



Department of Energy

Washington, DC 20585

August 10, 1990

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John J. Linehan, Director  
Repository Licensing Project Directorate  
Division of Waste Management  
U.S. Nuclear Regulatory Commission  
4-H-3  
Washington, D.C. 20555

Dear Mr. Linehan:

On behalf of the Office of Civilian Radioactive Waste Management the Los Alamos National Laboratory (Los Alamos) will host a technical workshop on radionuclide adsorption on September 11 and 12, 1990, in Los Alamos, New Mexico. You are invited to have two technical expert representatives intimately familiar with radionuclide migration, retardation and adsorption attend this workshop. Emphasis will be placed on adsorption processes and unsaturated flow and transport related to the Yucca Mountain site in Nevada. The workshop will include presentations by experts from outside the Yucca Mountain Project as well as presentations by experts from Lawrence Livermore National Laboratory and Los Alamos. A description of the workshop, a list of speakers, two recent articles from Los Alamos and a copy of the Nuclear Waste Technical Review Board (NWTRB) report to Congress are enclosed for your information.

Technical representatives from the NWTRB, the State of Nevada, the U.S. Geological Survey, Sandia National Laboratories and the Yucca Mountain Project Office have also been invited to attend the workshop. Though these representatives are not required to make formal presentations, they are expected to join in group discussions. If your representatives wish to present papers to the workshop and submit them for publication in the proceedings document of the workshop, they should contact Julie Canepa at Los Alamos.

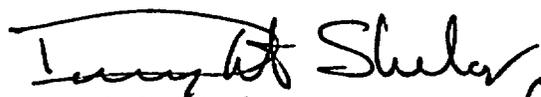
This workshop promises to provide a wide ranging technical dialogue among parties interested in the Yucca Mountain site. We hope that your most expert representatives can attend.

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For more details regarding the time and place of this workshop, please contact Richard J. Herbst at (505) 667-9286 or Julie A. Canepa at (505) 667-4109, both of Los Alamos, or Donald E. Livingston of the Yucca Mountain Project Office at (702) 794-7944.

  
Ralph Stein *for*  
Associate Director for Systems  
Integration and Regulations  
Office of Civilian Radioactive  
Waste Management

4 Enclosures:

1. Workshop Announcement
2. Confirmed List of Invited Speakers
3. Sorption of Radionuclides on  
Yucca Mountain Tuffs
4. Laboratory Studies of Radionuclide  
Migration in Tuff
5. NWTRB Report to U.S. Congress,  
March 1990

cc w/o enclosures: ,

J. A. Canepa, LANL, Los Alamos, NM  
R. J. Herbst, LANL, Los Alamos, NM

## RADIONUCLIDE ADSORPTION WORKSHOP

### DESCRIPTION

SEPTEMBER 11 AND 12, 1990

The Los Alamos National Laboratory is hosting a workshop on radionuclide adsorption for the U.S. Department of Energy (DOE)/Yucca Mountain Project. This workshop will be held September 11 and 12, 1990, in Los Alamos, New Mexico. The purpose of this workshop is described in the following excerpt from the First Report to the U.S. Congress and the U.S. Secretary of Energy from the Nuclear Waste Technical Review Board (NWTB).

"The Board recommends that the DOE organize a radionuclide adsorption workshop to be attended by the DOE and its contractors involved in the measurement and modeling of such adsorption. The workshop would have two general purposes, (a) to determine the applicability of available radionuclide adsorption data on tuff and models for predicting such adsorption under existing and postclosure conditions at Yucca Mountain, and (b) to establish what additional radionuclide adsorption research and model development are needed. Such research and model development should attempt to demonstrate that quantitative scientifically defensible predictions and radionuclide adsorption at Yucca Mountain are possible and show how such measured and predicted adsorption relates to compliance with the radionuclide release rate criteria set forth in 40 CFR 191."

The Los Alamos Yucca Mountain Project staff will present ongoing and planned studies or radionuclide sorption and migration through the course of the workshop. Data, conceptual models, and computational results will be presented to bring all participants up-to-date on work progress. Invited speakers will present papers related to the above stated purpose and goals stated below to generate discussion and make all attendees aware of technical progress related to the particular needs of the sorption and radionuclide migration program of the DOE/Yucca Mountain Project. A list of invited and confirmed speakers is enclosed. A proceedings document of the workshop will be published, therefore draft papers are requested at the workshop. The papers will be reviewed by knowledgeable experts, and final papers are required within two months following the workshop.

Specific goals of the workshop are: (1) to establish the technical state-of-the-art of sorption studies (saturated and unsaturated); (2) to evaluate the applicability of the current sorption database for the Yucca Mountain Project; (3) to evaluate processes with respect to radionuclide transport in a dynamic or advective systems (unsaturated flow); (4) to discuss a conservative approach that recognizes the need to prioritize the sorption and migration studies that are needed to meet regulatory requirements; (5) to discuss the relative importance of understanding geochemical processes as related to nuclide migration in an unsaturated environment; and (6) to discuss the relative inherent uncertainties in the geochemical process evaluation and radionuclide migration studies.

For more information regarding specific workshop information such as meeting location and times, Los Alamos hotel information and directions, please contact Julie A. Canepa at (505) 667-4109 or FTS 843-4109.

ENCLOSURE 1

CONFIRMED LIST OF INVITED SPEAKERS

Speakers

Affiliation

Jeff Serne	Pacific Northwest Laboratory
Peter Wierenga	University of Arizona
James Conca	Washington State University, Tri-Cities
V. Nguyen	E Wa, Inc., Minneapolis, Minnesota
R. J. Wagenet	Cornell University
Gail Cedarberg	ENVIRON Corp., Princeton, New Jersey
James Leckie	Stanford University
Inez Triay	Los Alamos National Laboratory
Arend Meijer	Los Alamos National Laboratory
Carol Bruton	Lawrence Livermore National Laboratory
Brian Vini	Lawrence Livermore National Laboratory

# SORPTION OF RADIONUCLIDES ON YUCCA MOUNTAIN TUFFS

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## ABSTRACT

A substantial database of sorption coefficients for important radionuclides on Yucca Mountain tuffs has been obtained by Los Alamos National Laboratory over the past ten years. Current sorption studies are focused on validation questions and augmentation of the existing database. Validation questions concern the effects of (1) the use of crushed instead of solid rock samples in the batch experiments, (2) the use of oversaturated stock solutions, and (3) variations in water/rock ratios. Sorption mechanisms are also being investigated. Database augmentation activities include determination of sorption coefficients for elements with low sorption potential, sorption on pseudocolloids, sorption on fracture lining minerals, and sorption kinetics.

Sorption can provide an important barrier to the potential migration of radionuclides from the proposed repository within Yucca Mountain to the accessible environment. In order to quantify this barrier, sorption coefficients appropriate for the Yucca Mountain groundwater system must be obtained for each of the important radionuclides in nuclear waste<sup>1</sup>. Los Alamos National Laboratories has conducted numerous batch (crushed-rock) sorption experiments over the past ten years to develop a sorption coefficient database for the Yucca Mountain site<sup>2</sup>. In the present site characterization phase, the main goals of the sorption test program will be to validate critical sorption coefficients and to augment the existing database where important data are lacking.

## DATABASE VALIDATION

The sorption coefficient database available at the present time<sup>2</sup> suggests that for all but a few of the important elements (i.e., U, Tc, Np) sorption coefficients are sufficiently large (i.e.,  $\gg 10$  ml/g) to make sorption an important barrier to the migration of radionuclides

in Yucca Mountain under most conditions anticipated for the site. An important question is, "Are the coefficients included in the database appropriate for modeling radionuclide migration in the Yucca Mountain ground water system?" For example, "Could crushing of the rock material used in the batch experiments artificially enhance the value of the sorption coefficient obtained for a given element?"<sup>3</sup> For the alkali and alkaline earth elements (e.g., Cs, Ba, Sr), the latter question can be answered with some certainty. Sorption of these elements on Yucca Mountain tuffs is dominated by ion exchange reactions involving zeolites and clays<sup>3</sup>. Ion exchange reactions on these phases are fairly well understood. Further, because these phases have large intracrystalline exchange capacities and because the crystal sizes are much smaller than the (crushed-rock) particle sizes used in the experiments, crushing should not substantially influence the sorption coefficients. This is borne out by comparisons of batch sorption coefficients obtained on crushed and solid samples of several rock types<sup>3</sup>. Because zeolites and clays are relatively abundant along flow paths between the proposed repository and the accessible environment<sup>4</sup>, we can say with some confidence that sorption coefficients for the alkali and alkaline earth elements will generally be large over the ranges of environmental conditions and radionuclide concentrations anticipated in the far-field of the proposed repository<sup>2</sup>.

For the actinides and lanthanides, the sorption reactions are not as well understood even though measured sorption coefficients are large for many of these elements<sup>2</sup>. Because the stable compounds of Am, and presumably Ce and Eu, have very low solubilities in Yucca Mountain ground waters<sup>5</sup>, some question exists as to whether the large sorption coefficient values listed in the present database for these elements<sup>2</sup> could simply reflect precipitation reactions. For example, the solubility limited concentration of Am in Yucca Mountain ground waters is on the order of  $10^{-9}$ M<sup>5</sup>. Because the sorption experiments reported in the database<sup>2</sup> were

**TABLE I**  
**Am SORPTION ON DEVITRIFIED TUFF/J-13**

Sample no.	Rd (sorption) (ml/g)	Rd (desorption) (ml/g)	Initial Concentration
GU3-688	14,000		$6.9 \times 10^{-12}$ M
G1-1833	4,200-5,300	5,900-8,900	$1.0 \times 10^{-7}$ M
GU3-433	2,900-3,800	6,000-14,000	$2.1 \times 10^{-7}$ M
JA-32	79-230	1,500-2,800	$1.0 \times 10^{-8}$ M
YM-22	1,100-1,500	1,900-3,100	$1.0 \times 10^{-7}$ M
YM-54	150-160	400-680	$1.0 \times 10^{-7}$ M

Solubility of Solid AmOHCO<sub>3</sub> =  $10^{-8}$  to  $10^{-10}$  M

carried out with stock solutions containing  $10^{-6}$  to  $10^{-7}$  M Am, if Am did not sorb onto Yucca Mountain tuffs, precipitation in the sorption experiments could produce an apparent sorption coefficient in the range of  $10^3$  ml/g. To investigate this possibility, a new set of experiments was carried out with solution concentrations of  $6.9 \times 10^{-12}$  M, well below the estimated solubility limited concentration level. At this concentration, normal counting techniques are not appropriate and a mass spectrometric isotope dilution technique was utilized. Preliminary results for a devitrified welded tuff from Yucca Mountain (GU3-688) are shown in Table I. Fortunately, the newly measured sorption coefficient is as large as the largest value measured in the earlier experiments on this type of rock (Table I). In fact, the formation of colloids<sup>6</sup> in the earlier experiments (e.g., samples JA-32, YM-54) may have resulted in a lowering of measured sorption coefficients due to imperfect separation of colloids from the solution phase<sup>5</sup>.

Although the new Am results indicate that sorption coefficients for this element should be large in Yucca Mountain tuffs, the batch experiments that produced these results do not provide much indication of the mechanism(s) by which Am is sorbed onto the tuffs. Some knowledge of such sorption mechanisms would not only enhance our confidence in the experimental results obtained to date but would also provide some basis for extrapolation of these results to environmental conditions not directly addressed by the experiments. As a start in this direction, a series of experiments have been initiated to determine the mechanism(s) by which neptunium sorbs to individual mineral phases found in Yucca Mountain tuffs<sup>4</sup>. Np was chosen as the first actinide element to be studied because it has a relatively high solubility in Yucca Mountain ground waters<sup>5</sup> and is therefore easier to analyze. Preliminary results of batch

experiments with Np and pure mineral phases are shown in Table II. These experiments were carried out to identify the mineral phase(s) with the greatest affinity for Np under conditions appropriate to the Yucca Mountain ground water system. Once such phases are identified, the mechanism(s) by which Np sorbs to each phase will be investigated in detail. The sorption coefficients listed in Table II have not been corrected for possible differences in the surface areas of the mineral samples although these differences are thought to be of second order. For example, the difference in the Np sorption coefficient measured for synthetic and natural calcite may reflect differences in surface areas for these two samples. Clearly, of the minerals listed in Table II, the iron oxides and oxyhydroxides have the greatest affinity for Np, followed by Mn oxides (romanechite and cryptomelane), the aluminosilicates montmorillonite and clinoptilolite, and finally calcite. Synthetic samples were used instead

**TABLE II**  
**Sorption of Np on Pure Minerals**

Mineral	Rd (ml/g) <sup>1</sup>
Hematite (synthetic)	$5.1 \times 10^4$
Goethite (synthetic)	$5.1 \times 10^4$
Cryptomelane (natural)	$7.8 \times 10^3$
Romanechite (natural)	$1.5 \times 10^3$
Calcite (natural)	390
Calcite (synthetic)	21
Montmorillonite (natural)	78
Clinoptilolite (natural)	30

<sup>1</sup>Distilled water buffered at pH = 8.5

of natural samples because the latter are often "contaminated" with small fractions of other mineral phases, complicating interpretation of the experimental data. Full details of these experiments will be presented elsewhere.

An important part of defining the mechanism(s) by which a given element sorbs to a mineral surface is the experimental characterization of the species of the element attached to the mineral surface. Spectroscopic techniques of the type required to characterize these species have only recently been applied to geochemical problems<sup>7</sup>. As part of an preliminary effort to apply these techniques to the investigation of sorption mechanisms of actinides on Yucca Mountain tuffs, we have designed an experiment involving Np sorbed onto goethite. Although hematite ( $\text{Fe}_2\text{O}_3$ ) appears to be the most abundant secondary iron oxide mineral in Yucca Mountain<sup>8</sup>, goethite ( $\text{FeOOH}$ ) was chosen for these experiments because well-characterized pure samples were available and because the experimental group had experience with this phase<sup>7</sup>. Np was chosen as the adsorbate because its compounds have relatively high solubilities in Yucca Mountain ground waters as noted above<sup>5</sup>. High solubilities are necessary to permit the transfer of a sufficient number of Np atoms onto the goethite surface, from an undersaturated solution, to obtain a reliable EXAFS signal. An adsorption edge for Np on goethite was obtained (Figure 1) to allow selection of an appropriate pH for the preparation of the EXAFS sample and to provide a basis for future surface complexation modeling efforts<sup>9</sup>. Similar experiments will be carried out with other elements and substrates.

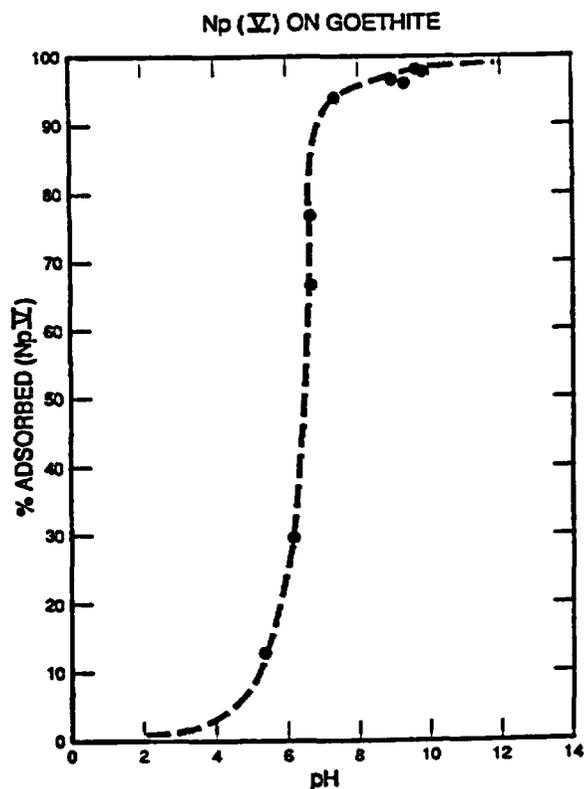


Figure 1. Neptunium adsorbed onto synthetic goethite. Initial concentration of neptunium in solution was  $5.0 \times 10^{-3} \text{M}$ .

**TABLE III**  
**WATER/ROCK RATIO EXPERIMENTS**  
**Zeolitic Tuff (G4-1502)/J-13**

Ultracentrifugation Experiments			
Rd's (ml/g)			
W/R Ratio	Ba	Cs	Sr
5:1	6,970 (2,400)	14,600 (4,200)	>10,500
10:1	46,700 (14,000)	13,900 (1,400)	>32,400
20:1	81,100 (3,900)	23,800 (2,200)	>27,900
30:1	123,000 (25,000)	31,100 (770)	108,000 (40,000)
Ultrafiltration Experiments			
Rd's (ml/g)			
W/R Ratio	Ba	Cs	Sr
5:1	69,200 (4,900)	17,900 (800)	92,500 (55,900)
10:1	106,000 (25,400)	33,500 (3,100)	169,600 (10,900)
20:1	236,000 (4,100)	43,200 (3,700)	207,900 (9,050)
30:1	433,800 (70,300)	44,700 (2,150)	322,100 (5,100)

The influence of different water/rock ratios on sorption coefficients is another validation question needing resolution<sup>10</sup>. The question is, "Could the relatively large water/rock ratios used in the experimental program bias the measured sorption coefficients in a non-conservative direction?" Theoretically, isotherm measurements should provide sufficient information to allow a correction to be made for differences in water/rock ratios in the experiments versus the site. Indeed this seems to be the case for experiments involving devitrified tuffs from Yucca Mountain<sup>3</sup>. However, for zeolitic tuffs the situation is less clear. As shown in Table III, sorption coefficients for Ba, Cs, and Sr on zeolitic tuffs increase with water/rock ratios contrary to theoretical expectation. If this trend is real and not some experimental artifact, it could have important implications for radionuclides which have small sorption coefficients (e.g., Tc, Np, U) as these coefficients might be even smaller at the lower water/rock ratios common to Yucca Mountain. Interestingly, the results for experiments in which solutions were separated from solids by ultrafiltration seem to be more in line with theoretical expectation than those in which ultracentrifugation was the separation method (Table II), although neither technique produced sorption coefficients that decreased with increasing water/rock ratios. A new set of experiments have been initiated using larger samples and larger filtration areas to attempt to resolve this question.

#### DATABASE AUGMENTATION

Additional batch sorption coefficient data are needed for elements with small sorption coefficients (e.g., Np, Pu, Tc, and U) because the errors associated with the determination of these coefficients are typically a larger fraction of the coefficient than the errors associated with larger coefficients. Experiments are planned to identify the phases with the greatest affinity for these elements. Once identified, the details of the mechanisms by which each of these elements sorb to these phases will be investigated. The results of these investigations should provide a basis for critical evaluations of whole rock sorption coefficients for these elements and thereby allow the derivation of more realistic error estimates.

In addition to sorption coefficient data, other types of information are required to fully quantify the influence of sorption processes on the potential rates of migration of radionuclides from the proposed repository in Yucca Mountain. These include sorption coefficients that pertain to fracture flow, sorption of radionuclides on pseudocolloids that may be present in the ground water system, and the kinetics of sorption reactions. Sorption coefficients that pertain to fracture flow will be estimated by weighting of sorption coefficients mea-

sured for each of the important radionuclides on pure mineral phases identified as fracture fillings in cores from Yucca Mountain. The sorption of radionuclides on pseudocolloids will be investigated through batch experiments, once the colloids present in Yucca Mountain ground waters have been characterized. The question of the kinetics of sorption reactions has been partially addressed (Rundberg)<sup>11</sup>. He concluded the kinetics of sorption reactions involving the alkali and alkaline earth elements were sufficiently fast to provide a large margin of safety given the large values measured for the sorption coefficients for these elements. For the actinides and presumably the lanthanides, the situation was less clear partly because the very little is known about the mechanisms by which these elements sorb onto Yucca Mountain tuffs. Plans for the investigation of sorption reaction kinetics and sorption mechanisms for these elements are in place.

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## LABORATORY STUDIES OF RADIONUCLIDE MIGRATION IN TUFF

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### ABSTRACT

The movement of selected radionuclides has been observed in crushed tuff, intact tuff, and fractured tuff columns. Retardation factors and dispersivities were determined from the elution profiles. Retardation factors have been compared with those predicted on the basis of batch sorption studies. This comparison forms a basis for either validating distribution coefficients or providing evidence of speciation, including colloid formation. Dispersivities measured as a function of velocity provide a means of determining the effect of sorption kinetics or mass transfer on radionuclide migration. Dispersion is also being studied in the context of scaling symmetry to develop a basis for extrapolating from the laboratory scale to the field.

These experiments have been performed under the Dynamic Transport task of the geochemistry program for the Yucca mountain project.

### INTRODUCTION

The theory of transport through porous media is well developed for chemical engineering (Sherwood, Pigford, and Wilke, for example). The theoretical methods have been developed with the principal purpose of designing efficient separations processes for the chemical industry using chromatographic columns. Chromatographic columns are generally homogeneous with respect to the both hydraulic properties, i.e., porosity and permeability, and chemical properties. Transport in geologic media is on the other hand complex hydrologically and chemically. Some of difficulties which must be overcome in order to predict the hydrologic transport of radionuclides are: 1) the solubility of many of the radionuclides is too low to allow the direct determination of the chemical structure of solution species by spectroscopic methods. 2) all of the chemical interactions between radionuclides and the minerals present in tuffaceous rock have not been identified. 3) all of the significant aqueous phase reactions occurring in groundwater have not been quantified. 4) The effect of heterogeneity is not considered in column chromatography. With respect to the fourth difficulty hydrologists have successfully applied the principles

developed for column chromatography by the use of the simplifying assumption of a representative elementary volume, REV<sup>2</sup>. However, the assumption of an REV is only valid under special circumstances. A general approach to modeling transport in complex hydrologic systems has yet to have been developed.

The transport of solutes in porous media is most often considered a Fickian diffusive process described by the convection-diffusion equation<sup>3</sup>,

$$\text{div}(D \text{ grad } C - UC) = \epsilon \frac{\partial C}{\partial t} \quad (1)$$

where

$D$  dispersion tensor;

$C$  concentration of solute;

$U$  Darcy's velocity vector;

$\epsilon$  effective porosity.

The dispersion tensor represents both diffusion and hydrodynamic dispersion. Hydrodynamic dispersion in this context refers both to dispersion caused by the variation in water velocity across pores and the dispersion caused by heterogeneity in the permeability of the hydrologic system. The use of a diffusive mechanism to describe dispersion would appear justifiable in light of the concept of representative elementary volume.

Modern stochastic models<sup>4,5,6</sup> capable of calculating the transport of conservative tracers describe the heterogeneity of aquifers in terms of the covariance of the permeability distribution. If the probability distribution of the velocity field is assumed to be gaussian the transport equation<sup>7</sup> can be written as.

$$\sum_k \sum_j \int_{t_0}^t C^{jk}(\tau) d\tau \frac{\partial^2 C}{\partial x^j \partial x^k} - \sum_j \bar{u}^j \frac{\partial C}{\partial x^j} = \frac{\partial C}{\partial t} \quad (2)$$

where

$C$  Covariance matrix of the velocity field;

$\bar{u}$  velocity.

These approaches predict increasing dispersion with time. Spatial covariance is a statistical property observed in Fractal geometry<sup>8</sup> and other nonlinear phenomena, such as, cellular automata. This opens a number of practical methods for generating realistic models of hydrologic transport. The spatial variation of the geochemical and/or sorptive properties with respect to transport has not been modeled. Of particular concern in terms of making accurate predictions of radionuclide migration is the covariance between permeability and sorption. For example, if the highly sorptive minerals, such as, smectites, were correlated with zones of low permeability the fastest moving radionuclides would in addition to having an above average water velocity would have a below average retardation factor. This could greatly increase the observed dispersion and lead to early breakthrough of small quantities of radioactive waste.

The Dynamic Transport task has as its primary mission the task of testing the assumptions made in the theory of chromatography and hydrologic transport by experimentally observing the transport of radionuclides in laboratory to field scale experiments. If there were no technical difficulties in determining the chemical species (performed in the solubility task) and determining the mechanism of interaction between radionuclides and minerals (performed in the sorption task) this would be the only purpose for this task. This is not the case however and the Dynamic Transport task has as its secondary mission the validation of sorption results in tuff columns of varying complexity. The simplest experiments are performed with crushed tuff uniformly packed in acrylic columns. These experiments utilize crushed tuff prepared in the same manner as the crushed tuff used by the sorption task. Significant discrepancies could indicate the presence of coexisting chemical species of the same element, colloid formation, and/or pseudocolloid formation. The kinetics of sorption can be studied by varying the water velocity and measuring the dispersion of the breakthrough curve as a function of velocity.

## EXPERIMENTAL

The radioactive tracers were prepared from commercially available isotopes, NEN and ICN corporations, diluted in J-13 water. All tuff columns were pretreated with J-13 water. Colloidal tracers were fluorescent carboxylated polystyrene sols available from POLYSCIENCES, INC. Radioactive tracers were assayed using standard radiochemical

procedures in accordance with the Los Alamos National Laboratory YMP QA procedure manual. The methods used were gamma ray spectroscopy using high resolution germanium detectors, and liquid scintillation beta and alpha spectrometry. For more details see reports referenced in the following sections.

## RESULTS

### Crushed Tuff Columns

The equation normally used to predict the retardation of radionuclides was derived by Heister and Vermeulen<sup>9</sup>,

$$R_f = 1 + \frac{K_d \rho}{\epsilon} \quad (3)$$

where  $K_d$  is the distribution coefficient,  $\rho$  is the dry bulk density, and  $\epsilon$  is the porosity. The derivation of this relation makes the following assumptions: 1) the solute is in equilibrium with the adsorbed phase. 2) the adsorption isotherm is linear. 3) the elution curve is constant pattern. In addition it is assumed that a single aqueous chemical species is in equilibrium with a single adsorbed species.

Crushed tuff columns are suited to testing the above assumptions because the crushed tuff used in the column experiments are nearly identical in composition to the batch sorption measurements, the columns can be packed uniformly to minimize dispersion, and have a high porosities and permeabilities making the experiments simpler to perform.

The validity of batch  $K_d$ s for the cations of cesium, strontium, and barium were checked using short crushed tuff columns<sup>10</sup>. The results were found to agree with the batch results if the batch experiments were performed on wet sieved crushed tuff. This is illustrated in Table I. Samples G1-2334, YM-22, and YM-38 were wet sieved to a size range of 75 to 500 micrometer diameter. This was necessary because the outlet frits in the crushed tuff columns have a pore diameter of 38 micrometers. The batch  $K_d$ s from crushed tuff treated in this manner yield retardation factors which agree with the observed retardation factors within a factor of three. Sample G1-3116 was not wet sieved and had a particle size ranging from 0 to 500 micrometers. The  $K_d$  for this material yields a retardation factor which is one or more orders of magnitude greater than the observed retardation factor. This result is due to the greater clay content in the unsieved material as compared to

Table I Comparison of Crushed Tuff Columns with Batch Sorption Experiments.

Sample	Element	Batch $K_d$	$R_c$ (calc.)	$R_c$ (meas.)
G1-2334	Sr	180	250	102
	Ba	1400	1940	1180
	Cs	1200	1670	1630
YM-22	Sr	60	128	50
	Ba	890	1890	723
	Cs	255	540	266
YM-38	Cs	13000	54000	49000
G1-3116	Sr	2300	9146	1065
	Ba	120000	480000	8300
	Cs	5900	23000	7100

the column material which has been sieved by flushing the column over the 38 micrometer frit.

Hydrodynamic dispersion in crushed tuff columns was examined in the context of sorption kinetics or mass transfer<sup>11</sup>. Figure 1 illustrates the dependence of dispersivity on water velocity. At low water velocity the dispersivity is dominated by longitudinal diffusion and thus increases with decreasing velocity, i.e., dispersivity increases as the residence time increases. At high water velocity mass transfer or sorption kinetics will dominate and the dispersivity will increase with increasing velocity. The crushed tuff columns did not exhibit a significantly large dispersivity at velocities as high as  $10^{-2}$  cm/s. The observed dispersivity as a function of velocity is shown in Fig. 2. The trend of the dispersivities were in general agreement with the theoretical curve in Fig. 1. Unfortunately there were no data taken at velocities near  $10^{-3}$  cm/s where the minimum in the curve is expected.

Crushed tuff columns were constructed for the specific purpose of determining the anion exclusion volume. These columns were 182 cm in length with an internal diameter of 0.7 cm. The dispersivities of these columns were on the order of 0.5 cm. Anion exclusion is the effect which causes anions to appear to migrate faster than tritiated water. This effect is due to the large size of anions and repulsion by the negatively charged mineral surfaces. The apertures of porous minerals such as zeolites and clays are on the order of a few Ångström units making it sterically impossible for anions to diffuse into the intracrystalline pore

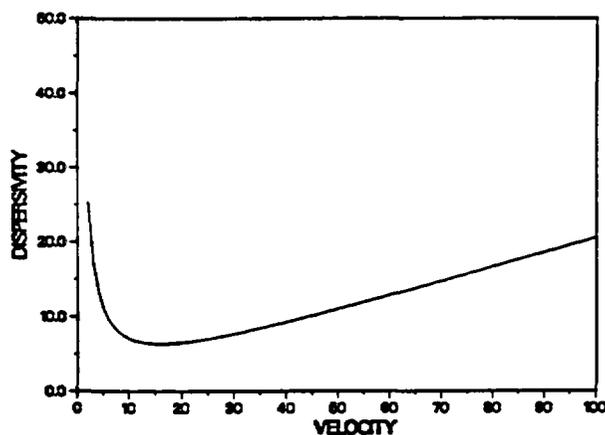


FIGURE 1. Dispersivity as a function of water velocity.

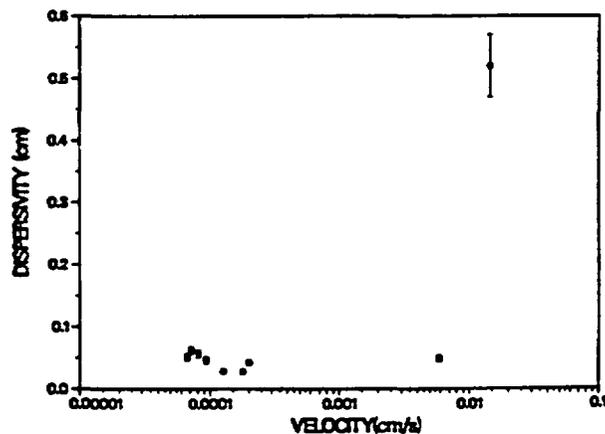


FIGURE 2. Measured dispersivity in crushed tuff column as a function of water velocity.

space. The anion exclusion volumes for tuff samples having high clay and zeolite contents were determined using  $^{95m}\text{TcO}_4^-$ , diameter 6.3 Å, see Table II. These anion exclusion volumes were found to agree with the estimated intracrystalline pore volumes based on the crystallographic data for the component zeolites and clays. The poorest agreement was for the sample USW-G2-339. This sample contained principally smectite clay. The intracrystalline pore volume was calculated for a monolayer of water in the clay interstices. If two layers of water were assumed in the clay structure the agreement would be within the experimental errors.

Table II Anion Exclusion Volumes

Sample Identification	Exclusion Volume (ml/g)	Calculated Exclusion Volume (ml/g)
USW-G2-339	$0.056 \pm 0.010$	$0.030 \pm 0.006$
USW-G2-1951	$0.20 \pm 0.03$	$0.13 \pm 0.04$
USW-G2-2017	$0.13 \pm 0.01$	$0.12 \pm 0.03$
USW-G2-2698	$0.069 \pm 0.009$	$0.08 \pm 0.01$
USW-G3-4868	$0.035 \pm 0.001$	$0.034 \pm 0.004$

The actinides neptunium, americium, and plutonium have exhibited unretarded breakthrough<sup>12</sup>. For americium and plutonium colloid the amount which elutes early is a small fraction usually a few percent of the total actinide injected. Plutonium colloid Fig. 3 and americium (open squares) eluted ahead of the tritiated water (filled circles). The difference in breakthrough volumes between the colloid and tritiated water is equal to the anion exclusion volume. This is presumably due to size exclusion. The puzzling observation is that neptunium and plutonium in the V and VI oxidation states, see Fig. 4, elute with the tritiated water, i.e., they are neither size excluded nor retarded. Ninety to ninety-five percent of the injected neptunium and twenty to eighty percent of plutonium VI and V has been observed to migrate through crushed tuff columns unretarded. This observation is in conflict with  $K_d$  values for neptunium ranging from 1 to 5 ml/g as determined by the batch technique. This raises questions as to whether the aqueous species in Yucca Mountain groundwater is the expected neptunyl ion,  $NpO_2^+$ . In any case one would expect the actinide molecules to be size excluded from the intracrystalline pore volume. It is conceivable that actinides are actually being weakly sorbed by a limited number of surface sites. Further study is needed to clarify this phenomenon before a nonunity retardation factor can be assigned to these elements.

#### Intact Tuff Columns

One step closer to field conditions is achieved by performing radionuclide migration experiments with intact tuff columns. These columns will not have the hydrologic simplicity that the uniform packing of sieved crushed tuff provides. They will however be free from the uncertainty that crushing causes in terms of the surface properties of minerals. These samples

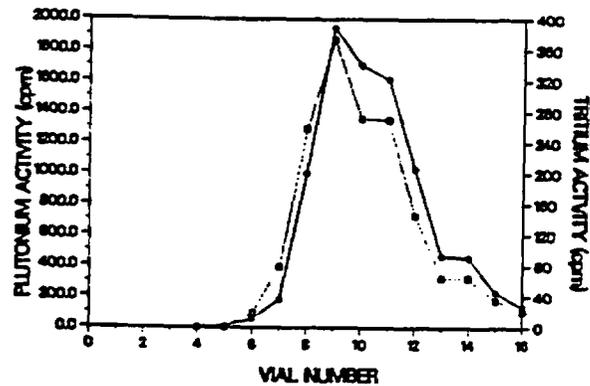


FIGURE 3. Plutonium(VI) (open squares) and tritiated water (closed circles) elution through USW-G2-1951 crushed tuff column.

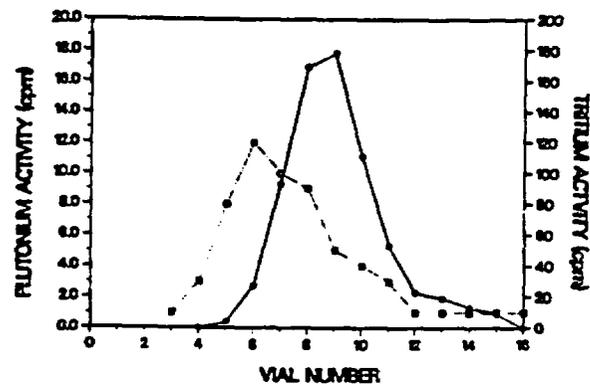


FIGURE 4. Plutonium colloid (open squares) and tritiated water (closed circles) elution through USW-G2-1951 crushed tuff column.

retain the natural hydrodynamic dispersion (valid for the laboratory scale) for porous flow through the tuff matrix. These experiments have produced interesting results.

Samples of densely welded tuff from the Topopah Spring member, Yucca Mountain, Nevada have exhibited elution curves which cannot be fit to the conventional advection-dispersion equation. ADE<sup>3</sup>. The curves can be fit however with a time dependent equivalent dispersion coefficient<sup>13</sup>. This effect has been previously observed by Coats

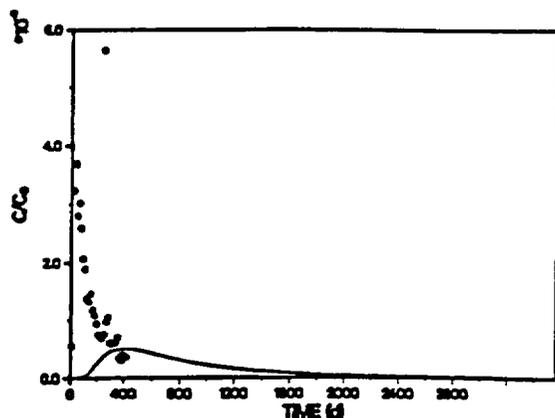


FIGURE 5. Comparison of predicted strontium elution, solid curve, with measured elution, open circles, through an intact Topopah Spring member tuff column.

and Smith<sup>14</sup> and more recently by Herr et al<sup>15</sup>. These authors have attributed the effect to that of local heterogeneities or deadend pores (Coats and Smith). The effect of heterogeneity is more generally described by the methods advocated by De Marsily and his coauthors<sup>4,7,13</sup>. This phenomenon was theoretically shown to be the result of the spatial distribution of permeability by Matheron and deMarsily<sup>4</sup>. The most dramatic consequence of the time dependent dispersion is the effect on the prediction of breakthrough times for sorbing tracers. If the conventional ADE is employed to predict the breakthrough of strontium the expected breakthrough in the solid tuff column would be at ~1.5 years, based on batch sorption measurements. The actual breakthrough, Fig. 5, occurs within a few weeks of the start of the experiment. This is a discrepancy of ~2 orders of magnitude. If the dispersion is given a time dependence the elution curve can be fit with the measured batch sorption coefficient, Fig. 6. The distribution of residual radioactivity in the tuff columns was measured by sectioning the column after elutions were observed. The distribution was found to be nonuniform. The heterogeneous distribution of sorbing minerals may be responsible, at least in part, for the reduced retardation. Dispersivities of tritiated water and pertechnetate are much greater than dispersivities observed in crushed tuff columns. Dispersivities for the sorbing tracers are significantly greater than dispersivities for tritiated water in the same tuff columns.

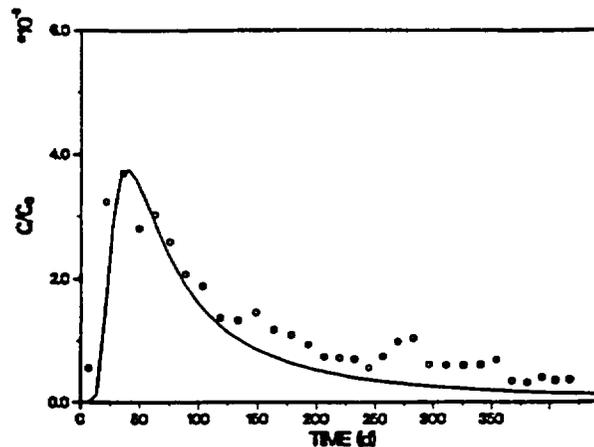


FIGURE 6. Fit to strontium elution, using time dependent dispersion, in intact Topopah Spring member tuff.

The observation of time dependent dispersion in laboratory scale migration experiments has provided new insight into the effect of heterogeneity on the retardation of sorbing radionuclides. In order to calculate the time dependence a priori at the very least a statistical characterization of the spatial distribution of sorbing minerals and the distribution of hydraulic conductivity must be made.

This effect will have an even greater importance as the scale of the hydrologic system increases to field and repository scales. Time dependent dispersion has been observed in the tritium and <sup>36</sup>Cl elutions from the CAMBRIC field test in tuffaceous alluvium on the Nevada Test Site for the Hydrology Radionuclide Migration project, HRMP<sup>16</sup>. The question which arises from these column experiments is when can one expect to observe the elution of sorbing radionuclides from CAMBRIC.

#### Fractured Tuff Columns

The next level of complexity is achieved with fractured tuff. In fractured rock the fluid flows through discrete fractures with a characteristic dispersion dominated by the variation in permeability within the fracture. Tracers will diffuse into the rock matrix perpendicular to the fracture as first pointed out by Neretnieks<sup>17</sup>. Radionuclide migration experiments in saturated tuff fractures have confirmed the importance of matrix diffusion. Elutions of conservative tracers can be described adequately by

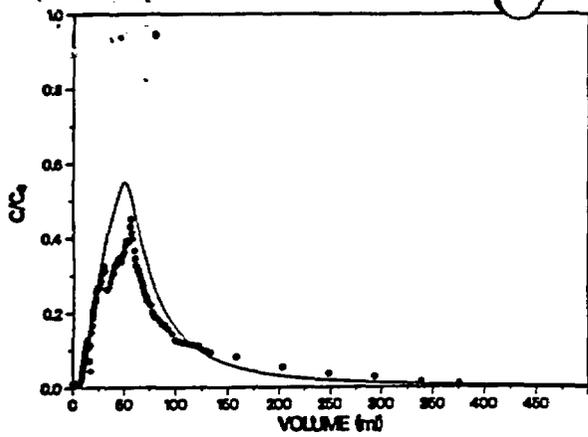


FIGURE 7. Comparison of pertechnetate elution through fractured Topopah Spring member tuff with the Tang, Sudicky, and Frind model.

the analytic solution to the advection dispersion equations of Tang et al.<sup>18</sup> Earlier experiments examining the movement of cationic tracers for the Dynamic Transport task exhibited a small fraction eluting early<sup>19</sup>. These observations may be attributed to pseudocolloid formation, channeling or time dependent dispersion in the fracture.

The permeabilities of these fractures were measured to determine the cubic law aperture. This aperture was found to be adequate to fit the elution profiles of conservative tracers. A Topopah Spring member tuff sample taken from an outcropping at Fran Ridge, near Yucca Mountain was recently used as a fractured tuff sample. The fractures in this sample were originally filled with calcite. After the tuff sample was cut and encapsulated the calcite was leached away with dilute hydrochloric acid. This was done in an effort to retain the in situ geometry of the fracture void. Transport in this fracture was not well described using the cubic law aperture determined from the fracture permeability. Adjustment of the fracture aperture was required to fit conservative tracer data. The fit achieved after adjusting the aperture is shown in Fig. 7 for pertechnetate anion.

Nonsorbing tracers have been found to be in fair agreement with prediction based on independently measured diffusivities and estimates of fracture aperture. The most recent work with these columns involved measuring the migration of colloidal polystyrene tracers. Polystyrene colloids with a ~1 micron diameter were found to have the lowest

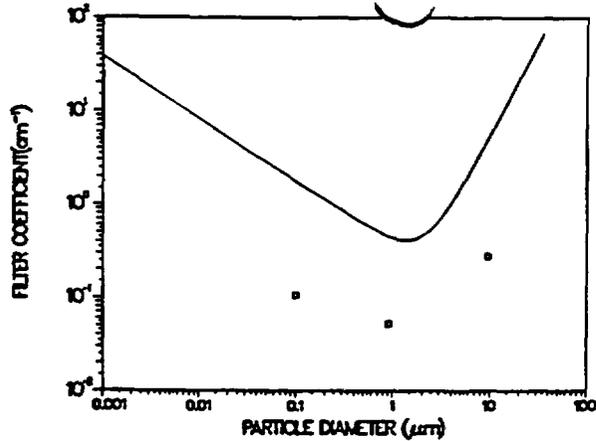


FIGURE 8. Comparison of colloidal filtration by fractured Topopah Spring member tuff with the Tien and Payatakes model.

filtration coefficient. This is in qualitative agreement with the filtration model of Tien and Payatakes<sup>20</sup>, see Fig. 8. Colloidal tracers have exhibited a peculiar shift in apparent fracture aperture with colloid diameter. This phenomenon has not been fully explained but is possibly the result of channeling. More transport experiments with tuff fractures and more detailed characterization of the water flow paths through the fracture are required to advance the understanding of radionuclide migration in discrete fractures. One meter scale fracture flow experiments are presently being planned to examine the effect of scale on migration in fractures.

The next level of complexity to be examined is the migration of radionuclides in unsaturated solid and fractured tuff. These experiments will challenge both the experimental and theoretical abilities of our project. Controlling tuff saturation over long periods of time is experimentally difficult and the fluid movement through unsaturated fractures may be a highly nonlinear problem, and may in fact be chaotic.

## CONCLUSIONS

The results of crushed tuff columns have yielded the following conclusions. The observed retardation factors for alkali metals and alkaline earths have agreed with those predicted from batch sorption measurements of  $K_d$  using the eq. 3. The actinides do not agree with the batch measurements. The elution curves observed for Pu colloid and americium exhibit

size exclusion. Neptunium and the higher oxidation states of plutonium have large fractions which migrate unretarded. The mechanism for sorption which leads to a nonzero  $K_d$  for neptunium and the reason for the absence of sorption in the column experiment remain unknown. Ongoing experiments in the solubility task and the sorption task will provide the explanation for these observations. Anions including the pertechnetate anion have also been studied in crushed tuff. The anion studies have been used to establish a relationship between the crystallographic structure of zeolites and clays and the magnitude of the anion exclusion effect. This relationship allows the prediction of retardation factors for pertechnetate given the mineralogical composition of tuff.

The solid tuff columns have exhibited time dependent dispersion. This observation points to the need for a more detailed characterization of the hydrologic and geochemical properties of Yucca Mountain tuff. The most important consequence of this observation is that without time dependent dispersion the elution of alkali metals and alkaline earths did not agree with batch sorption measurements. The apparent error in the predicted arrival time is greater than an order of magnitude. Future experiments will utilize optical and scanning electron microscopy along with microautoradiography to attempt to provide a forward basis for predicting the time dependence of the dispersion in the radionuclide migration. One would expect dispersion to increase as saturation decreases because it seems natural that the tortuosity of connected flow paths should increase. Future experiments examining migration in unsaturated tuff columns will test this hypothesis and demonstrate whether time dependent dispersion is more or less important in the unsaturated zone than in saturated tuff.

The fractured tuff columns have provided good agreement between matrix diffusion models and the observed elution of nonsorbing (conservative) tracers. With the exception that the aperture needed to be adjusted to fit the arrival time of the tritiated water in the case of the sample from the Fran Ridge outcropping. Sorbing tracers have exhibited the release of a small fraction appearing to unretarded. This result could be due to pseudocolloid formation as was observed for americium in the crushed tuff columns or channeling dispersion in the fracture. The next phase of experiments with saturated fractures will differentiate between these possible mechanisms. Colloid transport was observed through saturated fracture tuff with carboxylated polystyrene sols

ranging in size from 0.10 to 9.55 micrometer in diameter. Only the 0.91 micrometer diameter sol eluted a significant fraction (24 percent) of the input material. This is in general agreement with the predicted size dependence of the Tien and Payatakes filtration model.

In summary the crushed tuff columns have demonstrated a need for a better understanding of the chemical speciation of actinides in Yucca Mountain groundwater and a need for a mechanistic approach to sorption of actinides. Intact tuff and fractured tuff columns have demonstrated a need for the characterization of the distribution of hydrologic and geochemical properties in Yucca Mountain. There is also a need for a better understanding of the effect of heterogeneity on transport. These complications, which have been observed in saturated tuff, will add to the complexity of modeling radionuclide transport in unsaturated tuff.

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