE-25p#1	8.83	1.1×10^{-6}	0.5 (9.01)	0.8 (9.03)	0.7 (0.1)
	U	H-3	9.01	1.1×10^{-6}	5.8 (9.00)	6.5 (9.04)	6.2 (0.3)
	Se	J-13	NA	1×10^{-10}	0 (8.40)	2 (8.31)	1 (1)
	Se	UE-25p#1	8.83	1.9×10^{-9}	0.6 (9.01)	0.8 (9.03)	0.7 (0.1)
	Se	H-3	9.01	1.9×10^{-9}	4.1 (9.00)	2.0 (9.04)	3.1 (0.8)
	Se	deionized	8.46	1.9×10^{-9}	8.2 (8.65)	1.4 (8.31)	4.8 (2.4)
G-1-2233	U	J-13	8.72	2.7×10^{-6}	6.0 (8.89)	5.0 (8.78)	5.5 (0.4)
	U	UE-25p#1	8.99	1.1×10^{-6}	0 (9.29)	0.6 (9.26)	0.3 (0.3)
	U	H-3	9.26	1.1×10^{-6}	0.5 (9.27)	1.4 (9.22)	1.0 (0.4)
	Se	J-13	8.72	1.8×10^{-11}	1.8 (8.89)	1.7 (8.78)	1.8 (0.1)
	Se	UE-25p#1	8.99	1.9×10^{-9}	2.1 (9.29)	1.3 (9.26)	1.7 (0.3)

TABLE IV. SORPTION RATIOS FOR URANIUM AND SELENIUM IN SEVERAL WATERS (Cont)

Core ^a	Element	Water	Feed pH	Concentration (M)	R _d (M/g) ^b (pH)		Average ^c
G-1-2233	Se	H-3	9.26	1.9 x 10 ⁻⁹	5.7 (9.27)	6.6 (9.22)	6.2 (0.4)
	Se	deionized	8.59	1.9 x 10 ⁻⁹	5.7 (8.96)	6.3 (8.71)	6.0 (0.2)
G-1-2901	U	J-13	8.57	1.1 x 10 ⁻⁶	0.5 (8.94)	0.9 (8.92)	0.7 (0.1)
	U	UE-25p#1	8.90	1.1 x 10 ⁻⁶	3.0 (9.21)	2.4 (9.17)	2.7 (0.2)
	U	H-3	9.10	1.1 x 10 ⁻⁶	0.8 (9.12)	0.5 (9.25)	0.7 (0.1)
	U	deionized	8.72	1.1 x 10 ⁻⁶	2.4 (8.67)	2.5 (8.70)	2.4 (0.1)
	Se	J-13	8.57	1.9 x 10 ⁻⁹	3.9 (8.94)	2.8 (8.92)	3.4 (0.4)
	Se	UE-25p#1	8.90	1.9 x 10 ⁻⁹	4.3 (9.21)	3.0 (9.17)	3.7 (0.5)
	Se	H-3	9.10	1.9 x 10 ⁻⁹	2.0 (9.12)	2.3 (9.25)	2.2 (0.1)
	Se	deionized	8.72	1.9 x 10 ⁻⁹	6.8 (8.67)	6.1 (8.70)	6.5 (0.3)

^aParticle sizes were 75 to 500 μ m.^bSorption time was 6 weeks.^cNumbers in parentheses are the standard deviation of the mean.

TABLE V. A COMPARISON OF SORPTION RATIOS IN DIFFERENT GROUNDWATERS

Sample	Element	Sorption or Desorption	$R_d(\text{ml/g})$		
			J-13	UE-25p#1	H-3
GU-3-1301	Sr	Sorption	32	10	96
	Cs	Sorption	160	45	156
	Ba	Sorption	570	82	870
	Eu	Sorption	75	>17 000	130
	Sr	Desorption	90	32	150
	Cs	Desorption	180	55	180
	Ba	Desorption	660	140	770
	Eu	Desorption	110	>20 000	170
	U	Sorption	0	0.7	6.2
	Se	Sorption	1	0.7	3.1
	Sr	Sorption	48 000	2000	16 600
	Cs	Sorption	13 500	7500	7150
G-1-2233	Ba	Sorption	250 000	41 000	35 100
	Eu	Sorption	900	>5600	120
	U	Sorption	5.5	0.3	1.0
	Se	Sorption	1.8	1.7	6.2
	Sr	Desorption	90 000	3000	9500
	Cs	Desorption	23 000	8800	3860
	Ba	Desorption	240 000	59 000	14 100
	Eu	Desorption	5000	>7800	174
	Sr	Sorption	68	44	184
	Cs	Sorption	1290	900	1030
	Ba	Sorption	1600	1400	1720
	Eu	Sorption	160 000	38 000	3120
G-1-2901	U	Sorption	0.7	2.7	0.7
	Se	Sorption	3.4	3.7	2.2
	Sr	Desorption	67	35	266
	Cs	Desorption	1380	850	1420
	Ba	Desorption	1980	1100	1900
	Eu	Desorption	210 000	69 000	3500

TABLE VI. NEPTUNIUM SORPTION RATIOS IN SOME YUCCA MOUNTAIN WELL WATERS

Core ^a	Well Water Atmosphere	Feed pH	Feed Concentration (M)	Sorption Ratio ^b		Average ^c	Desorption Ratio ^b		Average ^c
				(mℓ/g) (pH)			(mℓ/g) (pH)		
GU-3-1301	<u>UE-25p#1</u>	6.9	4.2×10^{-11}	0.16 (6.72)	0.09 (6.69)	0.13 (1)	6.63 (7.30)	3.96 (7.07)	5.3 (1.2)
	<u>J-13</u> CO ₂	NA	2.5×10^{-11}	2.1 (6.65)	2.1 (6.63)	2.1 (1)	31 (6.15)	26 (6.14)	29 (3)
	<u>UE-25p#1</u>	8.8	4.3×10^{-11}	18 (8.87)	13 (8.77)	15 (2.6)	1000 (8.61)	640 (8.62)	830 (190)
	<u>J-13</u>	8.4	2.0×10^{-11}	1.8 (8.53)	1.7 (8.54)	1.8 (0.1)	18 --	18 (8.42)	18 (1)
G-1-2233	<u>UE-25p#1</u> CO ₂	7.0	4.1×10^{-11}	0.88 (6.84)	0.88 (6.79)	0.88 (0.1)	6.7 (7.12)	5.0 (7.27)	5.8 (1)
	<u>UE-25p#1</u> Ambient	8.8	4.3×10^{-11}	3.2 (8.91)	3.2 (8.93)	3.2 (0.1)	9.2 (8.7)	8.9 (8.7)	9.1 (1)

^aThe rock used was crushed and sieved to 75 to 500 μm.

^bSorption and desorption measurements were made for 6 weeks each.

^c The values in parentheses are the standard deviation of the mean.

GU-3-1301. The reason for this is not apparent. Analyses of rock-equilibrated UE-25p#1 water are under way and may shed some light on these findings.

2. Batch Sorption Measurements on Thorium, Uranium, and Selenium (B. P. Bayhurst and K. W. Thomas). Thorium batch sorption measurements were made on six Yucca Mountain tuffs in the CO₂-controlled atmosphere box (Table VII). The final pH values were ~5, which was lower than intended; however, these data will help bound thorium behavior in the pH 5 to 9 range. As in earlier data, there are no significant correlations of thorium sorption with tuff mineralogy. Samples G-1-3116 and G-4-1608 contain significant amounts of zeolites and have the highest sorption ratios; however, G-2-2017 has similar amounts of

TABLE VII. THORIUM SORPTION MEASUREMENTS USING J-13 WATER IN A CO₂-CONTROLLED ATMOSPHERE*

Core ^b	Traced Feed Concentration (M)	Traced Feed (pH)	Sorption Ratios (ml/g)		
			Experimental Values (pH)		Average Value ^c
G-1-2840	2.2 x 10 ⁻⁷	4.95	3900 (5.41)	2600 (5.48)	3300 (420)
G-1-2901	1.6 x 10 ⁻⁷	5.47	3700 (7.07)	3400 (6.45)	3600 (140)
G-1-3116	1.1 x 10 ⁻⁷	5.00	20 900 (5.40)	26 700 (5.41)	23 800 (2050)
G-2-2017	1.0 x 10 ⁻⁷	5.02	2000 (5.48)	4400 (5.48)	3200 (850)
GU-3-1203	9.7 x 10 ⁻⁸	4.88	2000 (5.30)	1700 (5.30)	1900 (140)
G-4-1608	1.5 x 10 ⁻⁷	4.84	717 900 (5.49)	22 700 (5.46)	20 300 (1700)

*Atmosphere enriched to ~5% in CO₂.

^bFraction size was 75 to 500 μm (wet-sieved).

^cNumbers in parentheses are standard deviation of the mean.

clinoptilolite and mordenite and does not exhibit increased sorption of thorium. Core GU-3-1203 has the lowest sorption ratio and is 40% glass. In any event, all the sorption ratios are high (>1800 ml/g).

Several uranium and selenium measurements were made using J-13 water in both air and CO₂-controlled atmospheres (Tables VIII-IX). As seen in previous studies, the uranium results in air are lower than those measured under the CO₂-controlled atmosphere, indicating that measurements made in air are conservative. For selenium, one tuff gave higher sorption in the CO₂ atmosphere and the other tuff was higher in air. Both of these tuffs are highly zeolitized.

TABLE VIII. SORPTION RATIOS FOR SELENIUM AND URANIUM USING J-13 WATER IN AIR

Core ^a	Element	Traced Feed pH	Traced Feed Conc. (M)	Sorption Ratio ^b (ml/g)		
				Experimental Values (pH)		Average Value ^c
G-1-2017	Se	7.33	1.90×10^{-9}	1.42 (7.36)	1.12 7.57)	1.27 (0.11)
G-4-1608	Se	7.75	1.90×10^{-9}	14.8 (7.51)	15.7 (7.60)	15.2 (0.31)
G-2-2017	U	7.33	1.07×10^{-6}	d (7.36)	d (7.58)	d
G-4-1608	U	7.75	1.07×10^{-6}	12.60 (7.51)	11.4 (7.60)	12.0 (0.45)

^aFraction size is 75 to 500 μm (wet-sieved).

^bSorption time was 6 weeks.

^cNumbers in parentheses are standard deviation of the mean.

^dNegative values caused by low value of standard; need to count again.

3. Long-Term Sorption of Neptunium and Technetium (S. D. Knight, F. O. Lawrence, M. R. Cisneros, and K. W. Thomas). The long-term sorption measurements on neptunium and technetium have been completed. Over a period of 15 to 16 months, there were no changes in the technetium sorption coefficients that were nearly zero. The neptunium values increased only slightly with time and were on the order of 5 ml/g. The increase was about 70% for GU-3-916, about 33% for GU-3-1301, and about 23% for G-4-1502. Tables X-XI list the final results that have been corrected for evaporative losses of the solution during the experiment. Previously reported results (Ogard and Vaniman 1985) were not corrected for these losses and are slightly lower than those reported here.

4. Neptunium Isotherm Measurements (F. O. Lawrence, M. R. Cisneros, and K. W. Thomas). Preliminary results of isotherm measurements on two Yucca Mountain tuffs

TABLE IX. SORPTION RATIOS FOR SELENIUM AND URANIUM USING J-13 WATER IN CO₂ ATMOSPHERE^a

Core ^b	Element	Traced Feed pH	Traced Feed Conc. (M)	Sorption Ratio ^c (mL/g)		
				Experimental Values (pH)		Average Value ^d
G-1-2698	Se	5.83	1.90 x 10 ⁻⁹	2.82	2.59 (5.71)	2.7 (0.1) (5.90)
G-1-2901	Se	5.93	1.90 x 10 ⁻⁹		7.22 (6.28)	5.76 (6.34)
GU-3-1203	Se	5.82	1.90 x 10 ⁻⁹		1.73 (6.03)	2.21 (6.13)
G-2-2017	Se	5.49	1.90 x 10 ⁻⁹		4.97 (5.70)	4.48 (5.84)
G-4-1608	Se	5.96	1.90 x 10 ⁻⁹		3.46 (6.27)	3.16 (6.21)
G-1-2698	U	5.83	1.07 x 10 ⁻⁶		17.9 (5.17)	18.6 (5.90)
G-1-2901	U	5.93	1.07 x 10 ⁻⁶		4.75 (6.28)	4.03 (6.34)
GU-3-1203	U	5.49	1.07 x 10 ⁻⁶		2.98 (6.03)	5.35 (6.13)
G-2-2017	U	6.95	1.07 x 10 ⁻⁶		4.99 (5.70)	5.32 (5.84)
G-4-1608	U	5.96	1.07 x 10 ⁻⁶		20.5 (6.27)	22.2 (6.21)

^aAtmosphere enriched to ~5% in CO₂.

^bFraction size is 75 to 500 μm, wet-sieved.

^cSorption time was 6 weeks.

^dNumbers in parentheses represent the standard deviation of the mean.

TABLE X. LONG-TERM TECHNETIUM SORPTION RATIOS USING J-13 WATER

Core ^a	Traced Feed pH	Traced Feed Conc. (M)	Sorption Time	Sorption Ratios ^b (ml/g)		
				Experimental Values (pH)		Average Value ^c
GU-3	8.57	6×10^{-10}	6 weeks	0.50 (8.51)	0.94 (8.57)	0.72 (0.2)
			13 weeks	0.33 (8.75)	1.3 (8.70)	0.81 (0.5)
			6 months	0.81 (8.61)	0.44 (8.66)	0.62 (0.2)
			9 months	0.14 (8.81)	0.11 (8.81)	0.13 (0.02)
			12 months	0.13 (8.83)	0.32 (8.90)	0.22 (0.1)
			16 months	0.08 (8.93)	0.17 8.92)	0.12 (0.05)
GU-3-1301	8.67	7×10^{-10}	6 weeks	0.058 (8.41)	0.022 (8.47)	0.04 (0.02)
			13 weeks	0.065 (8.63)	0.002 (8.69)	0.03 (0.03)
			6 months	-0.003 (8.60)	0.004 8.61)	0
			9 months	0.013 (8.70)	0.031 (8.72)	0.02 (0.01)
			12 months	0.17 (8.70)	0.30 (8.75)	0.23 (0.1)
			16 months	0.04 (8.79)	0.20 (8.79)	0.12 (0.08)

TABLE X. LONG-TERM TECHNETIUM SORPTION RATIOS USING J-13 WATER (Cont)

Core ^a	Traced Feed pH	Traced Feed Conc. (M)	Sorption Time	Sorption Ratios ^b (mℓ/g)		
				Experimental Values (pH)		Average Value ^c
G-4-1502	8.74	8×10^{-10}	6 weeks	0.042 (8.60)	-0.003 (8.60)	0.02 (0.02)
			13 weeks	0.06 (9.00)	-0.038 (8.81)	0.01 (0.05)
			6 months	-0.085 (8.65)	-0.09 (8.65)	0
			9 months	-0.06 (8.71)	-0.05 (8.75)	0
			12 months	0.001 (8.80)	-0.015 (8.82)	0
			16 months	-0.08 (8.83)	-0.03 (8.86)	0

^aParticle size was 75 to 500 μm .^bSorption time was 6 weeks.^cNumbers in parentheses are standard deviations of the mean.

with ^{235}Np and ^{237}Np solutions are presented in Table XII. A third tuff, GU-3-1203, has been studied, but the data have not yet been analyzed. The feed solution for the G-4-1608 study contained ^{235}Np and ^{237}Np and their protactinium and uranium daughters. The samples were counted by alpha counting in an ion chamber and, for comparison, by gamma counting in Na(I) well counters and a Ge(Li) detector. The results presented are based on alpha counts for all but the last sample that contained no ^{237}Np , the presence of which complicates the gamma counting analyses. The feed solution for the GU-3-433 core was prepared with a ^{237}Np solution that had had the daughter products removed just be-

TABLE XI. LONG-TERM NEPTUNIUM SORPTION RATIOS USING J-13 WATER

Core ^a	Traced Feed pH	Traced Feed Conc. (M)	Sorption Time	Sorption Ratios (mℓ/g)			Desorption Time	Desorption Ratios (mℓ/g)		
				Experimental		Average ^b Value		Experimental		Average ^b Value
				Value (pH)				Value (pH)		
GU-3-916	NA	6 x 10 ⁻¹¹	6 weeks	4.9 (8.76)	5.0 (8.65)	4.9 (1)	6 weeks (8.76)	35 (8.80)	32	33 (1)
			2.8 months	5.3 (8.69)	5.7 (8.68)	5.5 (1)				
			6 months	5.9 (8.48)	5.6 (8.54)	5.9 (1)				
			9 months	5.9 (8.24)	6.2 (8.08)	6.0 (1)				
			12 months	6.8 (8.51)	6.8 (8.58)	6.8 (1)				
			15 months	7.2 (8.40)	9.6 (8.60)	8.4 (1.2)				
GU-3-1301	8.4	2 x 10 ⁻¹¹	6 weeks	1.8 (8.53)	1.7 (8.54)	1.8 (1)	6 weeks	18 (-)	18 (8.42)	18 (1)
GU-3-1301	8.6	6 x 10 ⁻¹¹	3 months	2.3 (8.63)	2.1 (8.65)	2.2 (1)	6 weeks	23 (8.66)	26 (8.74)	25 (2)
			3 months	2.1 (8.65)	1.9 (8.67)	2.0 (1)				
			6.2 months	2.3 (8.55)	2.6 (8.62)	2.5 (1)				
			9.5 months	2.1 (8.46)	2.0 (8.47)	2.0 (1)				

TABLE XI. LONG-TERM NEPTUNIUM SORPTION RATIOS USING J-13 WATER (Cont)

Core ^a	Traced Feed pH	Traced Feed Conc. (M)	Sorption Time	Sorption Ratios (ml/g)			Desorption Time	Desorption Ratios (ml/g)		
				Experimental				Experimental		
				Value (pH)	Average ^b Value			Value (pH)	Average ^b Value	
GU-3-1301	8.6	6 x 10 ⁻¹¹	12.1 months	2.1 (8.28)	2.0 (8.44)	2.0 (1)				
			15.7 months	2.4 (8.37)	2.4 (8.45)	2.4 (1)				
G-4-1502	8.7	1 x 10 ⁻¹⁰	6 weeks	4.6 (8.55)	4.8 (8.62)	4.7 (1)	6 weeks	13 (8.71)	10 (8.70)	11 (2)
			3 months	5.2 (8.66)	3.6 (8.70)	4.4 (1)				
			6 months	5.2 (8.44)	5.2 (8.49)	5.2 (1)				
(8.37)	(8.53)		9.1 months	5.7	5.5	5.6 (1)				
12.1 months	5.8	5.8	5.8 (1)	(8.47)	(8.41)					
			15.1 months	5.8 (8.19)	5.8 (8.22)	5.8 (1)				

^aParticle size was 75 to 500 μm.^bThe numbers in parentheses are the standard deviation of the mean.

fore use. The samples from this core were counted in the same manner as above. In both cases, the sorption coefficient remained essentially the same over 7 orders of magnitude.

5. Plutonium and Americium Sorption Measurements (F. O. Lawrence, M. R. Cisneros, and K. W. Thomas). A two-part sorption measurement with plutonium has been completed. A standard batch sorption experiment was run for 6 weeks after which the

TABLE XII. NEPTUNIUM ISOTHERM SORPTION MEASUREMENTS USING J-13 WATER IN CONTROLLED-ATMOSPHERE CONDITIONS^a

Core ^b	Initial Np Feed	$R_d(\text{m}\ell/\text{g})^c$		
	Concentration	Measured		Average
	(M)	Run 1	Run 2	
G-4-1608	6.6×10^{-4}	2.0	2.7	2.3 (1)
	3.0×10^{-4}	1.3	0.58	0.94 (1)
	6.7×10^{-5}	3.5	3.2	3.3 (1)
	3.4×10^{-5}	3.4	3.1	3.3 (1)
	7.6×10^{-6}	4.7	5.1	4.9 (1)
	3.7×10^{-6}	4.5	5.4	5.0 (1)
	7.5×10^{-7}	5.1	4.7	4.9 (1)
	3.9×10^{-7}	4.4	5.9	5.2 (1)
	7.5×10^{-8}	4.8	(^d)	4.8 (^d)
	3.9×10^{-8}	6.0	4.7	5.3 (1)
	4.3×10^{-9}	3.0	7.8	5.4 (2.4)
	2.7×10^{-11}	5.2	5.5	5.4 (1)
GU-3-433	4.8×10^{-5}	2.6	1.6	2.1 (1)
	2.1×10^{-5}	0.60	0.17	0.38 (1)
	4.3×10^{-6}	3.4	4.9	4.1 (1)
	2.2×10^{-6}	4.6	5.0	4.8 (1)
	5.0×10^{-7}	5.3	5.1	5.2 (1)
	2.4×10^{-7}	5.5	4.3	4.9 (1)
	4.4×10^{-8}	6.2	6.1	6.2 (1)
	3.2×10^{-8}	9.6	2.6	6.1 (3.5)
	8.2×10^{-12}	0.82	0.67	0.74 (1)

^aAtmosphere enriched to 5% in CO₂.

^bAll crushed rock used was 75 to 500 μm in size. The sorption times were 6 weeks.

^cThe values in parentheses are the standard deviation of the mean.

^dOnly one measurement available.

aqueous phase was removed and contacted with fresh, pre-equilibrated tuff for an additional 6 weeks. The sorption ratio measured for the first phase of the experiment was 260 $\text{m}\ell/\text{g}$, which agrees well with the value of 250 $\text{m}\ell/\text{g}$ reported previously (Wolfsberg and Vaniman 1984). The second phase gave a sorption coefficient of 185 $\text{m}\ell/\text{g}$. It is not clear

TABLE XIII. SERIAL SORPTION MEASUREMENTS WITH PLUTONIUM USING J-13 WATER^a

Feed		<u>Initial Sorption</u>		
		<u>R_d (ml/g)</u>		
<u>pH</u>	<u>Concentration (M)</u>	<u>pH</u>	<u>Experimental</u>	<u>Average^b</u>
8.4	9.5 x 10 ⁻⁸	8.01	240	
		8.04	270	260 (14)

Feed		<u>Secondary Sorption</u>		
		<u>R_d (ml/g)</u>		
<u>pH</u>	<u>Concentration (M)</u>	<u>pH</u>	<u>Experimental</u>	<u>Average^b</u>
8.01	7.2 x 10 ⁻⁹	8.38	190	
8.04	6.6 x 10 ⁻⁹	8.23	180	185 (4)

^aSorption measurements were made for 6 weeks under ambient conditions using 75- to 500- μ m crushed rock from core GU-3-916.

^bThe values in parentheses are the standard deviation of the mean.

whether this small difference is due to statistical variations, the factor of 10 difference in plutonium concentration, or other effects. However, it does show that there is no great difference in the behavior of plutonium that sorbed in the first phase and that in the second. The data are presented in Table XIII. An extended experiment consisting of at least four phases is now planned. A comparison has been made of 6-week sorption ratios measured using a plutonium tracer prepared in a bicarbonate buffer solution and those obtained using our standard method of tracer preparation. Sorption ratios were measured at 1, 2, 3, and 6 weeks for the buffered tracer. The original buffered plutonium stock solution was spectrophotometrically monitored periodically for stability. Some changes were observed in the buffered tracer after 3 weeks. The 6-week sorption ratio for the buffered tracer was less than half that measured using the standard tracer preparation. It has been observed

in the past that plutonium sorption values can vary widely depending upon the method of plutonium tracer preparation. More experiments will be performed and comparisons will be made at times less than 6 weeks. Pertinent data are given in Table XIV.

A comparison has been made of 3-week sorption ratios measured using an americium(III) tracer prepared in a bicarbonate buffer solution and those obtained using our standard method of tracer preparation (Table XV). There was very little difference in sorption ratios for these two preparations. It was discovered, however, that an aliquot of the buffered solution did not remain stable for the duration of the experiment. Thus, it is uncertain what form the americium was in during the buffered experiment. The study will be repeated for shorter times. This work has shown that the buffer itself does not seem to affect the sorption measurement.

TABLE XIV. COMPARISON OF PU(V) AND MULTI-OXIDATION-STATE SORPTION RATIOS USING J-13 WATER^a

Stock Solution	Feed pH	Feed Concentration (M)	Sorption Time	Sample pH	Sorption Ratio (ml/g)	
					Experimental	Average ^b
NaHCO ₃ Buffered [Pu(V)]	8.38	2.5 x 10 ⁻⁷	1 week	8.4	27	32 (5.5)
				8.4	38	
			2 weeks	8.4	49	49(1)
				8.4	49	
			3 weeks	8.5	60	66 (6.2)
				8.4	72	
			6 weeks	8.6	190	170 (23)
				8.7	140	
Dried Acid Solution [Multi ox- idation state]	8.41	6.1 x 10 ⁻⁸	6 weeks	8.5	270	430 (160)
				8.3	590	

^aAll measurements were made on 75- to 500-μm crushed rock from core G1-1-2840 (a partially welded devitrified tuff from Tram member of Crater Flat).

^bThe values in parentheses are the standard deviation of the mean.

TABLE XV. COMPARISON OF Am(III) SORPTION RATIOS USING BUFFERED AND UNBUFFERED FEED SOLUTIONS WITH J-13 WATER^a

Stock Solution	pH	Feed Concentration	pH	Sorption Ratio (ml/g)	
		(M)		Experimental	Average ^b
NaHCO ₃ Buffered [Am(III)]	8.6	2.5 x 10 ⁻⁸	8.4	2000	2000 (64)
			8.5	2100	
Dried Acid [Am ^c]	8.4	2.1 x 10 ⁻⁸	8.6	2400	2400 (1)
			8.6	2400	

^a Measurements were made for 3 weeks on crushed core G-3-4868, a zeolitized tuff. Particle size was 75 to 500 μ m.

^b The values in parentheses are the standard deviation of the mean.

^c Speciation unknown.

6. Microbial Activity at Yucca Mountain (L. E. Hersman, F. O. Lawrence, M. R. Cisneros, and K. W. Thomas). The aim of this research is to determine if microbial activity can influence the mobility of plutonium at Yucca Mountain. Of special interest are those species capable of metabolizing and/or degrading drilling fluids that will be used extensively in exploration and repository construction at Yucca Mountain. Two sorption experiments were performed with tuff and bacteria this quarter. The first was designed to determine the effect of bacteria on plutonium sorption on crushed tuff. The second investigated the sorption of plutonium onto bacteria in the absence of tuff.

One gram of sterile crushed tuff, G-4-1501, was added to 20 ml of sterile Turco 5622 or ASP-700 drilling fluid medium. These slurries were inoculated with one of four bacterial species. Turco 5622 was inoculated with organisms "1A" or "6A,2" and ASP-700 was inoculated with species "9A2b,C" or "11A2b,C,2." These cultures were incubated at room temperature for 5 days. Cultures were transferred to sterile 50-ml centrifuge tubes and centrifuged at 12,000 rpm for 1 h. The supernatant was discarded, and 20 ml of

plutonium feed solution in J-13 water was added to the bacteria and tuff. A 5-day sorption experiment was then performed. The second experiment duplicated the first with the following exceptions: (1) no tuff was added to the bacterial cultures growing in the drilling fluid; (2) only the sterile tuff control was used in the second experiment because the first experiment demonstrated that other controls were unnecessary. The results are presented in Tables XVI and XVII.

In the presence of tuff, bacteria increased the sorption of plutonium, compared to the sterile control. The most significant increase was caused by species "11A2b,C,2." When tuff was absent, the bacteria still sorbed plutonium although not as effectively as did the tuff control. The species "11A2b,C,2" again appeared to be the best scavenger of plutonium. These studies demonstrate that bacteria do play a role in plutonium sorption.

Additional experiments are planned to address the effect of bacterial concentration on sorption. It also remains to be seen whether or not these bacteria are mobile in the underground environment of Yucca Mountain.

F. Dynamic Transport Processes (R. S. Rundberg, A. E. Ogard, J. L. Thompson, and A. J. Mitchell)

Crushed Tuff Columns. The technetium is believed to be present as an anion, the pertechnetate ion, in oxidizing water. If this is in fact the case, very little retardation

TABLE XVI. EFFECT OF BACTERIA ON PLUTONIUM SORPTION RATIOS

Experiment	Plutonium Sorption Ratio ^a (ml/g)		
	Run 1	Run 2	Run 3
Sterile Control	2.3	1.7	1.5
Turco 5622 Control	2.4	1.9	1.7
ASP-700 Control	2.9	2.5	1.9
Turco 5622 (1A)	3.5	2.3	1.9
Turco 5622 (6A,2)	3.6	2.0	1.9
ASP-700 (9A _{2b} ,C)	3.7	2.7	2.4
ASP-700 (11A _{2b} ,C,2)	4.3	3.7	2.7

^aThe crushed tuff used was 75 to 500 μ m from core G-4-1501. Sorption time was 5 days.

TABLE XVII. SORPTION OF PLUTONIUM BY BACTERIA

Experiment	Plutonium Sorption Ratio ^a (ml/g)		
	Run 1	Run 2	Run 3
Sterile Control	18.4	16.7	7.4
Turco 5622 (1A)	5.7	5.1	5.5
Turco 5622 (6A,2)	4.8	5.4	4.2
ASP-700 (9A _{2b} ,C)	13.3	9.0	2.3
ASP-700 (11A _{2b} ,C,2)	10.7	11.8	9.3

^aSorption time was 5 days. No crushed tuff was present.

of technetium can be expected at Yucca Mountain. Several well-understood anions were eluted through a large crushed tuff column containing G-2-2017 tuff; as reported in the previous progress report, these anions, with the exception of fluoride, exhibited the anion exclusion effect. The G-2-2017 tuff contains the zeolites mordenite and clinoptilolite, and the anion exclusion observed was in qualitative agreement with the intracrystalline volume of these zeolites. The ⁹⁵Tc was eluted through the G-2-2017, 2-m column to experimentally determine whether or not technetium is a single species, TcO₄⁻.

Ten milliliters of ^{95m}Tc-traced J-13 water was injected into the column followed by 50 ml of untraced J-13 water at a flow rate identical to that used for the single species anions. Samples of effluent were collected in an automatic fraction collector. The samples were assayed by gamma counting using an intrinsic germanium well detector. The resulting elution curve is shown in Fig. 1. The breakthrough observed is in excellent agreement with that previously observed for anions, 15.7-ml retention volume. However, the maximum concentration is only 76% of the initial concentration. This shows that 76% of the

Fig. 1. Elution of ^{95m}Tc through G-2-2017 crushed tuff column.

technetium is anionic, exhibiting the anion exclusion effect, and probably as the pertechnetate ion. The loss of 24% to the column is unexpected and indicates the presence of a cationic species. The G-2-2017 tuff is zeolitized and contains mordenite and clinoptilolite as major constituents. Unless the technetium sorbed through some unknown mechanism, cation exchange is unlikely. The technetium has been detected on the column verifying that some technetium has actually sorbed.

This type of speciation is difficult to detect by batch sorption measurements and demonstrates the usefulness of column studies. The cause of this observed sorption needs to be thoroughly investigated before a R_d can be assigned and used for performance assessment. Future studies will be performed to examine the interaction of controlled technetium species with tuff. The speciation of technetium under groundwater conditions will also be studied. An additional possibility is raised by references to autoradiolysis effects observed for ^{95m}Tc by Ianovici et al. (1981), which can produce reduced species under some chemical conditions. This possibility will be addressed through the use of ^{99}Tc , which has a much lower specific activity.

G. Retardation Sensitivity Analysis (G. Cederberg)

1. Comparison of TRANQL and Distribution Coefficient Approaches to Transport Modeling. Geochemical transport modeling plays a significant role in characterizing the macroscopic far-field environment and performance assessment of potential nuclear waste storage sites. Until the development of multicomponent transport models such as TRANQL, hydrogeologists have traditionally relied upon distribution coefficients (commonly referred to as K_d) to describe the rate of migration and retardation of a radionuclide within the porous medium. Once a K_d has been determined by laboratory field methods, it is used to define the retardation factor that in turn describes the velocity of the reactive solute relative to the average linear groundwater velocity (Freeze and Cherry 1979). Because this approach is conceptually and computationally simple, the use of distribution coefficients has been liberally applied to explain observed contaminant transport in soils and aquifers (Grove and Wood 1979; Krishnaswame et al. 1982; Schwartz et al. 1982; Jackson and Inch 1983). However, recent investigations (Reardon 1981; Miller and Benson 1983; Valocchi 1984) have shown that the use of distribution coefficients in pre-

dicting, rather than describing, observed contaminant migration may be inadequate and may not always be appropriate. Recently, more sophisticated multicomponent geochemical transport models (for example, TRANQL) have been developed. These models are able to incorporate all equilibrium chemical reactions that may be significant in describing and predicting transport such as aqueous-phase complexation, ion exchange, simultaneous adsorption, precipitation/dissolution, and dissociation of water. In this report TRANQL and the K_a approach to transport modeling are compared. First, multicomponent transport models and TRANQL are discussed. Second, the development and limitations of the K_a approach are discussed. Third, TRANQL and the K_a model are compared in terms of their predictive capability.

2. The TRANQL Approach. In the process of understanding groundwater contaminant transport, many geochemical transport models have been developed (Rubin and James 1973; Valocchi et al. 1981a; Charbeneau 1981; Valocchi et al. 1981b). Until recently only a single specific chemical reaction such as ion exchange or sorption for a small number of reacting solutes has been incorporated into mass transport models. Implicit in these models is the assumption that the solutes being modeled act independently of the bulk solution composition. Because most contamination sources are actually multispecies solutions, the need exists for models that are able to incorporate all known significant chemical interactions and processes that affect transport in any given groundwater system.

Several investigators have recently addressed the problem of modeling the transport of a multispecies solution in equilibrium with a groundwater system. Rubin (1983) provides an overall context in which the nature of the mathematical formulation is seen to depend upon the nature of the chemical reactions. Jennings et al. (1982), in their work on the groundwater transport of a multispecies solution composed of metals and ligands, suggest that there are two distinct techniques for modeling multispecies solutions. The first technique is to insert all of the interaction chemistry directly into the transport equations and to reduce the problem to one strongly nonlinear equation set. The second technique is to pose the equilibrium interaction chemistry independently of the mass-transport equations,

leading to a set of algebraic equations for the chemistry coupled to a set of differential equations for the mass transport.

Jennings et al. (1982), Rubin and James (1973), and Valocchi et al. (1981a) all follow the first approach. Jennings et al. (1982) presented a finite element solution to the modeling of the groundwater transport of a multispecies solution of metals and ligands for an arbitrary number of species. The chemical reactions they included were soluble complexation and competitive sorption among chemical species. Their model required the phase-exchange reactions (that is, sorption isotherms) to be known explicitly and be differentiable. The pH was also considered constant throughout the system. Rubin and James (1973) and Valocchi et al. (1981a) presented finite element solution models for describing the transport of equilibrium-controlled ion-exchanging solutes. Both considered binary and multicomponent ion exchange in solutions with constant pH. In this technique where the interaction chemistry is inserted directly into the transport equations, iteration of the entire equation set within each time step is required because the equation system is nonlinear. In this iteration procedure the finite element coefficient matrices must be updated and regenerated. Although this method can lead to accurate results by way of a conceptually satisfying algorithm, the method appears to be expensive except for a small number of solutes.

The technique of separating the algebraic equation set for the equilibrium chemistry from the differential equation set for the mass transport has been used with some success (Grove and Wood 1979; Jennings et al. 1982). Grove and Wood (1979) coupled mineral dissolution/precipitation and ion exchange for three reactive solutes to a one-dimensional transport model that neglected transverse dispersion. The algebraic equation set for the chemistry and the differential equation set for the mass transport were solved sequentially. The differential equation set was solved using a finite difference technique centered in space and time. Schulz and Reardon (1983) presented a combined two-dimensional mixing cell/analytical solution model that described multiple reactive solute transport in unidirectional groundwater flow regimes. The chemical equilibria for four solutes undergoing ion exchange and mineral precipitation/dissolution were calculated using a mixing cell model. The mixing cell model was coupled to and solved sequentially with an analytical

transport model. This model is limited in its application to groundwater sites containing one-dimensional flow, although both transverse and longitudinal dispersion were considered.

Miller and Benson (1983) also modeled one-dimensional transport in a saturated porous medium. They combined the differential equation set for the mass transport and the algebraic equation set for the chemistry into one differential/algebraic system of equations. The chemical reactions in their model included sorption of ions and complexes in the solid phase, formation of complexes in the aqueous phase, and dissociation of water. A Newton-Raphson iteration technique was used to solve the system of equations. In some cases, convergence of the system was difficult. Because the system of equations was solved for chemical concentrations along previously generated streamlines, transverse dispersion was ignored.

Posing the chemical equilibria equations and the transport equations independently and iterating between the two offer some advantages over inserting all the chemical equations into the transport equations. If the finite element method is used in solving the differential equations, as in the work of Jennings et al. (1982) and Valocchi et al. (1981a), reformulation of the finite element matrices within each time step is not required. The phase-exchange relations (that is, sorption isotherms) need not be known explicitly or be differentiable because the equilibrium chemistry is posed as a set of algebraic equations. Also, convergence of the equation sets may be less of a problem.

A general mass transport model (called TRANQL) has been developed using the second technique (Schulz and Reardon 1983). In the development of TRANQL, the algebraic equation set for the equilibrium interaction chemistry, MICROQL, contains all of the phase-exchange and/or mass-action equations necessary to describe all significant chemical processes affecting transport such as sorption, complexation, dissociation of water, ion exchange, and precipitation/dissolution. It is not necessary to assume the solutes being modeled act independently of the bulk solution composition. The differential equation set contains the mass balance of the multispecies system based only on the physical processes of advection and dispersion. The algebraic equation set, MICROQL, for the interaction chemistry is solved using the Newton-Raphson method, whereas the differential equation

set is solved using the Galerkin-finite element method. In TRANQL, a solution is found by iterating between the two equation sets. Specific details of the solution procedure can be found in Cederberg et al. (1985).

3. The K_d Approach to Transport Modeling

a. K_d Model Development. For the purpose of illustrating the development of the K_d approach, the following TRANQL simulations are limited to transport in a one-dimensional, homogeneous medium. The governing transport equation for a single reactive component in the aqueous phase is

$$\frac{\partial C}{\partial t} + \frac{p\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

In the K_d approach adsorption is usually incorporated into Eq. (1) by assuming local chemical equilibrium and using a special case of the Freundlich isotherm,

$$\bar{C} = k_1 C^{k_2} \quad (2)$$

where k_1 and k_2 are empirically derived coefficients. The Freundlich isotherm, which is purely empirical, assumes that the total solid-phase concentration of a component $\bar{C}$ is solely a function of the total solution-phase concentration (C). A special case of the Freundlich isotherm is

$$\bar{C} = K_d C \quad (3)$$

where K_d is referred to as a distribution coefficient (in liters per gram) and the exponent of C is unity. Equation (3) defines a linear relationship between $\bar{C}$ and C . Physically, the distribution coefficient is a measure of the partitioning of a component between the solid and solution phase. Thus, a high K_d value indicates a strong tendency for sorption and low mobility. Using Eq. (3) for predictive purposes is considered to be valid under the assumptions that local chemical equilibrium is attained, the component is present in trace amounts, the sorption isotherm is linear, and the determined K_d value is spatially and temporarily constant and independent of the bulk solution composition. Substitution of Eq. (3) into Eq. (1) yields

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (4)$$

where R is the retardation factor defined as

$$R = 1 + \frac{\rho d\bar{C}}{\theta dC} = 1 + \frac{\rho}{\theta} K_d \quad (5)$$

The transport equation, Eq. (4), then becomes

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - \frac{v' \psi}{\partial x} \quad (6)$$

where D' is the effective dispersion coefficient ($D' = D/R$) and v' is the rate of advance of the center of mass of the contaminant zone ($v' = v/R$). This zone is retarded relative to the rate of advection of the nonreactive contaminant zone, v .

The retardation concept is illustrated schematically in Fig. 2. The position of the 50th percentile concentration level or "average" position of an advancing slug of contamination, denoted by $X'_T(t)$, can be computed using R because $v' = v/R = dX'_T/dt$. This simple approach has the objective of predicting the advance rate of the average position of a contaminant zone emanating from a continuous or temporary source.

b. Limitations of the K_d Approach. Although the convenience and computational ease of the K_d approach is beyond dispute, it has had limited success in modeling observed behavior and its validity as a means of developing reliable predictions of the behavior of contaminants in actual groundwater systems is questionable.

Several recent investigations (Reardon 1981; Miller and Benson 1983) have shown that the use of distribution coefficients in problems involving multicomponent ion-exchange reactions where the isotherms are nonlinear may not be appropriate. Recently, Valocchi (1984) proposed the use of a constant, "effective" K_d to calculate the contaminant front velocity. An effective K_d is calculated from the ratio of the difference in sorbed concentrations across the advancing front to the difference in aqueous concentrations across the front. For selected cases of one-dimensional binary and ternary homovalent ion exchange, front locations calculated using this effective K_d with Eq. (4) agreed closely with concentration profiles calculated using a numerical model. However, even this effective K_d approach breaks down in systems where dispersion is an important process, where slug-type or temporary sources occur, and where multi-ion heterovalent exchange occurs.

Fig. 2. Schematic representation of the retardation concept.

Theoretical and experimental difficulties exist in determining K_d 's and using them to predict contaminant migration. The distribution coefficient is usually determined by laboratory or field methods under a given set of chemical and physical conditions that may or may not be representative of constant or changing (dynamic) conditions in the field. K_d values determined and reported in the literature are specifically associated with a given porous medium and a given solution composition within that medium.

Estimates of K_d values for inorganic contaminants are predominantly determined by laboratory batch experiments, observing retardation in the field, or in situ K_d tests. In a batch test a known mass of the geologic medium from a sediment core is mixed with a volume of solution representing the geochemical composition of the leachate or groundwater. The solution contains a specified concentration of the reactive contaminant of interest.

The solids and solution are agitated for several hours or days until chemical equilibrium has been achieved. The solution and solids are then separated and the total concentration of the reactive component in each phase is determined. This test is then repeated using different concentrations of the reactive solute and the relationship $C = K_d \bar{C}$, which is known as the adsorption isotherm, is obtained.

By mapping contaminant plumes and measuring breakthrough curves from known contaminant spills or tracer tests, the average velocity of the reactive solute can be compared to the average velocity of a nonreactive solute (Freyburg 1984; Jackson and Inch 1983; Pickens et al. 1981). A mean retardation factor and, thus, a value of K_d are determined from the ratio of these velocities. The information from these observations describes only how the center of mass of a contaminant plume travels relative to a nonreactive plume over a specific distance in the field. No information, however, is obtained on how the front or tail edges of the plume are advanced and dispersed through the aquifer.

Recently in situ column devices for determining distribution coefficients have been developed. One-dimensional flow of natural groundwater is established in the device, and the retardation of the reactive solute is determined by measuring the relative migration rates of a nonreactive and reactive tracer. Because the velocities used in the experimental device are often several orders of magnitude greater than the groundwater velocity, the

assumption of chemical equilibrium may not be valid. If an in situ K_d test is performed using a reactive solute in equilibrium with the native groundwater, then a reasonable measure of how that solute will be distributed between solution and solid phases should be obtained. What the test will not reveal is how the solute will be distributed at that point when a solution of different chemistry flows through. This is the situation that most often confronts contaminant hydrogeologists.

Although these methods exist for determining distribution coefficients, there still also exist many limitations and uncertainties inherent in the use of the K_d approach within the framework of the advection-dispersion equation. The limitations and uncertainties exist because of geochemical effects, the heterogeneous nature of the aquifer, and effects caused by the physical dynamics of dispersion and advection.

In both the batch test and the in situ K_d test, the distribution coefficients are measured under a very specific set of geochemical conditions such as pH, concentration of sorbing solute, concentration of other ionic species present, and physical properties of the medium such as mineral composition and surface area. Batch tests (Hajek and Ames 1968; Routson and Serne 1972) have shown that the measured K_d value can be influenced by the ratio of solution to solids used in the tests. Korte et al. (1976) showed that surface area, number of sorption sites, and pH are important in determining solute partitioning and, thus, the migration of trace elements. Other investigators (Hahne and Kroontje 1973; Korte et al. 1976; Garcia-Miragaya and Page 1976; Donner 1978; Donner et al. 1982; Means et al. 1978) have shown that the ionic strength of solution, the degree of inorganic complex formation, the type and concentration of other inorganic species present, and the pH of the system all affect the sorption and mobility of inorganic species in groundwater systems.

Even if the aqueous solution used in the determination of the distribution coefficient has the same composition as the leachate, the conditions in the field are dynamically different from those found in laboratory batch experiments. Dispersion and advection cause a spreading of the leachate and a continual mixing of leachate and native water that may differ markedly in chemical composition. The advancing zone of contamination continuously supplies updated, re-equilibrated concentrations of nonreactive and reactive

components to the native aquifer system. As the spreading of the plume continues, new equilibrium species concentrations must be calculated based on the transport of all system components. In the column experiments of Couchat et al. (1980), batch K_d values were found for ^{90}Sr to be inadequate in providing a good simulation of their experimental breakthrough curves.

The K_d approach to transport modeling does not account for changes in contaminant concentration caused by geochemical processes such as complexation or changes in pH. For contaminants that are hazardous at very low concentration levels, prediction of the arrival time of the front or tail of a contaminant zone can be more important than predictions of the arrival times of the mean locations of contaminant zones. Also, in areas concerning the toxicity of a component, one species containing that component may be more biologically toxic than another. Complexation in groundwater systems cannot always be ignored in contaminant problems.

4. Comparison of the TRANQL and K_d Approach to Transport Modeling

a. TRANQL Simulations. In contrast to the restrictive K_d approach, when using TRANQL to describe and predict contaminant transport it is not necessary to assume that the reactive components are present in trace amounts, the adsorption isotherm is linear, or the sorption reaction is independent of the bulk solution composition. By relaxing these specific assumptions and using TRANQL, the simulation of the transport of a reactive contaminant can include all equilibrium chemical reactions.

The effect of a conservative component, EDTA (ethylenediaminetetraacetic acid), on the transport of cadmium was investigated. The chemical reactions and the logarithms of their equilibrium coefficients are given in Table XVIII. This particular system of components and species was chosen as a model equilibrium system simulating components found naturally in groundwater environments. Because EDTA is a model ligand that strongly complexes with many inorganic contaminants, it was selected as a principal complexing conservative component. Formation of complexes in the aqueous phase and adsorption of free aquo cadmium at the solid/solute interface are the reactions given in Table XIX. The components Cd^{2+} , Ca^{2+} , HCO_3^- , EDTA^{4-} , SOH , and H^+ chemically combine to form the 18 species listed in Table XIX. The value of the binding coefficient, K_{18} , for the sorption

TABLE XVIII. CHEMICAL REACTIONS OF THE CADMIUM/EDTA SYSTEM

	Reactions		Species	Log ₁₀ K
1	Cd^{2+}	=	Cd^{2+}	0
2	Ca^{2+}	=	Ca^{2+}	0
3	HCO_3^-	=	HCO_3^-	0
4	EDTA_4^-	=	EDTA_4^-	0
5	SOH	=	SOH	0
6	H^+	=	H^+	0

Complexation

7	$3\text{H}^+ + \text{EDTA}_4^-$	=	H_3EDTA^-	6.16
8	$4\text{H}^+ + \text{EDTA}_4^-$	=	H_4EDTA	10.26
9	$\text{Cd}^{2+} + \text{EDTA}_4^-$	=	CdEDTA^{2-}	15.78
10	$\text{Cd}^{2+} + \text{H}^+ + \text{EDTA}_4^-$	=	CdHEDTA^-	18.50
11	$\text{Cd}^{2+} + \text{HCO}_3^-$	=	CdHCO_3^+	1.92
12	$\text{Ca}^{2+} + \text{EDTA}_4^-$	=	CaEDTA^{2-}	10.52
13	$\text{Ca}^{2+} + \text{H}^+ + \text{EDTA}_4^-$	=	CaHEDTA^-	13.00
14	$\text{Ca}^{2+} + \text{HCO}_3^-$	=	CaHCO_3^+	0.92
15	$\text{Cd}^{2+} - \text{H}^+ + \text{H}_2\text{O}$	=	CdOH^+	-10.28
16	$\text{Ca}^{2+} - \text{H}^+ + \text{H}_2\text{O}$	=	CaOH^+	-12.78

Dissociation of Water

17	$-\text{H}^+ + \text{H}_2\text{O}$	=	OH^-	-13.91
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Sorption

18	$\text{Cd}^{2+} + \text{SOH}$	=	CdSOH	5.01 pH = 7.46 5.35 pH = 7.97
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reaction of cadmium is a function of pH because proton stoichiometry was not included in the reaction. Therefore, two values of $\log_{10} K_{18}$ are given in Table XIX for two values of pH: at pH = 7.97, $\log_{10} K_{18} = 5.35$; at pH = 7.46, $\log K_{18} = 5.01$. A larger value of pH leads to a larger value of K_{18} . The values of K were calculated from data taken from laboratory batch experiments. The aquifer material used in the experiments came from a calcareous, sandy, unconfined aquifer near Borden, Ontario, Canada. Details of the experi-

TABLE XIX. CHEMICAL STOICHIOMETRY OF CADMIUM/EDTA SYSTEM

Species	Components	Cd	Ca	HCO ₃	EDTA	SOH	H	log ₁₀ K
1	Cd ²⁺	1	0	0	0	0	0	0
2	Ca ²⁺	0	1	0	0	0	0	0
3	HCO ₃ ⁻	0	0	1	0	0	0	0
4	EDTA ₄ ⁻	0	0	0	1	0	0	0
5	SOH	0	0	0	0	1	0	0
6	H ⁻	0	0	0	0	0	1	0
7	H ₃ EDTA ⁻	0	0	0	1	0	3	6.16
8	H ₄ EDTA	0	0	0	1	0	4	10.26
9	CdEDTA ²⁻	1	0	0	1	0	0	15.78
10	CdHEDTA ⁻	1	0	0	1	0	1	18.50
12	CdHCO ₃ ⁺	0	1	0	1	0	0	10.52
13	CaHEDTA ⁻	0	1	0	1	0	1	13.00
14	CaHCO ₃ ⁺	0	1	1	0	0	0	0.92
15	CdOH ⁺	1	0	0	0	0	-1	-10.28
16	CaOH ⁺	0	1	0	0	0	-1	-12.78
17	OH ⁻	0	0	0	0	0	-1	-13.91
								5.01 pH = 7.46
18	CdSOH	1	0	0	0	1	0	5.35 pH = 7.97

mental procedure are given by Leckie et al. (1983). Values for the operational binding coefficient, K_{18} , were calculated using the following stoichiometry: Cd²⁺ solid = Cd-solid and MICROQL. Formation constants for solution species were input (Table XIX) along with an estimate of the binding coefficient. Estimates were continued until the amount of predicted adsorbed cadmium matched that observed.

The values of the physical parameters used in the simulations are listed in Table XX. These values are typical of those found in groundwater systems. The initial and boundary conditions for the simulations are given in Fig. 3. The total concentrations of Ca²⁺, HCO₃⁻, SOH (total number of sorption sites), and pH are held constant throughout the simulations to isolate the effect of the EDTA concentration on the transport of cadmium. At time $t = 0$, a pulse of EDTA and cadmium is placed in the system. Four different concentrations of EDTA in the input pulse were used. Each EDTA input pulse in combination with the pulse of cadmium results in a different initial distribution of total aqueous cadmium. For

TABLE XX. PHYSICAL PARAMETERS USED IN THE EDTA/CADMIUM SIMULATIONS

v (mean velocity)	= 0.10 m/day
θ (porosity)	= 0.40
α_L (dispersivity)	= 0.06 m
ρ (bulk density)	= 1760 g/ ℓ

numerical purposes the background levels of EDTA and cadmium were assumed to be 2 orders of magnitude smaller than the peak concentration values of the pulse input. To reference the simulations back to the varying initial concentrations of EDTA, a notation that specifies each case is listed in Table XXI, e.g., case TRANQL:1 background concentration at 10^{-6} M EDTA and $\text{pH} = 7.97$.

Cases TRANQL:1-TRANQL:4 were used in this section to simulate the transport of a pulse containing EDTA and Cd_T . At time $t = 0$, the system is assumed to be at chemical equilibrium. A constant background concentration was used as the boundary condition at $x = -1.375$ m. The center of the pulse was assigned $x = 0$ at $t = 0$.

TRANQL was run to simulate a real time of 40 days, which was enough time to observe the effect of the different EDTA concentrations on the transport of cadmium. A time step of 12 h and a nodal spacing of 0.25 m were used in the simulations. For purposes of minimizing numerical oscillations in the solution, the time step and nodal spacing were chosen based on the transport of cadmium, the reactive component, not EDTA, the conservative component.

TABLE XXI. EDTA CONCENTRATIONS USED IN EDTA/CADMIUM SIMULATIONS

<u>Case</u>	<u>Peak Concentration</u>	<u>Background Concentration</u>	<u>pH</u>
TRANQL:1	1.0×10^{-4} M	1.0×10^{-6} M	7.97
TRANQL:2	1.0×10^{-5} M	1.0×10^{-7} M	7.97
TRANQL:3	5.01×10^{-6} M	5.01×10^{-8} M	7.97
TRANQL:4	2.51×10^{-6} M	2.51×10^{-8} M	7.97

Fig. 3. The initial and boundary conditions for the cadmium/EDTA TRANQL simulations.

Figure 4 shows the results of four TRANQL simulations, each with a different initial concentration of EDTA. The total concentration of aqueous cadmium, Cd_{aq} , is plotted as a function of distance for each of the four EDTA peak concentrations. From the figure it can be seen that as the initial concentration of EDTA increases (going from case TRANQL:1 to TRANQL:2), the concentration of Cd_{aq} increases. When the peak concentration of EDTA is a maximum (case TRANQL:1), most of the cadmium is complexed with the EDTA and, therefore, remains in the aqueous phase. In this case cadmium behaves in a manner similar to that of EDTA, the conservative component. As the initial peak EDTA concentration decreases, more and more cadmium adsorbs to the porous medium because of the decrease in cadmium complexation in the aqueous phase. A 1-order-of-magnitude decrease in peak EDTA concentration (case TRANQL:1 to TRANQL:2) results in a 40% decrease in the maximum observed concentration of cadmium. A 2-order-of-magnitude decrease in peak EDTA concentration (case TRANQL:1 to TRANQL:4) results in more than an order-of-magnitude decrease in the maximum observed concentration of cadmium. As the peak EDTA concentration decreases, cadmium becomes more and more immobile and the concentration distribution becomes asymmetric. The asymmetry in the cadmium distribution can be attributed to the changing speciation everywhere in the system over time. Also, in Fig. 4 the concentration of $\overline{Cd}$ is plotted as a function of distance for each of the four EDTA peak concentrations. The concentration of cadmium is a minimum when the EDTA peak concentration is a maximum. This corresponds to a maximum concentration of Cd_{aq} .

The transport of cadmium has been shown to be a complex function of the presence of other components in solution. In the presence of a conservative complexing component such as EDTA, the mobility or transport of cadmium increased significantly as the concentration of EDTA increased. A 2-order-of-magnitude increase in EDTA resulted in an order-of-magnitude increase in the predicted maximum concentration of aqueous cadmium.

The simulated behavior of cadmium in the presence of varying EDTA concentrations is consistent with the algebraic equation set in MICROQL (Table XIX) and observed field behavior. Given the mass- and material-balance equations built into MICROQL, it can be seen that as the concentration of EDTA increases, more cadmium will be complexed

Fig. 4. The effect of EDTA concentration on the aqueous-phase and sorbed-phase concentration of cadmium.

with the EDTA and remain in the aqueous phase. The EDTA competes with the sorption sites for the cadmium. As more and more cadmium complexes with the EDTA, there is less and less cadmium available to sorb. Means et al. (1978) reported this effect, where high concentrations of EDTA in the presence of radionuclides caused extensive complexing and, thus, a higher than expected contaminant mobility.

b. Spatial and Temporal Variation of K_d . The TRANQL runs used to investigate the effects of varying component concentrations (for example, EDTA) on the transport of cadmium now are reused as a basis for the comparison of the K_d and TRANQL approaches. The formulation and assumptions of the TRANQL and K_d approaches to transport modeling differ significantly. From simulations using TRANQL, the total concentration of a component (for example, Cd_T), the total aqueous-phase concentration of a component (Cd_{aq}), and the total sorbed-phase concentration of a component ($\overline{Cd}$) are calculated everywhere in the system. Using the TRANQL-simulated values for Cd_{aq} and $\overline{Cd}$ [for example, from Fig. 4 and Eq. (3)], an equivalent K_d^* value can be calculated everywhere in space and time, where K_d^* denotes a value of a distribution coefficient calculated from simulated data.

The spatial variability of K_d^* is demonstrated in Fig. 5, where K_d^* is plotted as a function of x at time $t = 40$ days. In Fig. 5, K_d^* is plotted for each of the four initial EDTA concentrations at $pH = 7.97$ (cases TRANQL:1-TRANQL:4). The K_d^* in Fig. 5 was calculated from values in Fig. 4. From Fig. 5, one can see that for any particular peak value of EDTA, the calculated K_d^* varies with distance and is not constant in space. For any one of the curves, K_d^* is lowest when the concentration of EDTA is a maximum. This is consistent with Eq. (3) because as EDTA increases, cadmium increases and thus K_d^* decreases. At background concentration levels, K_d^* is a maximum. The values of K_d^* vary 2 orders of magnitude over distance. It is apparent that in a multicomponent solution the distribution coefficient for an inorganic species, such as cadmium, is not a constant in space.

The distribution coefficient represents the ratio of the total amount of a component in the solid phase to the total amount of a component in the aqueous phase, irrespective of the geochemical speciation of the system. However, in systems involving inorganic con-

Fig. 5. The effect of EDTA concentration on the spatial distribution of K_d^* .

taminants, equilibrium component speciation will affect the total concentration of species in the solution and solid phase, and thus the expected value of K_d . Rearranging Eq. (3) yields

$$K_d^* = \frac{\bar{C}}{C} \quad (7)$$

Substituting the species in Table XIX into Eq. (7), the distribution coefficient for cadmium, Cd^{2+} , is

$$K^* = \frac{[CdSOH](\theta/\rho)}{[Cd^{2+}] + [CdEDTA^{2-}] + [CdHEDTA^-] + [CdOH^+]} \quad (8)$$

where (θ/ρ) is used for consistency in units. In Eq. (8) $[CdSOH]$ is the total sorbed-phase concentration of the component Cd^{2+} and the total aqueous-phase concentration of Cd^{2+} is the sum of the four species Cd^{2+} , $CdEDTA^{2-}$, $CdHEDTA^-$, and $CdOH^+$.

In this simplest of examples it is clear that for the K_d to remain spatially and temporally constant, the partitioning of the component Cd^{2+} between the solid and solution phase must remain constant even when a change in chemical speciation may occur because of varying concentration levels of chloride. In the previous section, it was clearly shown that the concentration of EDTA had a significant effect on the amount of cadmium sorbed in the system. As the EDTA concentration was increased, the amount of cadmium sorbed decreased because of the increased complexation of cadmium and chloride. Only under extreme circumstances, where no complexing ligands are present, would K_d remain a constant whether or not the component Cd^{2+} is present in trace amounts. If K_d experiments are conducted in the laboratory under conditions where the contaminant of interest exhibits a much different speciation than would occur under field conditions, the laboratory result has limited applicability to field predictions.

Because of this dependence upon the geochemical and physical properties of the system, the K_d of a particular solute is not uniquely dependent on soil properties but is rather an operational parameter of little or no thermodynamic significance. A K_d tells one nothing about specific chemical reactions occurring in the system nor what physical or chemical reasons exist for controlling the reactions.

5. Comparison of TRANQL and K_d Simulations

It has been demonstrated that a K_d^* for an inorganic (cadmium) component is not spatially constant during groundwater transport. The question addressed in this section is, how do the actual simulated transports by the TRANQL and the K_d^* approaches differ and by how much? A one-dimensional K_d transport model was used to simulate cadmium transport. The results were compared with simulations using TRANQL. To compare the TRANQL and K_d approaches fairly, a K_d^* was calculated using Eq. (7) at time zero at the peak and background concentrations for each of the cases TRANQL:1 through TRANQL:4. Table XXII lists the K_d^* used in the comparisons. For example, from the initial conditions of case TRANQL:1, a K_d^{*p} was calculated at $x = 0$ and a K_d^{*b} was calculated at $x = 1.5$ m. The center of the injection pulse where cadmium and EDTA are present in maximum concentrations is located at $x = 0$. At $x = 1.5$ m, cadmium and EDTA are present in background concentrations. In Table XXII and here, the superscript p refers to the distribution coefficients calculated at $x = 0$ and the superscript b refers to the distribution coefficients calculated at background. For all four cases, the K_d^{*p} at $x = 0$ is less than the K_d^{*b} calculated at background. The smaller the value of K_d^* , the more mobility the component will exhibit during transport. An effective K_d^{*e} was also calculated by using the definition of Valocchi (1984):

$$K_d^{*e} = \frac{C^{-p} - C^{-b}}{C^p - C^b} \quad (9)$$

Rearranging Eq. (9) yields

$$K_d^{*e} = K_d^{*p} \left[\frac{1 - C^{-b}/C^{-p}}{1 - C^b/C^p} \right] \quad (10)$$

As the concentrations of the total aqueous and sorbed phases at $x = 0$ (peak concentrations of cadmium and EDTA) become much greater than the concentrations in the background solution, the effective K_d , K_d^{*e} , becomes equal to the K_d^{*p} . From the results in Table XXII, K_d^{*e} is greater than K_d^{*p} by less than 1%. Therefore, in this example system the effective K_d approach would predict no more significant mobility or transport than would using the K_d^{*p} . For each K_d^* , a v' , the rate of advance of the contaminant zone, is calculated and listed in Table XXII. Because K_d^{*p} is less than K_d^{*b} in each case, it follows

TABLE XXII. CALCULATED VALUES OF K_d^* AND v'

$K_d^*(\ell/g)$		TRANQL:1	TRANQL:2	TRANQL:3	TRANQL:4
K_d^{*P}		3.21×10^{-6}	3.73×10^{-6}	8.0×10^{-5}	1.75×10^{-4}
	v'	0.0986	0.0859	0.0740	0.0565
K_d^{*E}		3.41×10^{-4}	3.18×10^{-3}	5.89×10^{-3}	1.03×10^{-2}
	v'	0.090	0.0067	0.0037	0.0022
K_d^{*O}		1.82×10^{-6}	3.48×10^{-5}	7.70×10^{-5}	1.79×10^{-4}
α_{On}	v'	0.0992	0.0867	0.0747	0.0560

that the respective retardation factor will be less and the velocity of the contaminant zone will be greater. Because the K_d^{*P} 's predict a faster mobility and represent a worst-case transport situation, the K_d^{*P} 's will be used in the comparison of the TRANQL and the K_d approaches.

The results and comparison of the TRANQL and K_d approaches are displayed in Figs. 6a-6d. The same initial conditions (see Fig. 3) were used in the comparison. The concentrations of Cd_{aq} at time $t = 40$ days are shown. In Fig. 6a where the concentration of EDTA is a maximum, the predicted results of the TRANQL and K_d simulations closely agree. The peak concentrations of cadmium are at the same position, although TRANQL predicts a slight decrease in concentration. The TRANQL approach predicts that cadmium will behave in a manner similar to that of EDTA, the conservative component. The TRANQL simulations (see Fig. 4) show that more than 95% of the cadmium was complexed with the EDTA. The K_d approach also predicts that the transport of cadmium will be similar to the transport of a conservative component. The rate of advance of the contaminant zone, v' , was calculated to be 0.0986, only 1% less than the average mean velocity, v (see Table XXII). Both approaches predict the observed simulated behavior.

As the concentration of EDTA in the pulse decreases, the simulations for the TRANQL and K_d approaches agree less and less favorably (see Figs. 6b-6d). As the concentration of EDTA decreases, TRANQL predicts increasing differences in the maximum observed concentrations and increasing cadmium mobility with respect to the K_d simulations. In Fig. 6d, where the EDTA concentration is a minimum, TRANQL predicts a maximum

Fig. 6a. The comparison of TRANQL and K_d model simulations: Case TRANQL:1.

Fig. 6b. The comparison of TRANQL and K_d model simulations: Case TRANQL:2.

Fig. 6c. The comparison of TRANQL and K_d model simulations: Case TRANQL:3.

Fig. 6d. The comparison of TRANQL and K_d model simulations: Case TRANQL:4.

concentration of cadmium, which is an order of magnitude smaller than the value predicted using the K_d approach. It can also be seen that TRANQL predicts a broader cadmium distribution with the front edge of the distribution ahead of that predicted by the K_d approach.

In general, the TRANQL and K_d approaches predict differences in the observed cadmium transport in the cases where the cadmium is not entirely complexed with the EDTA. Only when there is enough complexing ligand, EDTA, present in the system to complex with most of the cadmium in the aqueous phase do the two approaches closely agree. However, even in this case, as in all the examples, the K_d approach does not predict the geochemical speciation in the system. The nonsymmetric shape of the TRANQL simulations can be attributed to the geochemical complexation and speciation occurring everywhere in the system. As new total concentrations of components are being advected and dispersed in the system, MICROQL updates and calculates the geochemical speciation based on the new total concentration of components.

6. Conclusions. Results show that the classical distribution coefficient, K_d , for a trace metal is a function of several important system variables, such as availability and concentration of competing ligands and equilibrium formation constants. Thus, K_d may vary in both time and space and should not be considered a constant. In the context of predictive capabilities, the TRANQL simulations and the K_d simulations differ significantly in situations where sorption is considered an important controlling reaction. TRANQL provides estimates of the concentrations of the components in the advancing front and the chemical speciation everywhere in the system. Because the K_d approach does not include the effects of geochemical equilibrium reactions on the transport of components, the extensive use of K_d models may lead to errors in estimates of transport. Further investigations should be focused on the applicability of using K_d models or multicomponent models to predict radionuclide transport at potential nuclear waste storage sites.

H. Applied Diffusion (A. E. Norris, P. L. Wanek, and K. Wolfsberg)

The purpose of this task is to measure diffusivity values under field conditions at Yucca Mountain. The in situ measurements will be used to ascertain the accuracy of diffusivities extrapolated from laboratory experiments. The diffusivities are important for

calculating the rate of transport of nonsorbing radioactive wastes in water that might flow through the repository block.

The field experiments entail the introduction of tracers into boreholes in Topopah Spring Member and Calico Hills tuffs, sealing the boreholes while diffusion occurs, overcoring the diffusion sites, and analyzing the overcored material for the tracer concentrations as a function of distance from emplacement. Work this quarter concentrated on the development of tracer analysis techniques.

The natural isotope chemistry task has identified NaBr as a potential tracer with nonsorbing characteristics in the presence of Topopah Spring Member tuff. The high-performance liquid chromatography method used for the tracer selection study has neither the sensitivity nor the convenience that would be desirable for assaying the samples from the in situ diffusion experiments. A neutron activation technique for bromine analyses was tried previously (Rundberg et al. 1985), but the method was not as practicable as the ion chromatography used for the tracer selection study. A different neutron activation technique was tried recently with much more promising results. This technique differed from the previously reported neutron activation method in that the bromide solution was evaporated onto filter paper before irradiation, instead of being irradiated directly, the irradiation length was increased from 5 min to 2 h (both at a flux of $\sim 3 \times 10^{12}$ neutrons $\text{cm}^{-2}/\text{s}^{-1}$), and the time before counting was increased from a few hours to ~ 30 h to permit 75% of the ^{24}Na activity in each sample to decay. The sensitivity of the new method appeared to be limited to $\sim 0.02 \mu\text{g Br/ml}$ solution, because of the bromine content of the filter paper that was used. Filter paper with a lower bromine content may be found, but this method already is capable of measuring bromine in well J-13 water at a concentration 1 order of magnitude smaller than is possible with our best ion chromatography technique. This new neutron activation analysis method is sufficiently convenient that large numbers of aqueous samples can be analyzed for bromine with less labor and in a shorter time than with the currently used ion chromatography technique. The bromine content of well J-13 water was determined by this new neutron activation method to be $\sim 0.05 \mu\text{g/ml}$.

III. MINERALOGY-PETROLOGY OF TUFF (D. Bish, D. Broxton, F. Byers, B. Carlos, S. Levy, and D. Vaniman)

During this quarter, work was focused on the origin of soil and fault-related alteration mineralogy at Yucca Mountain and on the refinement of petrographic stratigraphy within the Topopah Spring Member. Ongoing studies of fracture mineralogy and of hydrous mineral stability will be reported next quarter. Also during this quarter an improved method for zeolite analysis by x-ray fluorescence was developed.

A. Studies on the Origins of Soil and Fault-Related Alteration Mineralogy at Yucca Mountain

Studies of soil and fault-related samples around Yucca Mountain, particularly in relation to faults exposed in trenches, were begun in late September 1984, at the request of NNWSI management. Concern was expressed that some of the mineral deposits associated with faults may be the products of deep-seated springs. Any future activity of deep-seated springs could compromise a repository at Yucca Mountain by providing aqueous transport of waste up to the surface.

The mineralogy of these soil and fault-related samples is being studied with four possible origins in mind:

- (1) The deposits may be pedogenic, reflecting only local dissolution and reprecipitation of material from the soil zone. This would be a local, low-temperature origin.
- (2) The deposits may have formed from a low-temperature spring. Such springs could be either perched or deep-seated.
- (3) The deposits may have formed from a high-temperature spring, with a deep-seated origin.
- (4) The deposits may include material that originated from early high-temperature alteration along with early faulting soon after tuff emplacement.

More than one of these hypotheses may be necessary to explain the full variety of minerals found in these faults, in the altered tuff cut by the faults, and in the nearby soils.

This is a multidisciplinary study because of the large variety of data relevant to the resolution of an origin for these deposits. Also for this reason, the studies are spread jointly between researchers at LANL and the US Geological Survey (USGS). At this time, J. O'Neil of the USGS is analyzing oxygen and carbon isotopes in samples from this collection.

No active springs of deep-seated origin have been observed at Yucca Mountain or vicinity. However, spring deposits of 30,000-yr age occur in southern Crater Flat, and a 78,000-yr-old spring deposit may occur at the southern end of Yucca Mountain (Szabo et al. 1981). It is certainly possible that other springs may have occurred with activity so old or rare that they have not been observed in surface mapping. Such springs could be recognized by the study of mineral deposits or alteration in trenches. The descriptions below concentrate on samples from Trench 14 on the eastern side of Yucca Mountain, at present our best known site.

1. Field Relations. Trench 14 was excavated across a north-south-trending fault on the west side of Exile Hill. From east to west, the trench exposes volcanic bedrock, bedrock with overlying alluvial cover, and alluvium. There is considerable calcite and silica accumulation within the alluvium. Several fault traces are exposed at the east end and central part of the trench; faults and associated fractures are coated with carbonate and silica. The samples studied fall into three categories:

- (1) material from pedogenic K horizon developed on alluvium (west end of trench; sample TR14-1);
- (2) material from faults within alluvium (east end of trench; sample TR14-2); and
- (3) material from faulted bedrock (east end of trench; samples T-14 TUFF, TR14-3a, TR14-3b, and TR14-3c).

2. Sample Descriptions

a. Representative Pedogenic K Horizon (TR14-1). This is the upper laminated portion of a Stage IV (most highly developed) pedogenic K horizon (Gile et al. 1966) developed in alluvium. The sample has a strongly nodular texture and is locally vesicular with crude horizontal layering. Principal components of the sample are carbonate nodules that are spherical to elongate and up to 3 mm across. The nodules are of three varieties:

- (1) laminated, round, with silicate and vitric sand nucleii of alluvial or eolian origin (abundance of heavy minerals, variety of rock types, high sphericity of many grains);
- (2) laminated, highly irregular, with interior void spaces and micritic or sparry pseudomorphs of plant material;
- (3) nonlaminated, round, with scattered carbonate and silicate inclusions.

The three varieties are partly segregated into poorly defined, discontinuous horizontal layers. The matrix is micritic calcite; the amount of micrite varies and its texture is locally nodular, laminated, or massive. Outer edges of the nodules are locally recrystallized to sparry calcite. Pore space is irregularly distributed but most abundant in layers containing irregular laminated nodules. Pores include spaces within and between nodules and discontinuous, semihorizontal fractures that locally follow nodule laminae. Botryoidal silica, showing slight birefringence, lines most pore spaces, especially fractures.

b. Material from a Fault within Alluvium (TR14-2). This is a sample of material filling a fault-related fracture in the weathered alluvium. The filling is crudely laminated parallel to the fracture walls. The principal mineral constituents are calcite, silica, and minor sepiolite; detrital silicate grains are rare. The texture closely resembles the irregular laminated, nodular texture present in parts of sample TR14-1. There are no plant remains or nodules with silicate nucleii. The nodular material encloses fragments of fine-grained calcite with very fine laminations that are still approximately parallel to the fracture walls; these are the remains of an older fracture filling. Pore spaces are lined with silica and locally filled with sparry calcite. Fine-grained acicular calcite is present as a pore lining overlain by silica and as a partial pore filling over silica. Small amounts of sepiolite also fill pores and may be overlain by or intergrown with silica.

c. Material from Faulted Bedrock (T-14 TUFF, TR14-3a, TR14-3b, and TR14-3c). These are examples of the bedrock partly below the alluvium at the east end of Trench 14. In this part of the trench, the alluvium is thin and bedrock is exposed at the base of Exile Hill. The rock is a highly altered volcanic tuff. Lithic inclusions of densely welded, devitrified tuff, up to boulder size, are abundant. Phenocrysts are predominantly quartz, alkali feldspar, and biotite. The highly altered matrix was very fine grained vitric ash with variable amounts of shards and crystal fragments. This material is nonwelded to slightly

welded, with local variation in degree of devitrification. Patches of secondary drusy quartz, formed by recrystallization of the matrix, are locally abundant. The matrix surrounding these patches of quartz is more coarsely devitrified than elsewhere (Fig. 7).

In all the tuff samples, the fine-grained matrix is partially to completely replaced by calcite. Some fine-grained crystalline lithic inclusions are also partially replaced. Nodular texture has developed locally within the calcite. Initially fine-grained calcite has recrystallized in places to produce coarse sparry crystals. For example, the segregated silicate residue and relict fracture fillings within a sparry calcite crystal (Fig. 8) indicate that this coarse-grained calcite formed by recrystallization of finer grained carbonate.

Silica similar to the material described in samples TR14-1 and TR14-2 (but more birefringent in places) has been deposited as fracture and void filling and as a replacement of carbonate and tuff matrix. Aggregates and rinds of fine-grained sepiolite or intergrown sepiolite-silica are locally abundant as fracture and void filling. Some aggregates appear deformed as a result of crystallization and recrystallization of adjacent carbonate.

The altered tuffs are highly fractured; both primary and secondary constituents are affected. Fracture fillings are mostly calcite, but include plant relicts, silica, and sepiolite.

3. Relations Between Samples. Preliminary study suggests a close textural and mineralogical similarity between the pedogenic material in weathered alluvium and the material deposited along faults within the weathered alluvium. Pedogenic calcite is transported in soils by downward-moving surface water and deposited from solution. Continuing deposition and recrystallization force the noncarbonate soil particles apart, leading to the formation of laminated, nearly pure carbonate horizons (Birkeland 1974). For carbonate deposition in a fracture, however, the geometry and permeability of the depositional environment are different. In addition, because tectonic fractures can conduct water well below the root zone, carbonate deposition may be less affected by plant CO_2 in such fractures than in the soil horizons. Nevertheless, the basic depositional processes are much the same. The material deposited along fractures may be nonpedogenic mainly in the sense that it transgresses soil horizons. The apparent greater abundance of coarse sparry calcite in fractured tuff and in caliche near the fault, compared to horizontal K-horizon caliche, may result from locally increased permeability along fractures and from possible fluid com-

Fig. 7. TR14-3a, plane light. Devitrified matrix around secondary quartz. Dark border is probably stylitic concentration of insoluble material. Remainder of matrix is replaced by calcite and silica. Long dimension 3 mm.

Fig. 8. T14 TUFF, plane light. Most of photo is a single crystal of calcite. Linear accumulations of insoluble residue, center left, and relict fracture filling, lower right, suggest recrystallization of finer grained calcite to form large single crystal.

position differences. Lattman and Simonberg (1971) showed that infiltration of rainwater into carbonate alluvium in southern Nevada was sufficient to cause local solution and re-precipitation of fine-grained carbonate as sparry cement to depths of more than 10 ft (3 m). Therefore, no additional source of water (for example, a spring) is required to account for the sparry calcite. It is in this pedogenic association that sepiolite is also found.

In contrast, the altered tuff also contains drusy quartz that could be the product of moderate temperature hydrothermal alteration. If this is true (see fluid inclusion studies, below), it would be important to establish the time of alteration and the relationship, if any, between alteration and fluid movement along faults. Further field study will determine the distribution of alteration within tuff and its relationship to the exposed faults.

4. Mineralogy. X-ray diffraction analysis of bulk samples of both soil- and fault-filling materials revealed the presence of major calcite and minor amorphous silica or opal CT. However, the 10% HCl-insoluble residue of the carbonate rocks contained major sepiolite and/or opal CT and lesser amounts of palygorskite and quartz. The presence of sepiolite and palygorskite, magnesium silicates with chain-like structures, is noteworthy because these minerals are thought to form at low temperatures. These two minerals are very common in calcic soils, pedogenic calcretes, and other surficial carbonates, such as paludal or lacustrine deposits, in the semiarid southwestern US. In fact, their presence in calcic horizons of the surficial deposits of the NTS area has been noted by Jones (1983). Lacking strong evidence for a hydrothermal origin for these deposits in Trench 14, we suggest that these deposits represent low-temperature pedogenic calcretes, similar to those documented in the NTS area. Khoury et al. (1982) showed that these magnesium-silicates can form under ambient conditions simply through the evaporation of surface water equilibrated with atmospheric CO₂.

5. Fluid Inclusions. Multiple thin sections from soil and fault-filling samples have shown no fluid inclusions large enough to analyze for temperature of homogenization. The largest inclusions found are less than 2 mm in size or occur as fracture-related secondary inclusions in opaline silica. However, the intergrowth of these carbonate-rich samples with sepiolite is strong evidence of low-temperature origin. Moreover, although the inclusions

found are very small, examination at high magnification reveals no bubbles that would be expected from formation at higher temperatures.

The drusy quartz crystals that occur in altered tuff also are poor in large inclusions, but the small inclusions that occur in abundance contain visible bubbles. The largest inclusion found so far (8 mm) yielded a homogenization temperature of 145°C. Further serial sections are being obtained to confirm this temperature. This preliminary datum plus the textural evidence for early growth of the drusy quartz suggest that some form of hydrothermal event preceded the calcite-opal CT-sepiolite-palygorskite-amorphous silica crystallization along the fault.

6. Isotopic Studies. Samples of pedogenic K-horizon carbonate, of fault-filling carbonate, and of amorphous silica from one of the trenched faults are being analyzed for carbon and oxygen isotopes by J. O'Neil of the USGS. A sample of the early-formed drusy quartz from altered tuff along the fault will also be analyzed. These data will be compared with those compiled for Yucca Mountain drill-hole carbonates by Scott and Costellanos (1984). Analysis of the drusy quartz will be particularly useful for comparison with the high temperature (145°C) so far indicated by fluid inclusion studies and may help to distinguish between a high-temperature spring origin or an origin during early high-temperature tuff alteration.

7. Preliminary Interpretations and Future Work. Of the four possible interpretations for the origin of fault-related minerals stated in the introduction, none can yet be explicitly ruled out. We can, however, state that more than one episode of alteration is recorded in these samples. An early episode of high-temperature quartz growth (either during early cooling of the tuff or by high-temperature spring activity) was followed by an episode of low-temperature sepiolite-carbonate-silica-palygorskite alteration (through either pedogenic or low-temperature spring activity). The problem remains of uniquely determining whether or not spring activity was involved in either the high-temperature or low-temperature stages of alteration. Our preliminary data lead us to suggest that a combined field and laboratory study will provide the answers to these questions by (1) comparing the formation conditions, including direct or indirect radiometric dating if possible, of early drusy quartz in Yucca Mountain faults with the formation conditions of

similar silica alteration that occurs elsewhere at Yucca Mountain, and by (2) comparing the later low-temperature alteration in the faults with the known spring deposit at Crater Flat and with the suspected spring deposits of southern Yucca Mountain.

B. Petrographic Stratigraphy Within the Topopah Spring Member

A milestone report covering the petrochemical variation of the Topopah Spring tuff matrix in drill hole USW G-4 (Byers 1984) was transmitted to the Nevada Operations Office this quarter and is now in review. The compositions of Topopah Spring feldspars in hole USW G-4 have been compiled on An-Ab-Or triangular diagrams (anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ - albite, $\text{NaAlSi}_3\text{O}_8$ - orthoclase, KAlSi_3O_8) and also on binary An-Ab and Ab-Or histograms. The petrographic stratigraphy of the Topopah Spring matrix has been extended to other cored holes in the Yucca Mountain exploration block including USW G-1, USW GU-3, and UE-25a#1. Slides cut from drill cores have also been supplied by R. W. Spengler and R. B. Scott of the USGS to fill gaps in the LANL sample suite from these holes. As a test in stratigraphic identification, K. Knauss of LLNL provided three slides of a specimen of Topopah Spring matrix collected from the south end of Fran Ridge for waste package environment studies (WBS 2.2.1.L). These slides were counted and averaged, and the data were graphed for comparison with data from samples of known stratigraphic position (see Fig. 9).

Our main emphasis this quarter has been thin section study of UE-25a#1 core samples (Spengler et al. 1979), which are more closely spaced than those in other cored holes in the Yucca Mountain exploration block. Moreover, this hole is closer to the south end of Fran Ridge, where the LLNL sample was taken. The petrographic diagram of the Topopah Spring matrix from UE-25a#1 is shown in Fig. 9. Also shown is the petrographic diagram of the LLNL sample at its inferred stratigraphic position. Inasmuch as the general locality of the LLNL sample is known, the general stratigraphic position is also known from the mapping of Scott and Bonk (1984) of the USGS. Despite this prior knowledge, we attempted to treat the LLNL sample as a complete unknown.

Data from the three thin sections were averaged to reduce sampling error. There is a wide deviation in feldspar content, owing to sporadic occurrence of relatively large (approximately 2-mm) phenocrysts, but three slides of the same hand sample averaged

DRILL HOLE UE-25A #1

Data by F. Byers, LAM, 1994; LLNL, outcrop sample, south end of Fran Ridge, collected by K. Knauss, LLNL.

*LLNL data

Fig. 9. Petrographic variation of Topopah Spring matrix textures and phenocrysts with depth (stratigraphic position) in drill hole UE-25a#1, Yucca Mountain. LLNL designation shows inferred stratigraphic correlation of sample collected from south end of Fran Ridge by Kevin Knauss, LLNL. Contacts in stratigraphic column from Spengler, Muller, and Livermore (1979).

out this error to the extent that the average feldspar ratio is consistent with those in the lower two-thirds of the Topopah Spring in the drill core (Fig. 9). Quartz phenocrysts are rounded, indicative of resorption, and are probably genetically xenocrysts, in part derived from underlying quartz-rich magma zones. Quartz therefore is the most useful criterion among the phenocrysts for indicating stratigraphic position, for it becomes less common stratigraphically upward and is absent or rare above the middle nonlithophysal zone (Fig. 9).

The LLNL sample of the Topopah Spring Member from the south end of Fran Ridge is most likely correlated with the lower part of the middle nonlithophysal zone, although the upper part cannot be completely ruled out. This correlation is based on the following criteria illustrated in Fig. 9:

- (1) low granophyric content (2%);
- (2) low abundance of cristobalite-filled vesicles or amygdules (0.3%);
- (3) cristobalite, as opposed to tridymite, in vesicles indicates the lower half of Topopah Spring (Bish et al. 1984); and
- (4) little or no cryptocrystalline groundmass indicates the top or bottom of the middle nonlithophysal zone.

In addition to the semiquantitative petrographic criteria listed above and shown on Fig. 9, the textures of relic shards and pumice were compared with slides of the middle nonlithophysal zone and those of the lower nonlithophysal zone. It should be noted also that the primary shard textures of the lithophysal zones are completely obliterated by large (greater than 0.5-mm) secondary circular spherulitic growths, whereas the primary shard textures are still easily recognizable under the incipient, very fine (less than 0.5-mm) axiolitic secondary overprint in the nonlithophysal zones. The shards and pumices of the middle nonlithophysal zone are clearly recognizable with a flattening ratio mostly between 2:1 and 4:1 (moderately welded), whereas those of the lower nonlithophysal zone are greatly compacted and strung out around lithics and phenocrysts and have a flattening ratio of greater than 5:1 (densely welded). The LLNL sample can be definitely correlated with the middle nonlithophysal zone on the above criterion. The feldspar phenocryst data from the rhyolitic portions of the Topopah Spring Member are uniform. It was originally

thought that feldspar phenocryst compositions might show significant progressive change or shift with stratigraphic position, reflecting increasing magmatic temperature and pressure with depth. To some extent this is indeed the case, but the shift is very gradual, and sanidine data are sparse in samples through the mid-stratigraphic portion. Based on Brown and Parsons' (1981) graphical geothermometer for coexisting feldspar phenocryst compositions, the original magma temperature of feldspar crystallization in the lower part of the lower nonlithophysal zone was 690°C; in the upper part of the lower lithophysal zone the temperature was 720°C. Data on sanidine phenocrysts in the middle nonlithophysal zone and the lower half of the upper lithophysal zone are lacking, owing to paucity of phenocrysts. The upper half of the upper lithophysal zone has feldspar temperatures of formation between 725 and 775°C, and the overlying caprock of 750 to 910°C. These temperatures correspond to a gradual increase in range of Ab content in sanidine from 35 to 40% at the base, to 50 to 56% in the caprock. The Ab content of plagioclase remains at essentially 75 to 80% up to the caprock, in which the range drops slightly to 70 to 75% Ab and finally to 60 to 67% in the caprock vitrophyre.

C. A New Technique for X-Ray Fluorescence Analysis of Zeolites

For many years, the best available analyses of zeolites have been obtained by atomic absorption or gravimetric methods. X-ray fluorescence analysis that is more rapid and potentially more accurate has seldom been employed because of the hydration-dehydration problem with pressed powders or because of explosive steam production in the preparation of fused discs for analysis. This problem has been overcome by preparing fused discs after the sample powder has been through a two-stage heating process. First, heating for 1 h at 110°C drives off most zeolite water. Second, heating at 1000°C for 4 h removes any remaining water and forms a structurally nonzeolitic powder residue that will not rehydrate as soon as it is cooled. This powder residue is easily made into fused discs that may be analyzed using standard x-ray fluorescence techniques. Preliminary comparisons with atomic absorption and gravimetric data indicate that accurate analyses are obtained through this method.

IV. TECTONICS AND VOLCANISM

Volcanic hazard investigations have focused on five topics: the mechanism of emplacement of shallow basalt intrusions, geochemical trends through time of volcanic fields of the Death Valley-Pancake Range (DV-PR) volcanic zone, the possibility of bimodal basalt-rhyolite volcanism, the age and process of enrichment of incompatible elements in young basalts of the NTS region, and the possibility of hydrovolcanic activity. The stress regime of Yucca Mountain may favor formation of shallow basalt intrusions. However, combined field and drill hole studies suggest that shallow basalt intrusions are rare in the geologic record of the southern Great Basin. The geochemical trends of basaltic volcanism through time in the NTS region provide no evidence of possible future increases in rates of volcanism. Existing data are consistent with declining volcanic activity comparable to the late stages of the southern Death Valley volcanic field. Drill holes USW VH-1 and VH-2 provided no evidence of past bimodal volcanism in the Crater Flat area. The hazards of bimodal volcanism in this area are judged to be low.

Several problems remain. First, two magnetic anomalies, one in Crater Flat and the other near the town of Lathrop Wells, need to be drilled to complete documentation of the volcanic history of the Yucca Mountain region and to further test for buried rhyolite centers. Second, the source of a 6-Myr pumice discovered in alluvial deposits of Crater Flat has not been found. Geochemical studies have shown that the enrichment of trace elements in the younger rift basalts must be related to enrichment of their mantle source rocks. This enrichment predates the basalts of the silicic episode and is, therefore, not a young event. Studies of crater dimensions of hydrovolcanic landforms indicate that the worst-case scenario, exhumation of a repository at Yucca Mountain by hydrovolcanic explosions, is unlikely. Theoretical models of melt-water vapor explosions, particularly the thermal detonation model, suggest that hydrovolcanic explosions are possible at Yucca Mountain. Additional calculations may be required on the radiological consequences of basaltic eruptions at Yucca Mountain using an eruption cycle that originates with hydrovolcanic activity.

V. SEALING MATERIALS EVALUATION (D. M. Roy and C. J. Duffy)

A. Introduction

Cementitious materials (grout, mortars, concretes) are being proposed as one major type of potential sealing material for a repository in Yucca Mountain. Introduction of any sealing materials will, in general, cause reactions between the host rock and the sealant because of chemical differences and the reactive nature of fine-grained minerals and glasses in the tuff.

Different concrete-type sealing materials are being evaluated for their potential chemical compatibility with the tuff chemistry. Two approaches to sealant/host rock compatibility were examined. The first concrete utilized indigenous sands and gravel in the formulation of the sealant; the second approach used more conventional concrete materials to control the bulk chemical composition of the concrete and thus approached more closely the tuff composition.

The purpose of this project is to evaluate the chemical stability of potential sealing materials. This evaluation will be based upon laboratory studies that represent a range of credible temperature conditions supplemented by other evaluations based upon thermodynamic considerations and durable analogs from other sources. Experimental thermodynamic studies, stability assessments, development of a grout dissolution model for fracture seals, thermodynamic properties calculations, and assistance in preparation of the materials recommendation and design requirements report are major activities during FY85.

B. Fault Seal Alteration and Dissolution

A detailed model that describes the kinetics of dissolution of a heterogeneous, multi-component assemblage of crystalline phases was developed after the mathematical model presented by Lasaga (1984). Two important properties of the dissolution of crystalline materials addressed in this paper make this type of analysis possible: (a) most crystalline materials display a linear dissolution behavior, and (b) a multicomponent system can be described as a weighted linear summation of the component parts.

Personnel from Los Alamos and Pennsylvania State University participated in a design requirements/materials recommendation workshop held in Albuquerque, November

13-15, 1984. A synopsis of past and current seal material activity, including both physical properties and geochemical studies, was presented and discussed. As part of the workshop, details of the kinetics model for dissolution of fault seals were reviewed. Because the dissolution model would require considerable new thermochemical data, it was decided that further work should concentrate on a simplified set of calculations that could provide Project guidance in the near term. To examine possible phase changes that might take place in fault and fracture seals because of repository heating, predictions for the assemblage of stable phases in cementitious solids were completed that reflect our best interpretation of the phases stable at ambient temperature, 150°C, and 200°C.

Cement clinker is usually ground in the presence of grinding aids to form a material commonly recognized as cement powder. The clinker composition is controlled in part by the composition of the raw feed stock that enters the kiln, the temperature to which it is heated, the length of time that it is heated at temperature, and the quench rate of the clinker at the end of the cycle. All portland cements contain as dominant crystalline phases Ca_3SiO_5 , Ca_2SiO_4 , and $\text{Ca}_2(\text{Al,Fe})\text{O}_5$ with lesser $\text{Ca}_3\text{Al}_2\text{O}_6$. Minor amounts of CaO , MgO , and K_2SO_4 can be present as well as a form of CaSO_4 introduced as a grinding aid and set regulator.

Admixtures of reactive silica or siliceous materials are incorporated into the cement powder in quantities necessary to stoichiometrically react with and minimize the amount of calcium hydroxide forming as a hydration product of both the di- and tricalcium silicates. Further, graded quartz sands are present in the mixtures, which will to a lesser extent enter the chemical reactions.

The tricalcium silicate reacts rapidly with water to form a nearly amorphous calcium-silicate-hydrate, which forms a strong, hardened cement paste. This material possesses a variable composition, often approaching a calcium to silica ratio that would yield the stoichiometry $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The dicalcium silicate reacts more slowly to form a similar hydrate. Both reactions also produce calcium hydroxide, which crystallizes as the mineral phase portlandite. Reactive siliceous admixtures present with the cement powder react with the calcium hydroxide to form additional calcium-silicate-hydrate.

Tricalcium aluminate reacts with the calcium hydroxide solutions to form an intermediate product, $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$, which in turn reacts with the calcium sulfate from the set regulator to form ettringite, $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$, and additional portlandite. Because in the original clinker there exist extensive solid solutions of cations other than calcium, silicon, and aluminum in each of these phases, what is represented here is a simplified model for the development of hydration products. The incorporation of additional cations into many of these structures slightly changes the stability fields for these phases. This can be advantageous.

At intermediate temperatures up to 150°C , the calcium-silicate-hydrate transforms from an x-ray amorphous material to crystalline tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{18}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Further, the ettringite becomes unstable and thermally decomposes, releasing sulfate ions to the pore water and further reacting the calcium aluminate component with the silica source to produce an aluminum-substituted tobermorite. This aluminum-substituted tobermorite was observed to persist for up to 1 month at 300°C , some 100°C above the usually accepted stability limit for non-aluminum-substituted tobermorite, but with time it converted to the more silica-rich truscottite. At 200°C , the truscottite, anhydrite, and quartz may constitute a stable phase assemblage.

C. Reports

A topical report titled "Ancient Concrete Studies as Analogs of Cementitious Sealing Materials for a Tuff Repository" was completed by Penn State and is being reviewed at Los Alamos. This report presents the results of an investigation of the durability/longevity of concrete in the environs of ancient Rome. Because tuff and volcanic ash were used in the concretes, the results are particularly applicable to a nuclear waste repository in a tuff environment. Evidence from detailed investigations of the analog materials suggests that sealing materials compositionally and microstructurally similar to the ancient pozzolanic cementitious materials will adjust slowly to such an environment, perform well, and remain stable.

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