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U.S. Nuclear Regulatory Commission
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Subject: Programmatic Review of Paper

Dear Mrs. DeMarco:

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

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

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

Budhi Sagar
Technical Director

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Enclosure

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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 Pearcy, 1992; Pearcy 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 (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}U and ^{238}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}U relative to ^{238}U (i.e., they have $^{234}U/^{238}U$ 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}U depletions in groundwater, which are less common than ^{234}U enrichments, are generally attributed to changes in environmental conditions leading to dissolution of previously ^{234}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. $^{234}U/^{238}U$ activity ratios in present groundwaters at Peña Blanca range up to 5 (Pickett and Murphy, 1999). $^{234}U/^{238}U$ 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}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}Ra half-life of 1,600 years is comparable to this period. In a closed system after 10,000 years, disequilibrium between ^{226}Ra and its relatively immobile ^{230}Th parent (e.g., ^{226}Ra depletion in rock due to mobilization) would evolve to within about one percent of equilibrium. Therefore, a $^{226}Ra/^{230}Th$ 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}Pu in spent fuel that has grown from alpha decay of ^{243}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}Pu atoms in these sites could be calculated from ^{243}Am decay; availability of these ^{239}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}U activity enrichments in natural groundwaters. Occurrences of $^{234}U/^{238}U$ 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}Pu, with a half-life of 24,110 years, shows negligible effects of colloids in PuO_2 solubility studies. In contrast, ^{238}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}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}Pu bearing colloids, isotope fractionation due to alpha recoil enhances formation of ^{238}Pu-bearing hydroxide colloids and diminishes stability of natural colloids with sorbed ^{238}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}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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