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

Dear Mrs. DeMarco:

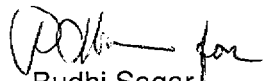
The attached manuscript is being submitted for programmatic review. This paper will be submitted for publication in the proceedings for the symposium on the Scientific Basis for Nuclear Waste Management, held at the Materials Research Society Annual meeting, November 26-29, 2001, in Boston, Massachusetts. The title of this paper is:

"Radioisotope Fractionation and Secular Disequilibrium in Performance Assessment for Geologic Disposal of Nuclear Waste" by W. Murphy and D. Pickett

This paper is a product of CNWRA and does not necessarily reflect the views or regulatory position of 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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Attachment

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# Radioisotope Fractionation and Secular Disequilibrium in Performance Assessment for Geologic Disposal of Nuclear Waste

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## ABSTRACT

Two potential applications of radioisotope fractionation and decay-series secular disequilibrium in performance assessment for geologic repositories for nuclear waste are preferential radionuclide release in source term analysis and characterization of system closure as a measure of the capacity of the geologic system to isolate waste. A primary mechanism of radioisotope fractionation is selective release and mobility of alpha decay products because of nuclear recoil effects, which is evident in natural system data. Preferential release of radioisotopes from nuclear waste forms or solubility limiting solid phases could affect repository performance; however, consequences of differential radioisotope releases are neglected in performance assessments. Decay-series disequilibria are useful also to characterize open/closed-system behavior in natural systems. Systems that are closed on time scales that are long relative to the half-lives of decay chain nuclides achieve secular equilibrium characterized by unit activity ratios among series nuclides. For geologic disposal of nuclear waste, measures focused on chemical system closure could capture the essential characteristics of the natural system with respect to radionuclide isolation and could be based quantitatively on uranium and thorium decay series secular equilibria/disequilibria.

## INTRODUCTION

Fractionation of isotopes in natural geochemical systems is useful in interpreting geochemical release and transport processes. Geochemical fractionation of stable isotopes of a given element is due to kinetic or equilibrium mass effects during phase transitions, molecular transformations, and diffusion. These effects tend to be insignificant for heavy isotopes, including most radioisotopes of concern in geologic disposal of nuclear waste.

Fractionation also occurs due to radioactivity [1]. Natural uranium and thorium decay series in systems that are closed on time scales that are long relative to the half-lives of the radionuclides achieve secular equilibrium, which is characterized by unit activity ratios among nuclides in the series. Secular disequilibrium (decay-series activity ratios other than unity) indicates open system behavior on a time scale relative to the half-lives of the nuclides. Ratios of activities of radioisotopes in a decay series are altered by processes that fractionate daughter isotopes from parents. A primary mechanism of fractionation in a decay series is selective release and mobility of alpha decay products and their daughters because of nuclear recoil effects. Progeny of alpha decay may be ejected from stable crystallographic sites or left in damaged and preferentially reactive sites. Consequently, natural groundwaters are commonly enriched by preferential release of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  (i.e., they have  $^{234}\text{U}/^{238}\text{U}$  activity ratios greater than 1). (Uncommon  $^{234}\text{U}$  depletions in groundwater are generally attributed to changes in environmental conditions leading to dissolution of previously  $^{234}\text{U}$  depleted source materials.)

Murphy and Pickett [2] presented a survey of isotope fractionation effects on radionuclide transport in relation to geologic disposal of nuclear waste, noting fractionation effects on radionuclide release, potential use of natural decay series isotope data for evaluating system closure, evaluation of “in situ” distribution coefficients, isotopic dilution, and radioisotope effects on differential colloid stability.

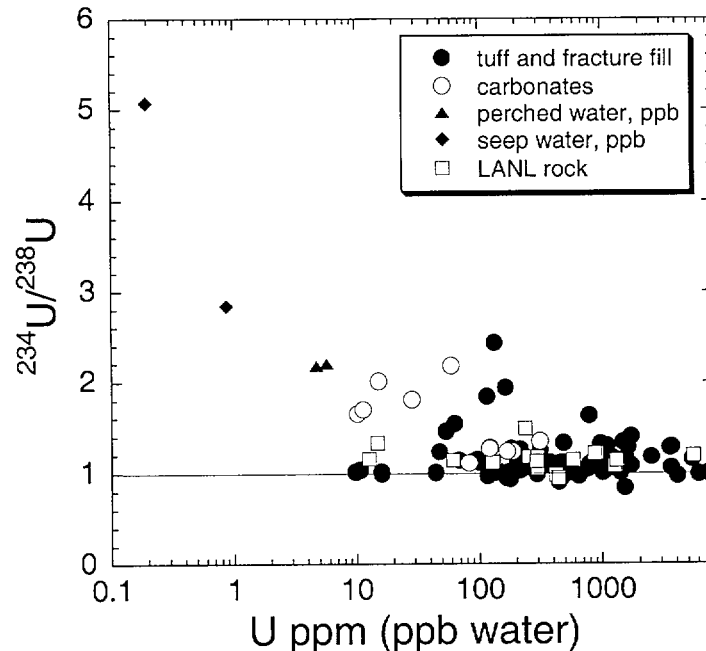
Preferential release of radioisotopes from nuclear waste forms or radionuclide solubility-limiting solid phases could affect repository performance. However, consequences of differential radioisotope release are generally neglected in performance assessment source term analyses. Furthermore, information on the degree of openness or closure of geologic systems and the time scale of chemical fluxes can be revealed in radioisotope systematics in the natural uranium and thorium decay series. Consequently, natural decay-series systematics may be used as a direct measure of the capacity of the geologic system to isolate radionuclides.

## NATURAL ANALOG DATA

Natural analog studies often use uranium decay-series data. Uranium decay-series fractionation in rocks and waters were used in the Alligator Rivers Analogue Project to help constrain quantitative, time-dependent release and transport models that allowed for differential release rates for  $^{234}\text{U}$  and  $^{238}\text{U}$  [3]. Uranium series isotopic disequilibrium in fractured granites was contrasted to secular equilibrium in unfractured granites from the Lac du Bonnet batholith, Manitoba, Canada, to characterize systems that were open and closed, respectively, to radionuclide transport [4].

The Nopal I uranium deposit at Peña Blanca, Mexico, is a natural analog of the proposed geologic repository at Yucca Mountain, Nevada [5-9]. 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, analogous to 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.

The distribution and fractionation of uranium decay-series nuclides at Nopal I are useful in characterizing transport phenomena and in judging the validity of transport modeling for performance assessment of the proposed repository at Yucca Mountain [9-12]. 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 range up to 5 [13].  $^{234}\text{U}/^{238}\text{U}$  ratios up to 2.4 in rocks and fracture filling materials outside the primary uranium deposit are due most likely to precipitation of uranium from solutions enriched in  $^{234}\text{U}$  by interactions with uranium rich source rocks [9,12]. Figure 1 shows uranium concentration and  $^{234}\text{U}$  enrichments in rocks and fracture fill material from Nopal I. With the exception of the carbonates, these  $^{234}\text{U}$  enrichments are minima because they do not reflect age corrections. The plot also shows the present-day relative  $^{234}\text{U}$  enrichment in unsaturated zone waters that have interacted with these rocks. Uranium decay series disequilibrium in fracture fill materials and rocks at Nopal I reveals multiple stage processes of radionuclide release, transport, deposition, and remobilization [12]. A separate uranium-series study at Nopal I [10] concluded that uranium mobility has been limited during the past 300,000 years, although radium mobility was indicated. Uranium-series results on caliches from near the deposit suggest that uranium release during the past few tens of thousands of years—characterized by  $^{234}\text{U}$ - $^{238}\text{U}$  fractionation—was also episodic [14].



**Figure 1.** Uranium concentration and  $^{234}\text{U}/^{238}\text{U}$  activity ratio in rocks and waters from the Nopal I natural analog site. Tuff and fracture fill rock data are from Prikryl et al. [9] and Pickett and Murphy [12], carbonate (i.e., calcite and caliche) data are reported in Pickett et al. [14], water data are from Pickett and Murphy [13], and Los Alamos National Laboratory (LANL) data on tuff and fracture rocks are from CRWMS M&O [10].

## PREFERENTIAL RELEASE

In performance assessments for geologic disposal of nuclear waste, relative radionuclide releases from waste form matrices are generally modeled to be proportional to isotopic inventories of the waste [15,16]. (Prompt or instantaneous releases of certain radionuclides are also commonly modeled.) However, fractionation of radionuclides, such as the preferential release of alpha decay products, which is evident in natural system data, is generally neglected in performance assessment modeling of the source term for radionuclide releases.

Preferential radionuclide release from nuclear waste forms has been addressed in a variety of experimental studies. For example, Eyal and Ewing [17] concluded in a study of effects of alpha recoil damage on dissolution of 17 year old borosilicate glass containing thorium that  $^{228}\text{Th}$  release was enhanced by fifteen to forty-five percent relative to its parent  $^{232}\text{Th}$ . In this study, alpha recoil damage led to preferential release of the daughter; direct alpha recoil into solution was not the fractionation mechanism. A review by Weber and Ewing [18] demonstrates the potential for order-of-magnitude increases in radionuclide release rates from ceramic waste forms due to decay-induced amorphization. Bibler et al. [19] examined releases of actinides and fission products from borosilicate glass and found their release rates to be no greater than releases of B, Li, or Na, which are used as standard measures for glass reactivity. However, it is unlikely that glasses tested in this study were sufficiently old to have accumulated the alpha damage that is primarily responsible for preferential release of alpha progeny. Similarly,

laboratory tests on spent fuel would not reflect alpha recoil and damage effects that accumulate only over long periods of time.

Theoretical effects of alpha recoil on dissolution of waste forms were addressed in a report supporting assessments of the proposed repository at Yucca Mountain [20]. This report concluded that such effects may be excluded from consideration in performance assessments for daughters of four nuclides ( $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{236}\text{U}$ ) based on low potential consequences. In the report, release rates due to direct alpha recoil to solution were calculated to be small compared to rates of release due to chemical dissolution of various waste forms. However, fundamental differences between alpha recoil (ejection) rates, dissolution rates, and overall release rates must be recognized in performance assessments. In addition to direct alpha recoil, release rates depend on solubilities and other properties of secondary phases that contain radionuclides and on occurrence of alpha progeny in damaged sites of increased reactivity. In general, conclusions reached in the Yucca Mountain report [20] fail to address general preferential release phenomena, such as those widely manifested by uranium decay-series disequilibria in natural systems.

Estimates of the potential significance of alpha decay effects for radionuclide release at the proposed Yucca Mountain repository can be based on inspection of inventory decay and ingrowth histories. The projected commercial spent nuclear fuel repository inventory includes numerous radionuclides resulting largely from ingrowth by alpha decay after waste emplacement (figure 3-9 and table 19-1 in [15]). Atoms of these radionuclides would be located in alpha-affected sites in the waste solid and may be preferentially released. Table I lists radionuclides that will be affected by alpha ingrowth. Shown are the factors by which a radionuclide content increases and the resulting percentage of atoms of that radionuclide in alpha decay sites. Potential dose effects were based on relative inventory abundance and estimated dose importance in performance assessments (e.g., [16]). Most notable is  $^{237}\text{Np}$ , a radionuclide important to dose in recent performance assessments for Yucca Mountain [16]. Neptunium-237 in spent fuel increases more than three-fold in approximately 1,000 years to the point that 71 percent of its inventory is alpha-affected. Neptunium-237 is also notable for considerable uncertainty concerning its solubility limit and release rate [21].

## NATURAL SYSTEM EVALUATION

Providing confidence in long-term safety of geologic disposal of nuclear waste requires systems with multiple barriers to radionuclide releases. In some cases, the mandate for multiple barrier systems is codified in subsystem performance requirements. For example, the general U.S. Nuclear Regulatory Commission (NRC) high-level nuclear waste regulation (10 CFR 60)—which was superseded by 10 CFR 63 for the proposed repository at Yucca Mountain—specifies a minimum groundwater travel time (GWTT) in the geologic setting (10 CFR 60). The GWTT requirement applies to the geologic system and is intended to ensure that the geologic setting provides a barrier function. Attempts to apply the GWTT requirement to the geologic system at Yucca Mountain raised questions concerning how GWTT could be defined, measured, and related to repository performance (e.g., [22,23]). Quantitative subsystem performance criteria are not included in the NRC site-specific regulation for the proposed repository at Yucca Mountain (10 CFR 63).

**Table I.** Radionuclides in commercial spent nuclear fuel at the proposed Yucca Mountain repository that may show enhanced release effects from alpha decay. The first seven listed radionuclides all grow in by several orders of magnitude toward equilibrium with their parents. Inventory from CNWRA [15].

Radionuclide	Maximum factor increase in inventory due to alpha decay	Percent of inventory occupying alpha decay sites at peak	Potential dose effect
<sup>210</sup> Pb	Large by 10 <sup>5</sup> y	100 %	High
<sup>226</sup> Ra	Large by 10 <sup>5</sup> y	100 %	High
<sup>227</sup> Ac	Large by 10 <sup>5</sup> y	100 %	Low
<sup>229</sup> Th	Large by 10 <sup>5</sup> y	100 %	High
<sup>230</sup> Th	Large by 10 <sup>5</sup> y	100 %	High
<sup>231</sup> Pa	Large by 10 <sup>5</sup> y	100 %	Low
<sup>233</sup> U	Large by 10 <sup>5</sup> y	100 %	High
<sup>234</sup> U	2.2 by ~400 y	53 %	High
<sup>235</sup> U	1.7 by 10 <sup>5</sup> y	41 %	Low
<sup>236</sup> U	1.5 by 10 <sup>4</sup> y	35 %	Low
<sup>237</sup> Np	3.4 by ~10 <sup>3</sup> y	71 %	High

Although the travel time of groundwater is potentially an indication of the ability of the geologic setting to isolate nuclear wastes, it focuses on a narrowly restricted part of the overall role of the geologic setting. Additional aspects of the role of the geologic setting are implicitly considered in containment and release subsystem performance criteria. For example, the chemical environments of containers and waste forms are conditioned by the geologic setting, and containment requirements and release requirements require consideration of this aspect of the geologic setting. However, for evaluating radionuclide transport in the geologic setting, the GWTT criterion fails to provide useful measures of critical geologic system processes including groundwater flux and retardation of radionuclide migration. With regard to radionuclide isolation, the efficacy of the geologic system is reflected in the extent to which it is geochemically closed with respect to migration of radioactive isotopes on an appropriate time scale. From this perspective, a quantitative evaluation of the degree of isotopic system closure could provide the basis for a measure of the essential radionuclide isolating capacity of the geologic site. Geochemical system closure can be demonstrated by natural radioisotope decay series data. Secular equilibrium and geochemical system closure are favorable natural system characteristics for geologic isolation of nuclear waste.

Decay-series natural system measures would be particularly applicable to 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 <sup>226</sup>Ra half-life of 1,600 years is comparable to this period. In a closed system after 10,000 years, disequilibrium between <sup>226</sup>Ra and its relatively immobile <sup>230</sup>Th parent (i.e., <sup>226</sup>Ra depletion due to its mobilization) would evolve to within about one percent of equilibrium. Therefore, a <sup>226</sup>Ra/<sup>230</sup>Th activity ratio in repository host rock outside a few percent from unity would indicate

radium mobility under site conditions within the past 10,000 years and its likely mobility during the regulatory period.

Decay-series radioisotope secular disequilibria evaluation would be specific to individual chemical species. Favorable characteristics for individual radionuclides could be based on safety and geochemical considerations, such as the magnitude of initial disequilibrium and waste form characteristics. Separate but complementary measures could be developed for decay series nuclides with contrasting geochemical characteristics, and generalizations could be developed to apply to anthropogenic species based on geochemical similarities.

## CONCLUSIONS

Radionuclide fractionation is most likely to affect performance of a geologic repository for nuclear waste through preferential release of alpha decay progeny 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. Activity ratios of released nuclides translate directly through conversion factors to dose ratios in performance assessments. Release models in performance assessments should recognize fractional isotopic release from solid waste forms particularly due to alpha decay effects.

For geologic disposal of nuclear waste, natural system evaluation focused on chemical system closure could capture the essential role of the natural system with respect to radionuclide isolation and could be based quantitatively on uranium and thorium decay-series secular equilibria/disequilibria.

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