

Rocky Mountain Peace and Justice Center

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4 September 2002

Ms. Christine S. Dayton
Environmental Systems and Stewardship
Kaiser-Hill Company
10808 Highway 93, Unit B, T130C
Golden, CO 80403-8200

RE: PLUTONIUM MIGRATION ISSUES

Dear Chris:

Thank you for your letter of 27 August responding to mine of 16 May 2002 regarding plutonium migration toward the Snake River Aquifer at the Idaho National Engineering and Environmental Laboratory (INEEL). You refer to a report and newsletter I sent you on this topic from the Institute for Energy and Environmental Research (IEER). You also comment on the Rocky Flats Actinide Migration Evaluation (AME) work in ways to which I wish to respond.

First, regarding the IEER documents, IEER relies on a National Academy of Sciences statement from 2000 about relatively rapid movement of plutonium through the vadose zone at INEEL toward the Snake River Aquifer. Perhaps what NAS says does not reflect "robust" science (your term), but NAS cites a dramatic change in the estimate of how long it will take plutonium to reach the Snake River Aquifer from a 1968 estimate of 80,000 years to a 1997 estimate of only 30 years. INEEL documents show that since 1972 plutonium has been detected in several aquifer wells; no one knows its exact source.

Second, regarding what you say about the history and accomplishments of the AME, I have several comments:

- The AME came into being in the context of the controversy surrounding the departure from Rocky Flats of environmental engineer M. Iggy Litaor. Litaor was well known for his published research on radionuclides in the environment on and off the Rocky Flats site. In the heavy rains of May 1995 Litaor documented significant real-time migration of plutonium in the Rocky Flats environment. In so doing, he countered assertions he and others had made previously to the effect that, once in the environment, plutonium remains more or less in place.
- Shortly after reporting this startling finding, Litaor was terminated by Kaiser-Hill. In a secret report done for Kaiser-Hill, scientists connected with the AME faulted Litaor for lacking the chemical speciation skills that they possessed and that they insisted were required to understand migration of actinides in the environment.
- Litaor, for his part, asserted from May 1995 forward that the principal means for plutonium migration in the Rocky Flats environment are the physical ones of transport by air and water erosion. Now, several years later, by its own expensive and circuitous route the AME group has reached essentially the same conclusion.

Third, I personally am not convinced that either Litaor or the AME is correct. I continue to wonder whether the chemical speciation approach has been as fully explored as is it

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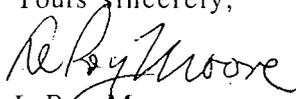
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should be. Attached is a letter I sent to you and the AME Team on 18 April 2000 raising a series of questions that were never satisfactorily answered. One of the key questions is whether oxidizing agents in the environment could change the oxidation state of plutonium, so that some portion of it could become soluble and could migrate rapidly away escaping detection, then be reconstituted in colloidal or particle form some distance away. Chemist Joel Selbin, a member of the AME Technical Review Group, says this could happen with uranium. When he asked at an AME meeting whether it could happen with plutonium, Greg Choppin of the AME team seemed to think it a not invalid question. But a definitive answer has never been given to this or to any of the other questions raised in my 18 April 2000 letter. As my letter says, "what is required is not assertions but demonstrations." At the public meeting where I presented this letter and asked for full answers in written form from the AME researchers, Dave Shelton of Kaiser-Hill stated bluntly that Kaiser-Hill would not spend its money on such. There the matter was left. And there it remains.

One of the articles to which my letter refers (Kersting et al, *Nature*, 7 January 1999) reports that plutonium migrated a distance of at least 1.3 kilometers in the subsurface environment at the Nevada Test Site over a period of 30 years. No one has explained how this could happen; the fact that it did certainly is pertinent for Rocky Flats. The second article to which my letter referred (Haschke et al, *Science*, 14 January 2000) showed that under certain conditions the oxidation state of plutonium may change from a condition where the material is insoluble to one where it can become soluble. I thought this might explain the relatively rapid migration at the Nevada Test Site. I also thought it might explain what Bruce Honeyman reported at an AME meeting on 20 August 1997 about plutonium solubility and mobility at Rocky Flats; emphasizing the solubility and therefore mobility of plutonium, he said the only question about its eventual migration off the Rocky Flats site was the rate of its movement. What Honeyman said would be forgotten by Kaiser-Hill and the AME team but for the fact that it was captured in minutes of the meeting. As for the *Nature* article, the AME team had one of the authors attend a meeting, but the results of the discussion were certainly inconclusive. I got the impression some of the AME people wanted to explain away an article that challenged their basic understanding. Of course the issue of possible solubility and thus greater mobility of plutonium is crucial, given present plans to leave a significant quantity of plutonium in the Rocky Flats environment after closure.

Given this situation, I do not think you or the AME team should assume that we have a definitive understanding of the behavior of plutonium in the Rocky Flats environment. I hope that before the AME work is finished we have convincing answers to the questions I have previously posed and am posing again by means of this letter.

Yours sincerely,


LeRoy Moore

cc: Rocky Flats Citizens Advisory Board
Rocky Flats Coalition of Local Governments
AME Technical Review Group

Rocky Mountain Peace and Justice Center

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18 April 2000

To: AME Team
Chris Dayton, Kaiser-Hill

From: LeRoy Moore, Ph.D.

Re: Outstanding questions re. plutonium mobility
that arise from the articles by Haschke et al
in *Science* (14 January 2000) and by Kersting
et al in *Nature* (7 January 1999)

On Wednesday, 1 March 2000, a public meeting was held to discuss the above mentioned articles relating to plutonium mobility. While the discussion was very interesting it did not really resolve key questions about the implications for Rocky Flats of the research reported in these articles. What is required is not assertions but demonstrations. What follows are some questions that have yet to be answered in a convincing manner.

1) The research of Haschke et al showed that up to 27% of the PuO_2 exposed to water as an oxidizing agent moved from PuO_2 to PuO_{2+x} or Pu(VI) , a form in which the Pu is more susceptible to solubility and thus also to mobility. Haschke et al thought this may have been a factor in the surprising long-distance migration of Pu (at least 1.3 km) discovered at NTS and reported on by Kersting et al in *Nature*, 14 January 1999. Is it possible that PuO_2 at NTS underwent transformation to PuO_{2+x} , in the process becoming soluble and migrating in this form, then being subsequently reconstituted as PuO_2 colloids, the form in which it was found by Kersting et al? If this could happen at NTS, could it not also happen at RF?

2) How far can Pu migrate in the sub-surface environment, whether in soluble form or in colloidal form? Kersting et al discovered Pu in colloidal form 1.3 km from the point of its origin 30 years earlier. They do not know whether it migrated further because no wells were drilled to find out. Given what they did find, shouldn't one conclude that over a relatively brief time by comparison with the half-life of Pu^{239} Pu can migrate quite considerable distances in the sub-surface environment, especially in groundwater?

3) At the March 1 meeting it was repeatedly asserted that nothing like what Haschke et al observed in their experiments has occurred at RF, because the Pu in the environment at RF has been observed only in oxide form, that is, only as PuO_2 . Is it possible that PuO_2 in the environment at RF transforms into PuO_{2+x} , becomes soluble, and flows away, so that the reason it is never observed is because it is gone? What would be required to demonstrate either that this never occurs or that it can occur?

4) Haschke et al observed that up to 27% of the PuO₂ involved in their study underwent transformation to PuO_{2+x} over a four year period. Over a longer period would not more of the PuO₂ undergo a similar transformation?

Wouldn't this process continue for an indefinite time, for as long as PuO₂ is available in the presence of some oxidizing agent? Four years is a relatively long period for a single laboratory experiment, but it is a very brief period for action in the physical environment of the real world. If PuO₂ in the environment at RF is gradually undergoing increased oxidation and possible solubility and mobility, what are the likely long-term consequences of Pu left in the soil?

5) If distilled water (as used in the Haschke et al experiments) acts as an oxidizing agent for PuO₂, what other elements could also foster enhanced Pu oxidation? What elements in the RF environment could play this role? What experiments could be conducted to demonstrate conclusively one way or the other whether or not such oxidation can occur and at what rate?

6) At a public meeting on 20 August 1997 Bruce Honeyman presented preliminary findings from some of his research on Pu speciation (attached is a photocopy of notes from this meeting later circulated as part of the record of the Actinide Migration Studies). In this meeting he stated that up to 90% of the Pu he was observing was in soluble form. He was asked whether this preliminary finding meant that the Pu is going to move offsite in the long term. He answered, "Yes, but additional work is needed to determine the rate of movement." What is the relation between what Honeyman claimed to have found at that time and the findings recently reported by Haschke et al?

7) What work plan can the AME devise to answer these and other questions that may arise regarding possible enhanced migration of Pu in the Rocky Flats environment?

John Law, John Hopkins, RMRS
John Corsi, Jack Hoopes, Chris Dayton, K-H

Record of Meeting Notes

Meeting: Actinide Migration Status Report

Date/Time: August 20, 1997; 4:30 p.m. to 6:30 p.m.

Location: Building 60, Rocky Flats

Attendees: DeAnne Butterfield, RFLII; Hank Stovall, Broomfield; Victor Holm, Chris Millsaps, Ken Korkia, CAB; Tom Marshall, RMPJC, CAB; Jim Stone, RFCC; William Kemper, Citizen; Ann Mary Nefcy, Citizen; Fran Burcik, WTDI; Mariane Anderson, John Rampe, Norma Cataneda, Purna Halder, Ken Braken, DOE-RFFO; John Corsi, Jack Hoopes, Chris Dayton, K-H; Rick Roberts, SSOC; John Law, John Hopkins, RMRS; Bruce Honeyman, CSM

Meeting Purpose: Provide the public with an update of the Actinide Migration Studies and present some preliminary results.

Significant Findings of Preliminary Results: Preliminary sampling indicates that the plutonium in the environment is in an organic form that could be relatively mobile; what initiates the mobility is still uncertain.

A final report titled "Summary of Existing Data on Actinide Migration at Rocky Flats" will be out by September 1997.

Dr. Bruce Honeyman followed Chris and presented the preliminary results that have been gathered from speciation studies to date. Speciation studies are essential in determining how mobile the actinide could be in the environment. Honeyman explained that the five potential species include: chemically exchangeable form, the carbonate bound form, the sesquioxide form, and the organic form.

Preliminary results indicate that the plutonium is in an organic form. This contradicts earlier data, that stated the predominant form of plutonium was thought to be in the sesquioxide form. This is only preliminary data and study has yet to determine what factors initiate the mobility.

Summary of comments and questions generated by Dr. Honeyman's presentation:

- Earlier findings indicated that plutonium in the environment was in an insoluble state (sesquioxide form), but now your data contradicts the earlier results and says that 90% of the plutonium is soluble.

Honeyman: Yes, when you include plutonium with organic complexes, it can become very soluble, and under certain conditions the plutonium can become very mobile in that form.

- Does this preliminary finding mean that the plutonium is going to move offsite in the long-term?

Honeyman: Yes, but additional work is needed to determine the rate of movement.

10. FACTORS AFFECTING RADIONUCLIDE TRANSPORT

10.1 INTRODUCTION

Radionuclide migration from the potential repository would be mitigated by several barriers, including the geochemical retardation due to solubility and sorption described in this section. One of the initial retardation factors is the solubility of the radionuclides themselves in any water that infiltrates the potential repository. The solubility of key radionuclides (e.g., Np, Pu, Am, and Tc) has been shown to be controlled by solution speciation and by the solubility-limiting actinide-bearing solid. Kinetic barriers are considered in this analysis and sometimes drive the conceptual choices of the phases to constrain some radionuclide concentrations. As such, this corresponds to metastable equilibrium in some cases and this ensures conservatism. This section summarizes factors affecting radionuclide transport under ambient conditions in the far field. Included are the results of the following investigations: radionuclide solubility and speciation, sorption, the effects of organics on sorption, matrix diffusion, and the conceptual models that describe these phenomena in transport codes. It also summarizes studies of colloid-facilitated radionuclide transport and of field testing of transport in the unsaturated and saturated zones. Section 10.1.1 considers the interactions of radionuclides with the products of canister corrosion such as iron oxides and cementitious materials that might be generated from concrete tunnel liners.

10.1.1 Radionuclides of Concern

Although the fission products ^{90}Sr and ^{137}Cs will dominate the radioactive inventory at the start of the potential repository's life (Choi and Pigford 1981), the half lives of approximately 30 yr. mean that these radionuclides will be decayed by the time the metal waste packages are projected to fail due to corrosion (a minimum of 1 k.y.) (Langmuir 1997). Therefore, little emphasis is placed on these elements. For spent nuclear fuel, the chief sources of radioactivity from 1 k.y. to 10 k.y. are Am and Pu isotopes (Langmuir 1997, Figure 13.18). From roughly 10 k.y. to 10 m.y., ^{237}Np contributes the most to radioactivity of the waste (Langmuir 1997, Figure 13.18). Therefore, scientific study has concentrated on the geochemical mobility of Am, Pu, and Np as the successively dominant contributors to radioactivity. In addition to these actinides, ^{233}U , ^{234}U , ^{129}I , and ^{99}Tc received attention in total system performance assessment (TSPA) exercises principally because there has been little demonstrated geochemical retardation from solubility or sorption for these radioactive isotopes. The radionuclides of concern singled out here (Tc, U, Np, Pu, and Am) were chosen from the most important species for the first 10 m.y. from the water-dilution figures of Choi and Pigford (1981) and from Langmuir (1997).

The geochemistry and thermodynamic solubility of the long-lived radionuclides are briefly reviewed in this section, followed by more extensive review of Np, Pu, and Am and their relevance to Yucca Mountain in subsequent sections.

Technetium—Technetium is a priority radionuclide due to its high solubility and low sorption. It is also the most important β^- -emitter in radioactive waste in the greater than 103-yr. time frame (CRWMS M&O 1994 Tables 5-11 and 5-12). Thermodynamic data for solids and solutions are being evaluated critically by scientists collaborating through the Nuclear Energy Agency; this review is scheduled to be published shortly. It is presumed by the TSPA that the waters at Yucca Mountain are oxidizing waters and that Tc will therefore exist in the Tc (VII) state as TcO_4^- . The tetrahedral arrangement of coordinating oxygens prevents the formation of stable solid precipitates and shields the Tc from mineral sorption sites. Release quantities calculated for solubility considerations would be limited by inventory, not precipitation equilibrium. However, interaction with reduced minerals, or in more reducing waters, may reduce the Tc to lower oxidation states (i.e., Tc [IV]), which would be orders of magnitude less soluble and more sorptive (Lieser and Bäuscher 1988). In reducing neutral waters, the predominant aqueous species would be $\text{TcO}(\text{OH})_2(\text{aq})$ in equilibrium with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}(\text{c})$ with a solubility of about 10^{-8} M (Rard 1983; Langmuir 1997, Figure 13.21). (Note: In this section, (c) indicates crystalline, (aq) indicates aqueous, and (am) indicates amorphous.)

At higher values of pH (greater than 10), amphoteric behavior starts to increase the solubility to approximately 10^{-7} M at a pH of 11. In the presence of high carbonate concentrations, carbonate complexes can form at pH values greater than 8.5, raising solubility to approximately 10^{-6} M by a pH of 11 for $P_{\text{CO}_2} = 10^{-2}$ bar (that is, approximately 33 times standard atmospheric CO_2 pressure). It is not anticipated that these pH and P_{CO_2} conditions will occur together unless alkaline plumes are generated by cement during the thermal pulse. However, cement will not be present in the current design except in small quantities. Little is known about the temperature effects on the Tc (VII)/Tc (IV) equilibrium, so extrapolation to the thermal range of 90° to 95°C in the near field of the repository is not possible. Furthermore, the intervening oxidation states (VI and V) are considered to be unstable with respect to disproportionation, but their stability under very dilute conditions or different temperatures is also not known. These comments on the effect of temperature on speciation, redox barriers, and, ultimately, thermodynamic solubilities can be made almost across the board for all the radionuclides discussed here (although Yucca Mountain water-specific solubility experiments will be

described below for Np, Pu, and Am). At this point, the only conservative, nonreproachable course of action is not to use solubility as a limiting factor in Tc release.

Iodine—Iodine occurs as iodate (IO_3^-) in highly oxidizing waters and as iodide (I^-) under less-oxidizing conditions, including most groundwaters (Pourbaix 1966, Figure 1, p. 621; Langmuir 1997, p. 520). Iodide salts are less soluble than iodate salts but are still too soluble to limit maximum possible I concentrations in groundwaters. Therefore, the concentration will be limited by the amount of I available from the inventory.

Uranium—Uranium has been studied extensively for over a century, and the relevant thermodynamics that control U solubility have been critically evaluated by Grenthe et al. (1992) under the auspices of the Nuclear Energy Agency. Spent nuclear fuel from nuclear power plants to be disposed of in the potential repository is largely in the form of UO_2 , so the discussion here starts with U (IV) complexes. Note that only U (IV) and U (VI) are considered to be important oxidation states of U, with U (V) quickly disproportionating (Newton 1975). Uranium (IV) is stable only at very reducing potentials, with the principal minerals being uraninite (crystalline UO_2), pitchblende (amorphous UO_2), and coffinite (USiO_4) (Langmuir 1997, p. 495). In the absence of carbonates, the principal solution species in equilibrium with uraninite/pitchblende (various degrees of crystallinity found experimentally) at pH values greater than 4 is

$\text{U}(\text{OH})_4^0(\text{aq})$, with a uranium solubility of less than 10^{-8} M to pH values greater than 12 (Ryan and Rai 1983; Parks and Pohl 1988; Rai et al. 1990, p. 263; Yajima et al. 1995, p. 1142). Given the formation constant of coffinite, its solubility should also be comparable to these values (Langmuir 1997, pp. 502, 503). Under Yucca Mountain conditions, the most important other ligand for U (besides OH^-) is carbonate. At very reducing conditions, the tetrahydroxide U (IV) complex is more stable in solution than the carbonates (Grenthe et al. 1992, pp. 120 to 122, 306 to 333), so U (IV) carbonates do not need to be considered further.

In the more oxidizing regions of uraninite (but not pitchblende) stability, the solution species in equilibrium over the U (IV) solid can be a U (VI) solution species, either a uranyl aquo/hydroxide species or a carbonate species (Langmuir 1997, Figures 13.8 to 13.9). In fact, several mixed-oxidation-state solids predominate at groundwater-relevant pHs before the U (VI) solid phases (schoepite ($\beta\text{-UO}_3 \cdot 2\text{H}_2\text{O}$) and [or] secondary uranyl solid phases, such as carbonates) predominate in the higher Eh values of the Eh/pH stability diagram. In ascending order of Eh values, important U solids formed in carbonate-free, near-neutral pH water include UO_2 , $\beta\text{-U}_4\text{O}_9$, $\beta\text{-U}_3\text{O}_7$, U_3O_8 , and UO_3 (Langmuir 1997, Figure 13.10). Important uranyl solution species under Yucca Mountain waters (e.g., UE-25 J-13, referred to henceforth as J-13) include, with increasing importance with pH, UO_2^{2+} , UO_2OH^+ , UO_2CO_3^0 , $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Grenthe et al. 1992, pp. 98 to 130, 306 to 330; Waite et al. 1994). Langmuir (1997, Figure 13.5) plotted the uranyl solubility as a function of pH with schoepite as the solubility-controlling solid for two P_{CO_2} cases. With no carbonate present, the solubility reached a minimum of just over 10^{-7} M at a pH value of just over 7. By a pH of 8.5 and, on the other side of the minimum, a pH of 5.5, the solubility increased to 10^{-6} M. With $P_{\text{CO}_2} = 10^{-2}$ bar ($\bar{}$), the minimum shifted to a pH of approximately 6.3 and to a value of about 10^{-6} M. The solubility increased from this value by an order of magnitude by pHs of 5 and 8. Typical Yucca Mountain waters (e.g., J-13) would produce solubilities intermediate between these two P_{CO_2} cases. The presence of other potential solid uranyl phases, such as rutherfordine or $\text{Na}_2(\text{UO}_2)(\text{CO}_3)_2$, was not considered. This fact implies that the present estimate is conservative, as a more stable uranyl carbonate solid would lower the solubility values, and less stable phases would convert to the schoepite.

Although the other actinides also exhibit oxide solubility-limiting solids rather than carbonates in J-13 water conditions (see below), schoepite has been reported to be a nonterminal phase: it dehydrates in dried-out conditions possible in the vadose zone and thereby its crystal structure is compromised, allowing it to be dissolved (Finch et al. 1992, p. 439). Secondary U mineralization subsequently occurs with weathering to form uranyl silicates (uranophane and soddyite), phosphates (autunite), vanadates (carnotite), or carbonates (e.g., rutherfordine), depending on what anions are available. Because many U deposits start out as uraninite and show these weathering/oxidation patterns, they can be used as natural analog systems for a radioactive waste repository to show mobility patterns of U over long periods of time (Curtis et al. 1994). An example of an analog for Yucca Mountain is the Peña Blanca deposit in northern Mexico, which occurs in an unsaturated and oxidized tuff located in an arid region (Pearcy et al. 1994; see Appendix 1 of this report). The formation of some of these secondary phases would limit the solubility of U further from that of schoepite. For instance, the formation of uranophane as the solubility-limiting phase, as is seen at Peña Blanca, should limit the U solubility to approximately 10^{-7} M (Langmuir 1997, pp. 513 to 514). Wilson (1990, p. 425) produced similar Ca-U (VI) silicate solids by leaching spent nuclear fuel with J-13 water.

Neptunium—TSPA results have shown that the inventory of Np from stored radioactive waste under current scenarios would be sufficient to consider Np a potential problem contaminant, with ^{237}Np being the largest contributor to the radioactivity of a radioactive waste repository at times between 10 k.y. to 10 m.y. (CRWMS M&O 1994; Wilson et al. 1994; Rechar 1995; Langmuir 1997). All of the TSPAs for the Yucca Mountain Site have considered neptunium to be the most hazardous radionuclide for repository times beyond 10 k.y. (CRWMS M&O 1994, Wilson et al. 1994, Rechar 1995); CRWMS M&O 1995; DOE 1998). In natural waters, Np (IV) is expected to be the dominant oxidation state under reducing conditions, while Np (V) is the dominant oxidation state in oxidizing waters (Katz et al. 1986; Lieser and Muhlenweg 1988, Section 2; Hobart 1990, p. 407). Although oxidizing conditions are generally expected to prevail in the unsaturated zone within Yucca Mountain, it is possible that reducing conditions may exist in the saturated zone (e.g., in the near field and far field) or locally in the near field (at least temporarily). Theoretical calculations using different thermodynamic data bases predict that the solubility-limiting solid phase would be either a Np (IV) or Np (V) compound, depending upon the redox state of the water (Wilson and Bruton 1990; Hakanen and Lindberg 1991; Janecky et al. 1995, 1997, p. 2). The solubility of solid phases with these different oxidation states is quite different, with the Np (IV) phase having a solubility several orders of magnitude less than that for the Np (V) phase. For Np (IV), solubility-controlling solids include $\text{Np}(\text{OH})_4(\text{am})$ and, especially, $\text{NpO}_2(\text{c})$. Important solution species include $\text{Np}(\text{OH})_4^0$ in low carbonate solutions (for pH greater than 3) and $\text{Np}(\text{OH})_3\text{CO}_3^-$ in higher carbonate solutions (e.g., total carbonate = 10^{-2} M, similar to UE-25 water, and a pH range from 5 to 11). Under conditions for the Np (IV) oxidation-reduction (redox) state, the solubility in water to at least a total carbonate concentration of up to 10^{-2} M is expected to be lower than 10^{-8} M (Langmuir 1997).

As for uraninite (described above), the stability field for $\text{NpO}_2(\text{c})$ extends into the Eh region in which Np (V) solution species may also exist (Langmuir 1997). The degree in which this extension occurs depends critically upon the database used. Neptunium (V) solubility-limiting solids include $\text{Np}_2\text{O}_5(\text{c})$, $\text{NpO}_2\text{OH}(\text{am})$, and in high ionic-strength carbonate media, the so-called double carbonate salts $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$ (where $x = 1$ to 3) (Volkov et al. 1980, 1981; Neck et al. 1994; Neck et al. 1995). In the absence of carbonates, the solution speciation of Np (V) is dominated by the highly soluble NpO_2^+ , which does not hydrolyze readily below a pH of 10 (Moskvin 1971; Rosch et al. 1987; Itagaki et al. 1992, Figure 2; Neck et al. 1992, Figure 3, p. 29; Tait et al. 1996, pp. 34 to 49). In J-13 type waters, where the higher carbonate complexes are not strong enough to be predominant even at higher temperatures, the carbonate-complexed Np (V) species of importance includes $\text{NpO}_2\text{CO}_3^-$ (Tait et al. 1996, p. 41).

Plutonium—Plutonium is a priority radionuclide, because a large quantity of it will exist in the inventory of a radioactive waste repository and, in oxidized form, it can be quite mobile. Unlike most metal cations, Pu can exist in multiple oxidation states simultaneously. The III, IV, V, and VI states of Pu are readily attainable under environmentally relevant conditions, and therefore redox conditions do not necessarily preclude a low release. In general, the solid state is dominated by Pu (IV), specifically $\text{PuO}_2(\text{c})$, $\text{Pu}(\text{OH})_4(\text{am})$, and radiocolloids (suspended PuO_2 polymer). The aging of Pu solubility-limiting solids might start with the formation of radiocolloids, which gradually dehydrate/polymerize to mixtures of $\text{Pu}(\text{OH})_4(\text{am})$ and (or) $\text{PuO}_2(\text{am})$, which, in turn, eventually go on to $\text{PuO}_2(\text{c})$ (Hobart et al. 1989, pp. 118 to 124; Clark 1994, p. 9). The final aged form should be $10^{6.6}$ times less soluble than $\text{Pu}(\text{OH})_4(\text{am})$, but modeling suggests that even aged $\text{PuO}_2(\text{c})$ contains $\text{Pu}(\text{OH})_4(\text{am})$ units on its surface, lessening this effect (Efurd et al. 1996, p. 7, Table 2). Mobility of the suspended radiocolloid and Pu-particle sorption (pseudocolloids) form can be significant, especially in highly fractured matrices in which filtration, redox reactions, and so forth are of diminished importance (Penrose et al. 1990; Triay, Simmons et al. 1995). Oxidation states can redistribute through disproportionation (e.g., Pu [V] disproportionates to Pu [IV] and Pu [VI] in acidic conditions at a rate inversely proportional to $[\text{pH}]^4$ [Newton 1975]) and from radiolysis effects. These radiolysis effects can cause either reduction (Cleveland 1979a, 1979b) or oxidation (Runde and Kim 1994) to occur, depending on the initial plutonium oxidation state and the chemical composition of the solution. As with Am, radiolysis can also complicate the solubility measurements due to radiation damage of the solubility-limiting solid.

In the solution phase, dilute Pu solutions expected in the environment are likely to have a distribution of oxidation states dominated by the +5 oxidation state, although Langmuir (1997, Figure 13.30) shows a large region of predominance for $\text{Pu}(\text{OH})_4^0(\text{aq})$ in the Eh-pH diagram for dilute Pu. As for Np (V), PuO_2^+ does not readily hydrolyze (Bennett et al. 1992, p. 18), in sharp contrast to the other oxidation states (Lemire and Tremaine 1980; Lemire and Garisto 1989; Langmuir 1997). Hydrolysis of the other plutonium oxidation states is high, occurring by a pH of 5 for PuO_2^{2+} , a pH of approximately 1.5 for Pu (IV), and a pH of approximately 8 for Pu (III). Plutonium (IV) undergoes extremely strong hydrolysis, leading to the universally seen formation of radiocolloids at neutral pHs and Pu concentrations greater than

approximately 10^{-7} M (Nitsche et al. 1993). All oxidation states have strong complexes with carbonate (Langmuir 1997), cutting into the Pu^{3+} and $\text{Pu}(\text{OH})_4^0$ predominance zones even at relatively low total carbonate concentration (10^{-2} M).

Americium—As noted above, in the 1- to 10-k.y. period, Am is, for a while, the largest contributor to radioactivity of the nuclear waste. Unlike other transuranic species, Am exists primarily in one oxidation state, namely as Am (III) (Silva et al. 1995, p. 73). The published Nuclear Energy Agency database for Am (Silva et al. 1995) puts Am and U alone as the actinides, whose databases could be agreed upon. At least two complicating factors do exist for interpreting Am data. Like Pu, Am can also exist in colloidal form (Penrose et al. 1990; Bates et al. 1992), so phase separation of truly soluble species is problematic, and there is another route for radionuclide migration. Furthermore, because ^{241}Am is intensely radioactive, it is difficult, if not impossible, to form a good crystalline solid as the solubility-controlling phase.

Americium (III) forms strong hydroxo, carbonato, and, for solids, mixed hydroxo-carbonato species (Silva et al. 1995, pp. 151 to 166). Important solution species at a P_{CO_2} of $10^{-3.5}$ bar (atmospheric CO_2 , producing water similar to J-13 at pH values between 7 and 9) include, with pH increasing from a pH of 6, Am^{3+} , AmOH^{2+} , AmCO_3^+ , $\text{Am}(\text{OH})_2^+$, $\text{Am}(\text{CO}_3)^{2-}$, and, beyond a pH of 9, $\text{Am}(\text{CO}_3)_3^{3-}$ (Silva et al. 1995). The only solid found in Yucca Mountain experiments in J-13 water was AmOHCO_3 (Nitsche et al. 1993), consistent with the large stability field of this solid over different values of pH and P_{CO_2} (Silva et al. 1995). Other important solids include $\text{Am}(\text{OH})_3(\text{c})$ ($\log P_{\text{CO}_2}$ less than -4, pH greater than 7.5) and $\text{Am}_2(\text{CO}_3)^3$ ($\log P_{\text{CO}_2}$ greater than -1, neutral pH) (Runde et al. 1992). Solubilities in Yucca Mountain-specific waters are discussed below. Thermodynamic studies of $\text{AmOHCO}_3(\text{c})$ at room temperature and $P_{\text{CO}_2} = 10^{-3.5}$ bar by Felmy et al. (1990, p. 196, Figure 2) show a solubility of $10^{-7.5}$ to $10^{-8.5}$ M for pH values from 6.5 to 9. Above a pH of 9, the solubility increases due to the formation of $\text{Am}(\text{CO}_3)_3^{3-}$ in solution.

10.1.2 Mineralogy and Strata Characteristics Affecting Radionuclide Transport

The two predominant modes of alteration in Yucca Mountain tuffs are (1) devitrification of the central portions of ash flows to form fine-grained assemblages of feldspars and silica minerals (quartz-tridymite-cristobalite) and (2) zeolitization, principally in the margins of ash flows. The first corresponds with the syngenetic alteration described in Section 5.2.1.1; the second is the principal mode of diagenetic alteration described in Section 5.2.1.2. Those tuffs that have experienced neither syngenetic nor diagenetic alteration retain most of their original glass (vitric tuffs).

Both Na and Ca in clinoptilolite exchange readily with a wide range of potential radionuclides, including Cs, Rb, Sr, and Ba (Ames 1960; Breck 1984, pp. 529 to 588). Potassium, on the other hand, is more difficult to remove from the clinoptilolite structure, exchanging well with Cs and Rb but exchanging poorly with Sr and Ba (Ames 1960). Although the compositional effects are most important for sorption of simple cations in solution, studies for the Yucca Mountain Site Characterization Project have focused on the utility of zeolitic horizons in retarding transport of complex transuranic species, most of which are poorly sorptive. Modeling by Robinson et al. (1995) illustrated the cumulative importance of thick zeolitic horizons in Np sorption; moreover, the data available at present indicate that the compositions of zeolitic rocks may also be an important factor, with Na-K clinoptilolite providing about twice the Np sorption capability of Ca clinoptilolite. The modeling done by Robinson et al. (1995) assumed a Np distribution coefficient (K_d) range of 1.1 to 3.9 for zeolitic rock in the unsaturated zone; in that report, it was concluded that there was no further need for Np sorption studies of vitric and devitrified tuffs, because the impact of the tuffs was negligible. However, a later report (Triay et al. 1997, pp. 85 to 86) assigned the most effective (i.e., larger) Np K_d s to iron-oxides anticipated from corrosion of the multipurpose container (assuming that such a container is actually used and emplaced at the Yucca Mountain site) and assigned the smallest maximum Np K_d for the natural site lithologies in the unsaturated zone to zeolitic tuff (unsaturated zone Np maximum K_d s were assigned as 15, 6, and 3 mL/g for vitric, devitrified, and zeolitic tuff respectively [Triay et al. 1997, pp. 85 to 100]). Despite differences in the assignment of K_d s for these different lithologies in various models, the dependence of model results on lithologic type remains. Furthermore, variations in geochemical properties, such as exchangeable-cation composition in zeolites, remain a factor to be considered.

In the unsaturated zone, exchangeable cations within clinoptilolites on the western side of the exploratory block consist primarily of Na and K (Broxton et al. 1986, p. 22). Clinoptilolites in the unsaturated zone on the eastern side of the exploratory block have mixed Na-K and Ca-K compositions. In the saturated zone, clinoptilolite compositions tend to