

# GEOCHEMISTRY OF THE YUCCA MOUNTAIN SITE: An Overview of the Approach to Characterization

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## ABSTRACT

Radionuclide retardation by geochemical processes is a potentially favorable natural condition of the Yucca Mountain site, the candidate site for the nation's first Mined Geologic Disposal System for high-level, radioactive waste. The extent to which geochemical processes can be used in the evaluation of alternative conceptual models for the Yucca Mountain site and relied upon as barriers in a multibarrier concept for the isolation of waste will be evaluated. A comprehensive geochemical investigation of the Yucca Mountain site is planned. The investigation comprises mineralogic characterization, rock/water interaction, radionuclide solubility, sorption, dynamic transport (diffusion, dispersion, sorption kinetics, diffusive/advective coupling), and integrated transport modeling studies.

## INTRODUCTION

Geochemical processes potentially provide a significant barrier to the migration of radionuclides from the repository to the accessible environment. The most likely mechanism for transport of radionuclides from a waste repository to the accessible environment is by dissolution of the stored solid-waste form and subsequent transport in water. As water containing radionuclides moves away from the repository, it will contact the altered volcanic tuffs of Yucca Mountain (zeolite and clay mineral assemblages) which have great capacity for cation sorption. Therefore, an assessment of the potential for radionuclide retardation must be based on knowledge of the petrology and mineralogy along likely groundwater flow paths; the groundwater chemistry; the solubility and speciation of the radionuclides; and sorption and retardation processes. Since likely flow paths for the groundwater may include fractures and faults, the mineralogic characterization must include the characterization of fracture and fault mineral coatings.

## PETROLOGY AND MINERALOGY

Yucca Mountain is a structural block consisting of a sequence of silicic volcanic rocks that are mostly pyroclastic deposits of mid-Miocene age. The major units underlying the candidate repository area extend up from the thick (450- to 700-m) Crater Flat Tuff (~13.9 Ma), through the informally named tuffaceous beds of Calico Hills (25 to 110 m, 13.8 Ma) into the Paintbrush Tuff (410 to 425 m, 13.4 to 12.9 Ma). The candidate host rock for a high-level waste repository is within the devitrified Topopah Spring Member of the Paintbrush Tuff.

Beneath the potential host rock, the stratified layers of devitrified (mostly quartz plus feldspar) and nonwelded (mostly glass or zeolite) tuffs provide significant mineral variability along both unsaturated and saturated transport pathways. The major alteration observed in the unsaturated tuffs below the host rock is zeolitization of glasses within 100 to 200 m above the present water table. This zeolitization happened more than 11.6 Ma ago, according to the pre-Timber Mountain age of tectonic tilting recorded by geopotential features that formed toward the end of the major zeolitization episode.(1) The fractures in the candidate host rock contain a complex development of cristobalite, zeolites (mostly clinoptilolite and mordenite), Mn-minerals, and calcite.(2) This is in marked contrast to the rock matrix,

which is composed predominantly of feldspars and silica minerals (quartz, cristobalite, and tridymite). Figure 1 illustrates the 3-dimensional distribution of minerals based on data from six drill holes.

The Yucca Mountain mineral variability includes all four categories of sorptive minerals described by Kent et al.(3) in the context of a surface-complexation model for radionuclide sorption and suggests mineralogic robustness for sorption at Yucca Mountain. The categories are 1) oxide minerals (including iron oxides and silica minerals), 2) multiple-site-type minerals (including the feldspars), 3) fixed charge minerals (including micas, clays, manganese oxides, and zeolites), and 4) salt-type minerals (including calcite).

It must be determined whether the minerals now present are stable such that the capacity for geochemical retardation does not diminish significantly over time (10,000 yr). Mineral alteration, either natural or induced by groundwater chemistry changes or a thermal effect, must be understood. A preliminary natural mineral alteration model has been developed which assumes that the continuing transformation of the metastable phases in Yucca Mountain is controlled by the activity of aqueous silica.(4) This model predicts small changes in mineralogy.

## GROUNDWATER CHEMISTRY

Knowledge of the groundwater chemistry at the site and the expected spatial and temporal ranges of variability is crucial to understanding mineral alteration and radionuclide solubility. The groundwater chemistry before waste emplacement must be characterized and a groundwater chemistry model must be formulated to enable this understanding. The results of hydrologic investigations (groundwater chemistry analyses) by the US Geological Survey are being integrated with the petrologic and mineralogic characterization by Los Alamos to develop this model.

## RADIONUCLIDE RETARDATION

The current geochemistry investigations have been conducted under laboratory conditions that mimic those conditions expected in the far-field environment at Yucca Mountain, an environment not significantly perturbed by

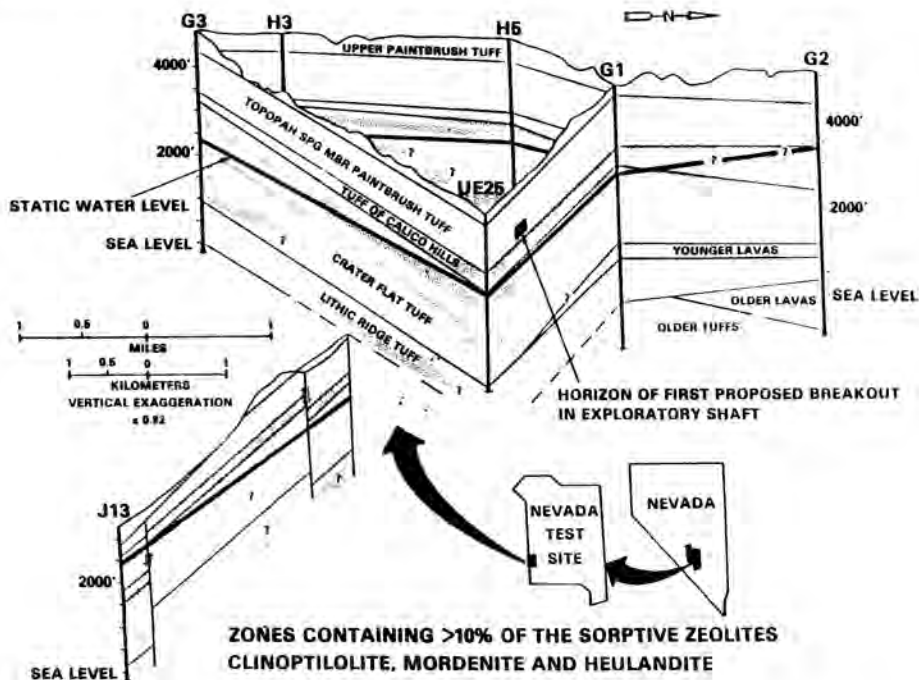


Fig. 1. Mineral Distribution at Yucca Mountain: Zone of Zeolitization.

the presence of the repository. These investigations include solubility, sorption, and dynamic transport.

#### Solubility (Dissolved Species Concentration Limits)

It is understood that chemical speciation and the ground water chemistry may affect the interaction between selected radionuclides and the minerals present at Yucca Mountain. For this reason, solubility studies must determine the speciation (oxidation state and molecular) and the dissolved species concentration limits for all key radionuclides in a variety of water compositions. These studies have been focused on the longer-lived, soluble actinides: americium, neptunium, plutonium, and uranium.(5) Solubility limits were determined in primarily Well J-13 water as well as other waters from the vicinity of Yucca Mountain. The limits were also measured as a function of pH and temperature, two characteristics that could be altered over time. To fully characterize the solution, the solute concentration, oxidation state, molecular complexation, and oxidation potential (Eh) were measured. Figure 2 summarizes some recent results with plutonium. It should be noted that 1) plutonium concentration decreases with increasing temperature; 2) plutonium solubility shows no trend as a function of pH; and 3) Pu(V) and Pu(VI) were detected in plutonium supernatants, with Pu(VI) increasing at the expense of Pu(V) with increasing pH.

Actinide species must be measured at expected concentration levels [ $10^{-6}$  to  $10^{-12}$  Molar (M)], which are levels also used for complimentary batch sorption and dynamic transport experiments. Classic spectroscopic methods have detection limits at  $10^{-6}$  M. Furthermore, if plutonium is released from the waste form by contact with near-neutral

pH ground water, plutonium colloid formation is very likely.(6) The formation characteristics, and stability of Pu(IV) colloid as a function of pH, Eh, and ionic strength are being investigated. An initial conclusion is that the colloid is structurally very similar to finely divided  $\text{PuO}_2$ . These conclusions are reported in Hobart et al.(7) Analytical tools such as photoacoustic and photothermal spectroscopies are being developed. These methods improve the detection limits to well below  $10^{-6}$  M and enable distinction of radionuclide oxidation species.

#### Sorption and Retardation

Sorptive processes can delay or retard the migration or transport of the radionuclides. Sorption has been investigated by studying the interaction between a radionuclide and Yucca Mountain tuff samples (crushed) using a batch sorption method. Batch sorption coefficients,  $R_d$ , were determined as a function of mineralogy, ground water chemistry, sorbing element concentration, atmospheric conditions, and temperature. Details of the batch sorption method and many of the results were summarized by Daniels et al. (8) and Thomas.(9) These results are most reliable for the simpler cations such as strontium, barium (analog for radium), and cerium, and for technetium, iodine, thorium, and europium. The complex solution chemistry of some of the actinides, however, complicates the interpretation of batch sorption results. In general, the batch sorption coefficients determined for the actinides were variable and inconsistent. For plutonium, neither the sorption mechanism nor the species in near-neutral pH solutions are known with certainty. Desorption coefficients for plutonium often exceeded sorption coefficients by more than an order of magnitude. Further, there was no

	Steady-state Concentration (M)			Oxidation state in Supernatant Solution		
	25°C	60°C	90°C	25°C	60°C	90°C
pH 5.9	NA	$(2.7 \pm 1.7) \times 10^{-8}$	$(6.2 \pm 1.9) \times 10^{-9}$	NA	III + poly: (10 ± 2)% IV: (2 ± 1)% V: (17 ± 5)% VI: (72 ± 5)%	III + poly: (9 ± 5)% IV: (6 ± 5)% V: (79 ± 7)% VI: (6 ± 5)%
pH 7.0	$(1.6 \pm 0.2) \times 10^{-6}$	$(3.8 \pm 0.8) \times 10^{-8}$	$(8.8 \pm 0.8) \times 10^{-9}$	III + IV + poly: (2 ± 3)% V: (68 ± 3)% VI: (27 ± 9)%	III + poly: (3 ± 1)% IV: (2 ± 1)% V: (44 ± 9)% VI: (52 ± 4)%	no conclusive result
pH 8.5	NA	$(1.2 \pm 0.1) \times 10^{-7}$	$(7.3 \pm 0.4) \times 10^{-9}$	NA	III + poly: (5 ± 4)% IV: (13 ± 1)% V: (58 ± 2)% VI: (24 ± 1)%	III + poly: (11 ± 2)% IV: (10 ± 2)% V: (85 ± 4)% VI: (0 ± 6)%

Fig. 2. Summary of Plutonium Solubility Experiments.

sensitivity to the concentration of cation-sorbing minerals.(10) Uncertainty in actinide sorption coefficients requires more detailed study of speciation and sorption kinetics (through dynamic transport tuff column studies). The sorption of actinides by trace mineral phases such as by Fe and Mn oxyhydroxides also is an intended study.

The batch sorption results are very sample specific and, therefore, difficult to generalize and apply throughout the mountain. Current sorption studies are focusing on the sorption behavior of individual, pure minerals such as the zeolites and in particular manganese and iron oxyhydroxides. These data might permit the generalization of sorption data as a function of the mineralogical composition of tuff. This, in turn, should permit the prediction of sorption coefficients along flow paths of known mineral content.

Sorption results also must be interpretable and applicable to dynamic and heterogeneous systems. Therefore, it is necessary to have an understanding of the mechanisms of radionuclide transport and retardation in tuff. Dynamic transport column and diffusion experiments complement and extend the batch results and sorption mechanistic data to these systems.

The dynamic transport, or column experiment concept has evolved from a crushed rock one to the more complex whole and fractured rock one. Figure 3 (11) shows a matrix of parameters to be measured by the various column experiments and static diffusion experiments. Each experiment measures a primary parameter, and in this way, the chemical and physical processes can be decoupled. For example, nuclide speciation and kinetic phenomenon affecting sorption, including ionic and molecular diffusion, are manifest in crushed rock experiments. Sorption coefficients can be calculated from the results of crushed tuff column experiments.(8) Generally, values obtained for the simple cations,

e.g., the alkaline earths, are not significantly different. However, values obtained for actinide and rare earth elements are lower than those obtained by batch experiments. Rate-limited or kinetic effects may explain the disparities. Likewise, speciation may contribute to the disparity in the results.

The diffusive/advective coupling can be studied by experiments involving the transport of tracers through fractured tuff columns. These experiments may be the most difficult to interpret because nearly all the processes shown in Fig. 3 are acting. These experiments are also the most important given the fractured nature of some of the tuff units at Yucca Mountain, most notably the Topopah Spring Member. Thus far, fracture flow experiments have been conducted with conservative tracers and colloids.

The conservative tracer experiments (HTO,  $\text{TcO}_4^-$ , and sulforhodamine B dye) were successfully modeled with a formulation for a single, parallel-sided fracture in a porous matrix.(12) The fraction of eluted tracer varied in proportion to the molecular size of the tracer. This condition suggests that an increasing proportion of the pores were inaccessible to the larger species (i.e., size exclusion). The colloid experiments (13) used three different sizes of fluorescent, carboxylated polystyrene spheres (nominally 0.1, 1.0, and 10.0 microns) and were modeled in the same way. Colloid effluent concentrations 1-3 orders of magnitude greater than observed was predicted. This difference is being attributed to filtration. These analyses are preliminary.

#### Transport Modeling

A preliminary assessment of the potential for radionuclide retardation has been made through modeling the transport of key radionuclide species. The computational code TRACR3D (14) was used to model the

	$R_d$	Speciation	Colloids	Kinetics	Matrix diffusion	Longitudinal diffusion	Hydrodynamic dispersion	Channeling	Heterogeneity
Crushed tuff columns	p	p	a	a	n	a	a	n	n
Mass transfer kinetics									
Sorption kinetics	a	a	a	p	n	p	a	n	n
Solid tuff columns	a	a	a	a	a	a	p	n	p
Unsaturated tuff columns	a	a	a	a	n	a	a	a	a
Fractured tuff columns	a	a	a	a	a	n	p	p	p
Filtration	n	n	p	n	n	n	a	n	n
Diffusion studies	a	a	a	a	p	n	n	n	n

## Key:

- a = effect will be observed, but parameter will be fit or derived from other experiment.  
 n = negligible effect.  
 p = primary source of data

Fig. 3. Dynamic and Diffusion Study Test Matrix.

integrated transport of uranium and technetium from the repository to the water table.<sup>(15)</sup> A nominal-case flow scenario (0.5 mm/yr) and a worst-case flow scenario (4.5 mm/yr) were used in the calculations. In summary, with uranium, the estimated transport was only moderately sensitive to the magnitude of the flow rate because sorption affected retardation significantly (Fig. 4). With technetium, when sorption was neglected, the flow rate dominated the transport (Figs. 5a, 5b).

## SUMMARY

Mineralogy and petrology studies have shown that the units beneath the proposed repository at Yucca Mountain have rock characteristics and mineralogy that probably will retard the migration of a number of important radionuclides. Additional characterization and determination of the 3-dimensional distribution of these minerals is planned as part of the site characterization.

Actinide solubility measurements are continuing to strengthen the thermodynamic data base and provide needed information in support of the sorption and dynamic transport experimental effort. Actinide colloids also are being characterized for the same purpose. Sorption coefficients have been determined by batch and column techniques. The batch data for the actinides is proving difficult to verify in more heterogeneous and dynamic systems. The adsorption kinetics are rapid for the simpler cations, and therefore, reasonable agreement between the batch and column measurement has been obtained.

Diffusive/advective coupling can be studied by fractured core column studies. Experiments have been initiated with nonreactive tracers and colloids. Diffusion and size

exclusion effects were observed. The colloid experiment showed that filtration partly mitigated the exclusion.

A geochemical/physical model of the retardation process is supported by preliminary transport modeling showing that sorption is the dominant retardation mechanism for a weakly sorbed tracer. The effectiveness of the geochemical barrier will continue to be examined as new data are obtained.

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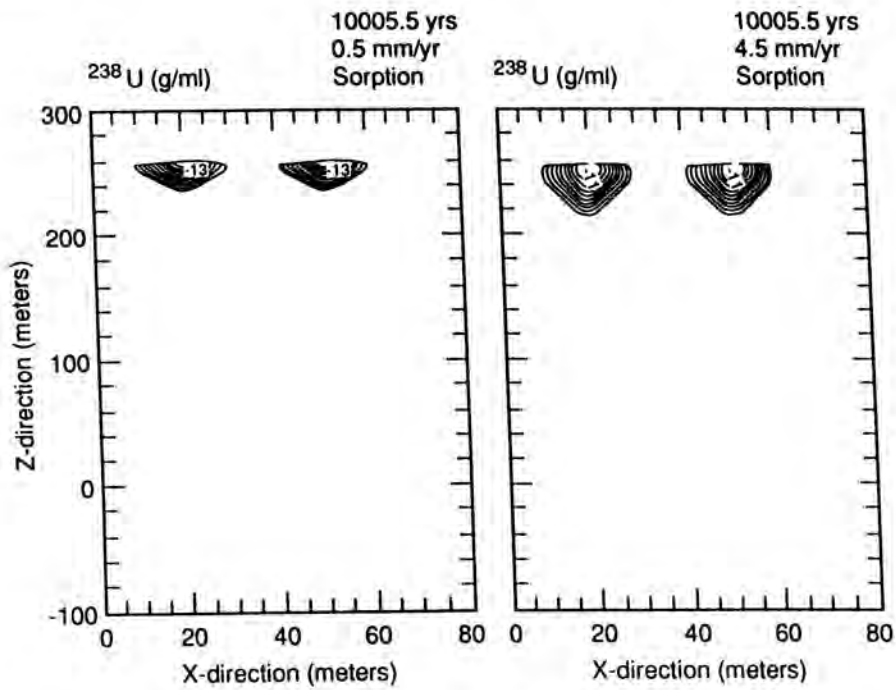


Fig. 4. Comparison of Liquid-Phase Concentrations of  $^{238}\text{U}$  After Transport for 10,000 yr at Different Flow Rates (Adjacent Lines Differ In Concentration by a Factor of 10).

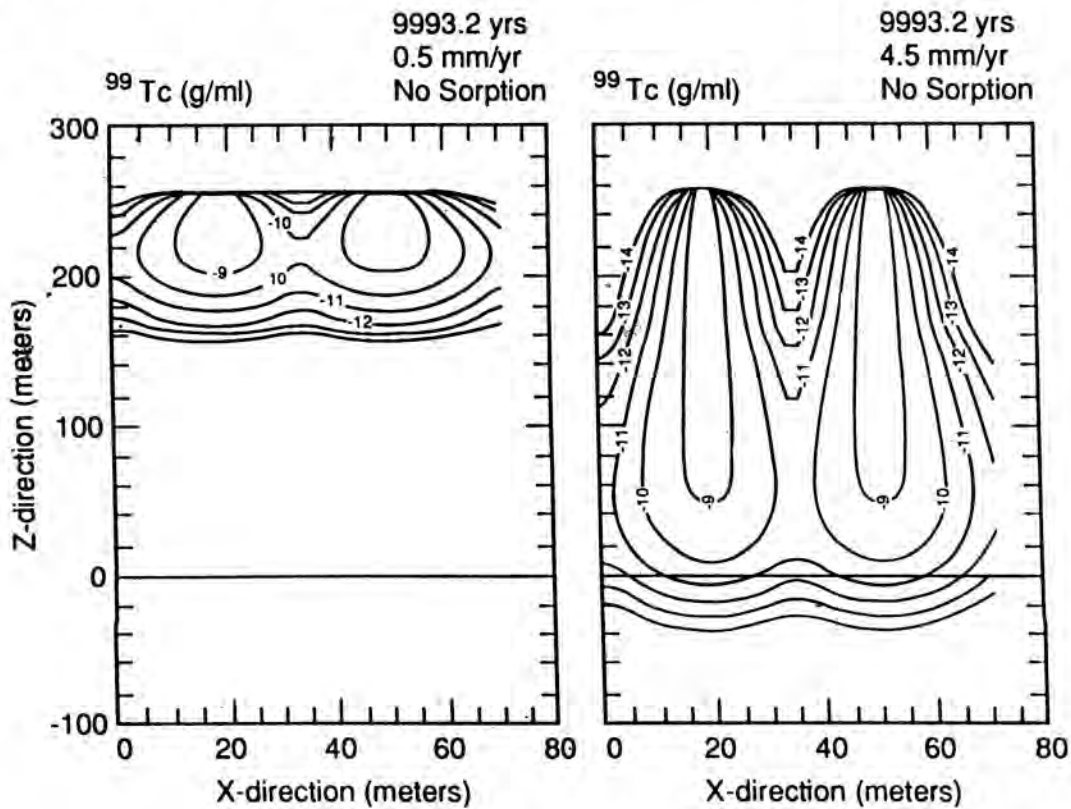


Fig. 5a. Comparison of Liquid-Phase

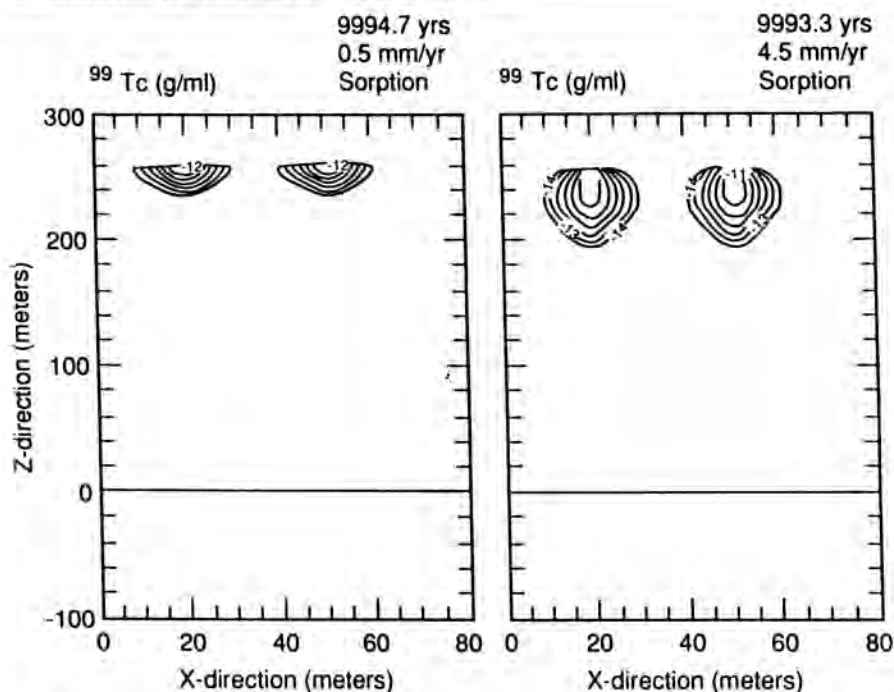


Fig. 5b. Comparison of Liquid Phase Concentration of  $^{99}\text{Tc}$  After Transport With Sorption for 10,000 yr at Different Flow Rates.

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