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June 8, 2001  
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U.S. Nuclear Regulatory Commission  
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11545 Rockville Pike  
Mail Stop T8A23  
Washington, DC 20555

Subject: Programmatic Review of Poster

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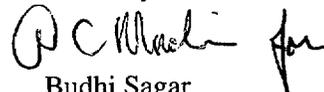
The enclosed poster is being submitted for programmatic review. This poster will be submitted for presentation at the Water-Rock Interaction Conference, to be held June 10-16, 2001, in Sardinia, Italy. The title of this poster is:

“Molecular Dynamics Simulation on the Uranyl Ion Near Quartz Surfaces”  
Jeffery A. Greathouse, Gregory Bemis, and Roberto T. Pabalan

This poster is a product of the CNWRA and does not necessarily reflect the view(s) or regulatory position of the NRC.

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Sincerely,



Budhi Sagar  
Technical Director

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Enclosure

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# Molecular Dynamics Simulation of the Uranyl Ion Near Quartz Surfaces

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<sup>2</sup>Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, Texas, U.S.A.



## INTRODUCTION

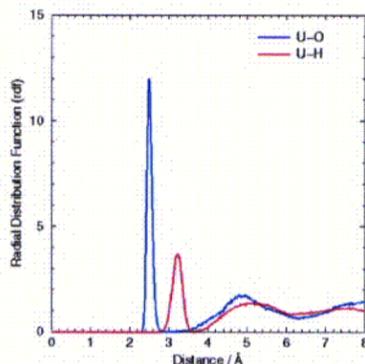
Sorption processes are potentially important mechanisms for retarding radionuclide migration from nuclear waste repositories to the biosphere. The effectiveness of sorption processes and their dependence on the characteristics of mineral sorbents and the chemistry of radionuclide-bearing water typically are determined through macroscopic sorption experiments. In this study, molecular simulation techniques were used to provide a molecular-level description of sorption phenomena that may complement data from sorption experiments.

## SIMULATION METHODS

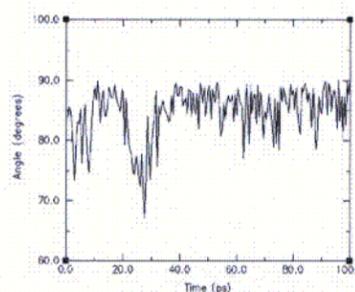
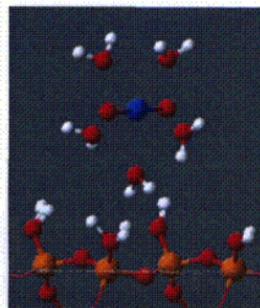
All simulations were performed using the Open Force Field modules of Cerius2 (Molecular Simulations, Inc., San Diego, CA). Potential parameters were based on the consistent-valence force field (CVFF) using the Lennard-Jones form of the short-range nonbonded interactions. CVFF parameters were used without modification for water, and slight modifications were made in the partial charges for the carbonate ion. Potential parameters for the uranyl ion and quartz atoms were taken from previous studies (Gilbaud & Wipff 1996, Pabalan & Lupkowski 1997). Bond stretch and angle bending parameters were included for all relevant species, except that the quartz surface was held rigid throughout the calculations.

We used the Crystal Builder module of Cerius2 to create a 32-unit cell slab of  $\alpha$ -quartz and the Surface Builder module to create the (010) surface. The simulation supercell was created with  $x$ - and  $y$ -dimensions of 19.68 and 21.65 Å, respectively, corresponding to four unit cells of quartz in each direction. The depth of the quartz slab was approximately 8 Å, or approximately 2 unit cells. The  $z$ -dimension of the supercell was fixed at 32 Å to allow room for water molecules and aqueous species.

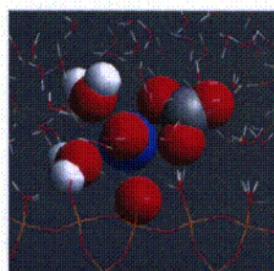
After energy minimization, molecular dynamics simulations were performed in the constant ( $NVT$ ) ensemble with the Nosé-Hoover thermostat (Allen & Tildesley 1987). Temperature was set to 300 K with a 0.1 ps relaxation time. A cutoff of 9 Å was used for short-range interactions, and Coulombic interactions were treated using the three-dimensional Ewald sum (Allen & Tildesley 1987) with a reciprocal-space cutoff of 0.5 Å<sup>-1</sup>. Total simulation time was 100 ps with a timestep of 0.0005 ps. Table 1 provides supercell composition and parameters for the simulations performed in this study. Averaged structural data and water self-diffusion coefficients ( $D_w$ ) are given in Table 2.



**Figure 1. (left)** U–O and U–H radial distribution functions in bulk water. **Figure 2. (right)** Equilibrium snapshot in the ( $x,z$ ) plane of water near a singly protonated quartz surface (Simulation 2). Si atoms are orange, O atoms are red, and H atoms are white.



**Figure 3. (a)** Equilibrium snapshot of the  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  complex near the quartz (010) surface. The U atom is blue. **(b)** Time evolution of the O–U–O vector relative to the quartz surface normal.



**Figure 4. (left)** Equilibrium snapshot of the uranyl surface complex,  $\text{UO}_2(\text{H}_2\text{O})_2(\text{CO}_3)(\text{O})$  (large spheres), near a partially deprotonated quartz surface (Simulation 6). The quartz surface and nonsolvating species are indicated in stick format.

## RESULTS

Simulations 1 and 2 were conducted in order to validate the nonbonded interaction parameters and model for the quartz-solution interface. Simulations 3–7 were conducted to investigate uranyl solvation and surface complexes near the quartz (010) surface. The quartz slab remained rigid during the simulations except for the surface H atoms, which were allowed to move relative to adjacent oxygen atoms.

From simulation 1, we see that the equilibrium  $\text{UO}_2^{2+}$  solvation shell consists of five water molecules in a bipyramidal geometry with uranyl oxygen atoms in the axial positions. The U–O rdf (Figure 1) contains two peaks, one corresponding to the primary solvation shell at 2.49 Å and a second broader peak at 4.85 Å. This average U–water–O distance of 2.49 Å is in excellent agreement with the experimental value of 2.42 Å, obtained from proton NMR and X-ray diffraction experiments (Aberg et al. 1983). The first sharp U–H peak occurs at 3.21 Å, indicating that the solvating water molecules are oriented such that their  $C_{2v}$  rotational axes are bisected by the bipyramidal plane.

Next, we tested our model of the quartz-water interface in simulation 2, which included 300 waters and a singly protonated quartz (010) surface. A snapshot of the simulation supercell during the equilibrated portion of the run is shown in Figure 2. The  $z$ -axis in this supercell was held constant at 32 Å, which provides ample separation for water far from the surface to exhibit bulk-like properties. The first O–O rdf peak is located at 2.79, which compares well with simulation results for pure water (data not shown). The second O–O peak at 4.67 Å is not consistent with bulk water, and we believe that disruption in long-range order in water is due to the quartz surface.

For simulation 3, the initial configuration consisted of a uranyl ion approximately 4 Å from a singly protonated surface. The uranyl ion formed an outer-sphere surface complex while remaining fully solvated by water molecules. One solvating water molecule formed hydrogen bonds with surface O atoms (Figure 3a). Trajectory analysis of the O–U–O vector relative to the quartz surface normal is shown in Figure 3b. A value of 90° indicates that the  $\text{UO}_2^{2+}$  ion is perpendicular to the surface throughout the simulation.

For simulations 4–7, we created a partially deprotonated region of the quartz surface by moving six adjacent surface hydrogen atoms to nearby surface oxygen atoms. Carbonate ions were also introduced in the aqueous layer for simulations 6 and 7. Tables 1 and 2 indicate that inner-sphere surface complexes formed only when the initial U–surface distance was small. Such a complex is seen in Figure 4. The uranyl ion formed a monodentate, inner-sphere surface complex, with a U–surface O distance of approximately 2.6 Å. Uranyl-carbonate complexes are characterized by a shorter U–O distance (Table 2), which was seen in uranyl-hydroxide complexes (data not shown).

**Table 1. Composition and parameters for molecular dynamics simulations.**

Simulation Number	Surface Composition	Time / ps	Number of waters	Aqueous species	Initial U-surface distance / Å
1	—	100	224	1 $\text{UO}_2^{2+}$	—
2	Singly protonated	100	300	—	—
3	Singly protonated	100	299	1 $\text{UO}_2^{2+}$	4.0
4	Partially deprotonated	100	300	1 $\text{UO}_2^{2+}$	2.5
5	Partially deprotonated	100	300	1 $\text{UO}_2^{2+}$	2.0
6	Partially deprotonated	100	295	1 $\text{UO}_2^{2+}$ , 1 $\text{CO}_3^{2-}$	1.5
7	Partially deprotonated	100	295	1 $\text{UO}_2^{2+}$ , 2 $\text{CO}_3^{2-}$	1.9

**Table 2. Results of molecular dynamics simulations.**

Simulation Number	Uranyl solvation complex <sup>a</sup>	U–O Distance / Å <sup>b</sup>	$D_w / 10^{-10} \text{ m}^2 \cdot \text{s}$ (nearest third) <sup>c</sup>	$D_w / 10^{-10} \text{ m}^2 \cdot \text{s}$ (middle third) <sup>d</sup>
1	$\text{UO}_2(\text{H}_2\text{O})_5^{2+}$	2.49	—	15.6 <sup>e</sup>
2	—	—	6.4	13.7
3	$\text{UO}_2(\text{H}_2\text{O})_5^{2+}$	2.50	7.2	12.9
4	$\text{UO}_2(\text{H}_2\text{O})_5^{2+}$	2.50	5.1	12.9
5	$\text{UO}_2(\text{H}_2\text{O})_4(\text{O})^{2+}$	2.50	6.4	12.2
6	$\text{UO}_2(\text{H}_2\text{O})_2(\text{CO}_3)(\text{O})$	2.35, 2.49	7.6	18.2
7	$\text{UO}_2(\text{H}_2\text{O})_3(\text{CO}_3)$	2.37	6.2	15.7

<sup>a</sup>Uranyl complexes in Simulation 5–7 include surface oxygen atoms, denoted by (O). Charges due to (O) are not included.

<sup>b</sup>U–O distances were obtained from the first peak in the U–O radial distribution functions.

<sup>c</sup>Water self-diffusion coefficients ( $D_w$ ) calculated for the third of water molecules nearest the quartz surface.

<sup>d</sup>Water self-diffusion coefficients ( $D_w$ ) calculated for water molecules in the middle third of the simulation supercell.

<sup>e</sup>Calculated for all water molecules.

## CONCLUSIONS

Molecular dynamics simulations of  $\text{UO}_2^{2+}$  ion were conducted in bulk water and at the quartz-water interface to provide molecular-level information on uranyl sorption phenomena. In all cases, the uranyl ion maintains a solvation shell of five oxygen atoms, consisting of water molecules, carbonate ions, or deprotonated surface sites. The uranyl ion adsorbed on the quartz surface retains a five-fold solvation shell, with the carbonate ion readily replacing two water molecules. The O–U–O axis aligns perpendicular to a singly protonated surface, and simulations involving a partially deprotonated surface resulted in inner-sphere surface complexes.

Water molecules near the quartz surface undergo limited translational motion, resulting in self-diffusion coefficients that are approximately half that of water near the middle of the simulation supercell (Table 2). Water mobility is also influenced by the type of uranyl-surface complex formed. In general, water is less mobile when the uranyl ion has formed an outer-sphere surface complex. Inner-sphere surface complexes do not protrude far into the aqueous region (Figure 4), resulting in increased water mobility.

## REFERENCES

Aberg, M., D. Ferri, J. Glaser & I. Grenthe 1983, *Inorg. Chem.* 22:2986; Allen, M.P. & D.J. Tildesley 1987, *Computer Simulation of Liquids*, Oxford, UK: Clarendon Press; Gilbaud, P. & G. Wipff 1996, *J. Mol. Struct. (THEOCHEM)* 366:55; Pabalan, R.T. & M. Lupkowski 1997, SWRI-IRD-20-9875, San Antonio, Texas: Southwest Research Institute.

## ACKNOWLEDGMENTS

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June 8, 2001  
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U.S. Nuclear Regulatory Commission  
ATTN: Mrs. Deborah A. DeMarco  
Two White Flint North  
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Subject: Programmatic Review of Paper

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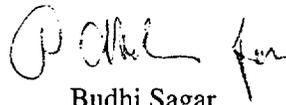
The enclosed paper is being submitted for programmatic review. This paper is being submitted for presentation at the GEOTRAP V Conference, held May 5-7, 2001, in Aspo, Sweden. The title of this paper is:

“Isotope Fractionation Effects on Radionuclide Transport in Geologic Disposal of Nuclear Waste”  
William M. Murphy and David A. Pickett

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# Isotope Fractionation Effects on Radionuclide Transport in Geologic Disposal of Nuclear Waste

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## 1. Introduction

Understanding the behavior of radionuclides in geochemical systems is essential to demonstrating the safety of geologic disposal of nuclear waste. Geochemical phenomena such as aqueous speciation, solubility, solid solution, colloid formation, and surface complexation depend primarily on the electronic properties of atoms and not on their isotopic mass. Hence, aside from differing radioactivities, performance assessments for geologic disposal of nuclear waste reasonably neglect differences in chemical properties of isotopes of the same element. Nevertheless, isotopes are fractionated in geochemical systems. Fractionation is due to kinetic or equilibrium mass effects during phase transitions, molecular transformations (which may be enhanced in biogeochemical processes), and diffusion. These effects are negligible for heavy isotopes, including most that are of concern in nuclear waste. For radioisotopes, fractionation also occurs due to radiation effects including decay and alpha recoil. Chemical variations due to isotopic fractionation are generally subtle compared to those resulting from differences in geochemical characteristics such as oxidation-reduction potential, pH, ionic strength, and mineralogy.

So why consider isotopic fractionation in the context of geologic disposal of nuclear waste? This paper examines two general reasons. (i) Information on transport characteristics of geochemical systems can be revealed by isotopic variations. In particular, information on the degree of openness or closure of the system and the timing of chemical fluxes can be revealed in the systematics of radionuclide activities in the uranium and thorium decay series. Also, chemical transport properties (such as mineral-water distribution coefficients) of elements composed of multiple radionuclides may be determined, in principle, from natural system data on the chemical behavior of the isotopes. For example, *in situ* sorption and desorption rates may be deduced in theory by solving simultaneously mass conservation equations for the distribution of several isotopes of the same element having the same sorption reaction properties but different half lives and fractionation effects due to nuclear processes. (ii) Fractionation phenomena, which are particular to individual radioisotopic systems or processes, may affect radionuclide release and transport in a repository system. For example: (a) The stability of colloidal plutonium depends on its isotopic composition because of radiological effects on colloid formation and degradation. (b) Release rates of alpha decay products from solid matrices are enhanced because of alpha recoil effects, leading

to isotopic fractionation that could affect performance. (c) Dilution effects due to mixing cause variations in isotope ratios and could affect releases and transport of individual radionuclides. Differential isotopic behavior in waste disposal may be especially significant if dose conversion factors vary among isotopes.

## 2. Natural Analog Data from Peña Blanca

The Nopal I uranium deposit at Peña Blanca, Mexico, has been extensively studied as a natural analog of the proposed geologic repository for high-level nuclear waste at Yucca Mountain, Nevada (Ildefonse et al., 1990; Murphy and Percy, 1992; Percy et al., 1994; 1995; Prikryl et al., 1997). Silicic volcanic rocks similar to those at Yucca Mountain host a natural uranium deposit at Nopal I. The hydrologic environment of the uranium deposit is presently unsaturated and the chemical environment is oxidizing, which are also the conditions at Yucca Mountain. Uranium at Nopal I was initially reduced uraninite ( $\text{UO}_{2+x}$ ) analogous to spent nuclear fuel, but it is now almost entirely oxidized. An estimated limit on the oxidation rate of uraninite at Nopal I has been used as a constraint in alternate performance assessment source term models for Yucca Mountain (Murphy and Codell, 1999). The distribution and fractionation of uranium and uranium decay series isotopes at Nopal I have been useful in characterizing transport phenomena and in judging the validity of transport modeling for performance assessment of the proposed repository at Yucca Mountain. Uranium decay series data from Peña Blanca (Prikryl et al., 1997; CRWMS M&O, 2000a,b; Pickett and Murphy, 2001) can be used to illustrate the utility of studying isotope fractionation to characterize geochemical transport phenomena.

Uranium isotope and daughter nuclide fractionation in rocks and waters were also used in the Alligator Rivers Analogue Project, with varying success, to help constrain quantitative, time-dependent release and transport models (International INTRAVAL Project, 1992). For example, the models allowed for differential release rates for  $^{234}\text{U}$  and  $^{238}\text{U}$  due to recoil and related effects.

## 3. Hydrogeochemical System Characterization

### System Closure

In a system that is closed on a time scale that is long relative to half-lives of the daughters, the activities of radionuclides in the uranium and thorium decay series become equal. This secular equilibrium is an indication of geochemical system closure, which is a favorable natural system characteristic for geologic isolation of nuclear waste. Radioisotope disequilibrium (decay-series activity ratios other than unity) indicates open system behavior. Geochemical mechanisms of openness of a system in radioisotope disequilibrium may be interpreted based on the chemical properties (e.g., solubility, speciation, sorption) of the radionuclides and variations in the hydrogeochemical environment. Natural groundwaters are commonly enriched in  $^{234}\text{U}$  relative to  $^{238}\text{U}$  (i.e., they have  $^{234}\text{U}/^{238}\text{U}$  activity ratios greater than 1) because of radiation effects such as alpha recoil (Osmond and Cowart, 1976). Daughters of alpha decay may be ejected from stable crystallographic sites or left in damaged and preferentially reactive sites. These

daughter isotopes are released preferentially to solution. ( $^{234}\text{U}$  depletions in groundwater, which are less common than  $^{234}\text{U}$  enrichments, are generally attributed to changes in environmental conditions leading to dissolution of previously  $^{234}\text{U}$  depleted source materials.) Preferential release of alpha decay products is a primary mechanism for fractionation of heavy radioisotopes.

Uranium decay series isotopes in the geologic and hydrochemical environment of the uranium deposit at Nopal I are commonly out of secular equilibrium.  $^{234}\text{U}/^{238}\text{U}$  activity ratios in present groundwaters at Peña Blanca range up to 5 (Pickett and Murphy, 1999).  $^{234}\text{U}/^{238}\text{U}$  ratios up to 2.4 in rocks and fracture filling materials outside the primary uranium deposit at Nopal I is due most likely to precipitation of uranium from solutions enriched in  $^{234}\text{U}$  by interactions with uranium rich source rocks (Prikryl et al., 1997; Pickett and Murphy, 2001). Uranium decay series disequilibrium in fracture filling materials and rocks at Peña Blanca reveals multiple stage processes of radionuclide release, transport, deposition, and remobilization (Pickett and Murphy, 2001). Another uranium-series study at Nopal I (CRWMS M&O, 2000a) concluded that uranium mobility has been limited during the past 300,000 years, although radium mobility was indicated. Similarly, uranium series isotopic disequilibrium in fractured granites from the Lac du Bonnet batholith, Manitoba, Canada, has been interpreted to represent open system behavior, whereas isotopic equilibrium in the unfractured granite marks a closed system (Gascoyne and Miller, 2001).

Potentially, system closure as demonstrated by uranium and thorium decay series secular equilibrium could be evaluated as a quantitative criterion for performance characteristics of the natural hydrogeochemical system of a nuclear waste repository site. This approach would be particularly useful for radionuclides with half-lives comparable to the regulatory time scale. For example, consider a hypothetical repository in which containment of radium is a safety concern within a 10,000-year time frame. The  $^{226}\text{Ra}$  half-life of 1,600 years is comparable to this period. In a closed system after 10,000 years, disequilibrium between  $^{226}\text{Ra}$  and its relatively immobile  $^{230}\text{Th}$  parent (e.g.,  $^{226}\text{Ra}$  depletion in rock due to mobilization) would evolve to within about one percent of equilibrium. Therefore, a  $^{226}\text{Ra}/^{230}\text{Th}$  activity ratio in repository host rock outside a few percent from unity would indicate that radium was mobile under site conditions within the past 10,000 years and would be likely to be mobile during the regulatory period. Decay-series radioisotope secular equilibrium criteria would be specific to individual chemical species, and acceptable limits could be based on safety and geochemical considerations, such as the magnitude of initial disequilibrium. Separate but complementary criteria could be developed for other decay series nuclides with contrasting geochemical characteristics, and generalizations could be developed to apply to anthropogenic species.

### *In Situ $K_d$*

Performance assessments for geologic repositories for nuclear waste commonly and conveniently invoke constant mineral-water distribution coefficients for individual radioelements to simulate retardation of radionuclide migration. A theoretical framework has been developed relating distribution coefficients for radioelements in the uranium and thorium decay series to the activities of radionuclides in natural water-rock systems (e.g.,

Ku et al., 1992). Mass balance relations for each of the multiple isotopes of individual chemical elements in the uranium and thorium decay series (notably isotopes of Th, Ra, and Pb) provide multiple constraints for each element on chemical properties such as distribution coefficients. Chemical properties such as equilibrium constants, diffusion coefficients, and precipitation rate constants vary insignificantly among isotopes of the same element in these series. Thus, mass conservation relations, involving dissolution, precipitation, sorption, radioactive decay, and migration, can be written for each of the isotopes and solved simultaneously to determine the chemical properties. For example, Ku et al. (1992) present equations relating activities of five thorium isotopes, which can be solved simultaneously for the five parameters: dissolution rate, precipitation rate, adsorption rate, desorption rate, and surface area. The distribution coefficient or *in situ*  $K_d$  is in turn related to the ratio of the sorption and desorption rate constants.

Extracting *in situ*  $K_d$ 's from natural system data is complicated by the characteristic complexity of nature relative to models. Critics note the complexity of processes that control the distribution of chemical species among the aqueous phase, sorption sites, and bulk solids, as well as ambiguities associated with analytical methods. Processes neglected or incompletely represented in various theoretical approaches and interpretations of data include nonlinear sorption, sorption site saturation, precipitation, coprecipitation, colloid formation and transport, and disequilibrium between sorbed species and the bulk solid. In particular, McKinley and Alexander (1993) warn against potentially dangerous applications of distribution coefficients or retardation factors in performance assessments for radioactive waste disposal systems when the coefficients cannot be shown to provide conservative results. Nevertheless, evaluation of *in situ*  $K_d$ 's provides an alternate line of evidence that may be used to judge laboratory-based data.

#### **4. Fractionation Effects on Release and Transport**

##### **Preferential Release and Transport**

In nuclear waste repositories, aqueous release is influenced by the phase setting and radiolytic history of particular radionuclides. Daughter radionuclides may occupy crystal sites that have been damaged by alpha and beta emission and alpha recoil. For example,  $^{239}\text{Pu}$  in spent fuel that has grown from alpha decay of  $^{243}\text{Am}$  (half-life 7,400 years) may occupy more damaged crystal sites than other Pu isotopes, and so may be preferentially released. The projected proportion of  $^{239}\text{Pu}$  atoms in these sites could be calculated from  $^{243}\text{Am}$  decay; availability of these  $^{239}\text{Pu}$  atoms to solution could be predicted based on theoretical considerations and comparison to natural systems and laboratory studies using shorter-lived parent-daughter pairs. Effects on radionuclide release due to damage during reactor operation could be tested by analyzing for individual isotopes during laboratory leaching/degradation studies. Analogous preferential release leads to common  $^{234}\text{U}$  activity enrichments in natural groundwaters. Occurrences of  $^{234}\text{U}/^{238}\text{U}$  activity ratios up to 5 in groundwaters from Peña Blanca (Pickett and Murphy, 1999) suggest that fractionation leading to isotopic disequilibrium could have an important effect on ultimate doses due to radionuclide release to the biosphere. Release models in performance assessments should not necessarily assume isotopically proportional release from solid waste forms.

Differential isotopic stability of plutonium colloids is also due to alpha recoil effects (Kim, 1986).  $^{239}\text{Pu}$ , with a half-life of 24,110 years, shows negligible effects of colloids in  $\text{PuO}_2$  solubility studies. In contrast,  $^{238}\text{Pu}$ , with a half-life of only 88 years, shows appreciable effects. Alpha recoil is believed to foster generation of colloids from hydroxide precipitates of  $^{238}\text{Pu}$  causing enhanced solubility effects. In natural geochemical systems, plutonium may be also transported by sorption on groundwater colloids, which tend to be destroyed by alpha recoil effects (Kim, 1986). Therefore, relative to  $^{239}\text{Pu}$  bearing colloids, isotope fractionation due to alpha recoil enhances formation of  $^{238}\text{Pu}$ -bearing hydroxide colloids and diminishes stability of natural colloids with sorbed  $^{238}\text{Pu}$ .

### **Isotopic Dilution**

The isotopic composition of a radioactive contaminant can also be altered by mixing with a naturally or artificially occurring source of the element. This mixing could result in isotopic dilution of the contaminant radionuclide and could mitigate contaminant migration under certain circumstances. For example, depleted uranium (predominantly  $^{238}\text{U}$ ) has been proposed as a chemical buffer material for disposal of spent nuclear fuel (Forsberg, 2001; Forsberg et al., 2001). If mixing of the two components results in a concentration at the geochemically imposed solubility limit, then precipitation of the mixed element would limit contaminant transport. Under other circumstances, transport of the contaminant could be augmented if the addition of the natural component leads to saturation of sorption sites. In general, mixing under natural geologic conditions is unlikely to lead to high aqueous concentrations, because the concentration in the mixture will be intermediate to that of the two components, and isotope dilution will not mitigate or enhance contaminant transport. In any case, radioelements such as plutonium that are rare in nature would not be subject to isotope dilution by natural sources.

## **5. Implications for Performance Assessment**

Radionuclide fractionation is most likely to affect performance of a geologic repository for nuclear waste through the preferential release of alpha decay products or differential isotopic release from multiple phases. Natural system data show that preferential release can lead to activity ratios in solution several times that occurring in source minerals.

A survey at the GEOTRAP 5 meeting of practitioners of performance assessment for geologic disposal of nuclear waste indicates that isotopic fractionation effects have been neglected in performance assessment models. Improved understanding of isotopic fractionation in nuclear waste disposal is likely to come primarily from observations of natural geologic occurrences of radionuclides and interpretations of experimental data. If significant processes are identified, including them in performance assessment models should be practical. For example, modeled radionuclide release rates could be isotope-specific, and sensitivity of dose to isotope fractionation could be tested by varying differential isotope release rates in performance assessment models (Murphy and Pickett, 2001).

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