

**RESPONSE TO LEROY MOORE'S LETTER
ACTINIDE MIGRATION EVALUATION ADVISORY GROUP:
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In response to Dr. Moore's letter of September 4, 2002 regarding plutonium (Pu) migration issues, the Actinide Migration Evaluation (AME) advisors have provided a series of short discussions that we hope will offer convincing answers to your questions.

First, regarding the Institute for Energy and Environmental Research (IEER) and National Academy of Science (NAS) citations of the estimate of how long it takes for contaminants to reach the Snake River Aquifer - this now infamous graph was developed to refer to contaminants in general, and not Pu in particular. Unfortunately it was re-published by an NAS panel, and now no one seems to be able to identify the original source of the graph, or even the data used to construct it. Based on these observations, this situation definitely does not represent "robust science". The lack of data, documentation, and peer-review makes it impossible to comment beyond the notion that it is certainly not robust. It is unfortunate that this NAS panel published this graph, and thereby failed to maintain the high scholarly standards that we have come to expect from the NAS. We also reiterate that Idaho National Engineering and Environmental Laboratory (INEEL) has not gone through a detailed pathway analysis, and are still in an early stage in understanding of contaminant migration. This situation is quite different from the Rocky Flats Environmental Technology Site (RFETS or Site), where we have a much more detailed understanding of the transport pathways for Pu and americium (Am) migration.

Regarding Dr. Litaor, and his assertion that physical transport was the principal means of Pu migration at RFETS - the AME was developed to deploy a multidisciplinary approach to develop a further understanding of actinide migration to benefit the closure design of the Site, and to attempt to answer questions raised by Litaor, not to ignore them. It is also worth recalling that Dr. Litaor had hypothesized that reducing conditions caused by the May 1995 storm event resulted in Pu reduction to Pu(III), and subsequent re-dissolution and transport as a soluble species. At that time, Stakeholders were focused on the use of K_d models and soluble transport in order to account for surface water exceedences. Indeed, this more integrated multidisciplinary effort employed by the AME has forced the Site and the regulators to abandon the use K_d models in favor of scientifically-based erosion and sediment transport models. Moreover, the particles, colloids, and

chemical forms of actinides has also been characterized, and taken together affords a much better understanding of actinide migration at RFETS. In this regard, we have come a long way towards answering the questions raised by Dr. Litaor.

In the main body of Dr. Moore's letter, he frames a hypothesis that oxidizing agents in the environment can change the oxidation state of Pu, so that some portion of it could migrate rapidly away escaping detection, then become reconstituted in colloidal form some distance from the source. He cites Haschke's *Science* article (*Science*, 2000, 287, 285) as proof that Pu changes its oxidation state, and Kersting's *Nature* article (*Nature*, 1999, 397, 56) as proof that Pu can migrate. To properly address Dr. Moore's assertions, we must reiterate some fundamental aspects of Pu chemistry.

Pu oxidation states. Depending on the redox conditions available, Pu both can and will change oxidation states in the environment. Since the solubility of Pu compounds will depend largely on the oxidation states, the AME group spent a good deal of time discussing oxidation states in the beginning of the AME study, making comparisons to uranium (U) behavior, and discussing the natural analog sites such as Oklo, Africa, and Koongarra, Australia. When Pu and U are in the same oxidation states their chemical behaviors are similar. However, no such similarity is found for U and Pu in different oxidation states. Under natural oxic aquatic conditions, U prefers oxidation state VI for soluble species, while Pu prefers oxidation state V for the soluble species, and IV as an insoluble species. Therefore, because U may demonstrate a given behavior does not mean that Pu shows the same behavior. This is the fundamental flaw in Dr. Selbin's assertion that Dr. Moore's proposed mechanism might be feasible for U, and therefore that Pu may show similar behavior. The fundamental fact that the oxidation state characteristics of U and Pu are different has been known for about 25 years as reflected in it being a pervasive theme in our public discourse throughout the period of the AME activity.

Based on decades of study, it is well-known that in natural waters, Pu solubility is limited by the formation of amorphous $\text{Pu}(\text{OH})_4$ [sometimes referred to as $\text{PuO}_2 \cdot 2\text{H}_2\text{O}$] or polycrystalline PuO_2 , both of which represent Pu in oxidation state IV. A reasonable conservative estimate for the solubility product (K_{sp}) of $\text{Pu}(\text{OH})_4$ is approximately 10^{-54} , and the most recent detailed review (Neck, *Radiochim. Acta*, 2001, 89, 1) suggests that the correct value is approximately 10^{-58} , with a corresponding solubility of ca. 10^{-10} M in a low ionic strength solution (typical of natural waters). This estimate puts an upper limit on the amount of Pu that can be present in solution, even if Pu(V) or Pu(VI) are more stable solution forms under a given solution condition. As a result, even if Pu(V) or Pu(VI) are present in solution,

the total solubility is still limited by the formation of the highly insoluble amorphous $\text{Pu}(\text{OH})_4$. The high stability and low solubility of $\text{Pu}(\text{IV})$, and the strong tendency of $\text{Pu}(\text{OH})_4$ to sorb on surfaces is a dominant and often controlling feature of Pu (geo)chemistry.

For many years it had been asserted (see, for example, Harnish -*USGS/WRIR-93-4175, 1994*) that PuO_2 was the likely chemical form of Pu in RFETS soils. These assertions lacked definitive scientific data to support or refute the claim. The AME group employed state-of-the-art scientific techniques to examine soils from the Site. Key x-ray absorption studies identified not only that the Pu oxidation state was IV, but also that the chemical composition was PuO_2 . Moreover, ultrafiltration studies (see, for example, Santschi, *Environ. Sci. Tech.* 2002, 36, 17) provided additional data demonstrating that the Pu in RFETS soils was associated with small particles and colloids. Taken together, these data provide the "demonstration" that Dr. Moore is seeking, namely that Pu is highly insoluble and that Pu observed in RFETS waters is associated with small particles and colloids. Therefore, Pu migration at RFETS occurs not because Pu is in a soluble form, as Dr. Moore asserts, but rather, because migration of a small amount of the insoluble form takes place through the movement of small particles and colloids. These findings are consistent with our basic understanding of Pu geochemical behavior from the past 60 years of scientific investigation, and are based on sound, defensible scientific data.

Haschke's Science Article. Dr. Moore cites Haschke's article in *Science* (2000, 287, 285) as proof that Pu in the form of PuO_2 may "change from a condition where the material is insoluble to one where it can become soluble". Dr. Moore also implies that the AME group was dismissive of this report because it challenged our fundamental understanding. For the record, Haschke's article reports indirect evidence (Pressure-Volume-Temperature data) that the composition of Pu oxide can change from stoichiometric PuO_2 to a non-stoichiometric solid of composition PuO_{2+x} , where x varies between 0 and 0.2. Up to this point in the article, Haschke offers credible data to support a change in stoichiometry, which is quite fascinating based on its intrinsic scientific interest. However, based on stoichiometry alone, Haschke went on to infer that the oxide must contain a higher oxidation state of VI, and extrapolates that it must, therefore, be more soluble. This portion of the Haschke article has most certainly been dismissed by the AME advisors, as it has by leading international experts on Pu solution chemistry, because it lacks direct experimental data on the actual oxidation state, and it speculates on the solubility of the oxide phase in the total absence of data. Haschke's interpretation of solubility is based on interpretation of Pu data prior to 1979, and does not offer any data or any proof of an oxidation state or solubility change. By ignoring all the research of

the past 21 years, Haschke failed to cite the more recent data that disagreed with his hypothesis. Citing Haschke's reference as proof of an oxidation state change is inappropriate and indefensible.

Many recent studies on the solubility of Pu(IV) have appeared. The most recent exhaustive study by Kim (*Radiochim. Acta* 1999, 86, 101) was available, but ignored by Haschke at the time of the *Science* publication (2000, 287, 285). More recent detailed reviews by Neck (*Radiochim. Acta*, 2001, 89, 1) and Fanghanel (*Pure Applied Chem.*, 2002, 74, 1895) point out the difficulty with the early solubility studies - namely that they suffered interference from radiocolloid formation and oxidation state disproportionation reactions under the high concentrations used in laboratory experiments, which generated Pu(III) and Pu(VI) as contaminants. Therefore, while Haschke's (2000) work provided an improved description of the range of solid-state characteristics of Pu oxides, it does not change our understanding of the solubility behavior that has been extensively studied, and extensively reviewed by international experts on actinide solubility and solution chemistry.

In the absence of explicit oxidation state or solubility information on PuO_{2+x} , the AME group adopted the pragmatic approach of asking whether PuO_{2+x} could form in the RFETS environment, and whether it would be identifiable using a direct experimental approach such as X-ray Absorption Fine Structure (XAFS) spectroscopy. In the interest of learning more about PuO_{2+x} and how it relates, if at all, to RFETS, an authentic sample of formula $\text{PuO}_{2.2}$ was obtained from one of Haschke's original scientific team, and the XAFS studies on this new material were found to be distinctly different from that of PuO_2 , and the Pu in RFETS soil samples. The RFETS soil samples were nearly identical to PuO_2 . Therefore, based on direct XAFS experimental evidence, the AME group does not believe that PuO_{2+x} is an important chemical species for RFETS soils, nor does a change in stoichiometry from PuO_2 to PuO_{2+x} provide a credible mechanism that alters the solubility of Pu and enhance its environmental migration.

The identification of some amount of PuO_{2+x} in PuO_2 does not alter the observed experimental fact that Pu oxide is very *insoluble* in natural waters. The solubility of Pu dioxide is so low that it has always been subject to ambiguities regarding the true identity of the solid and solution phases, and decades of study reveal a range of solubility centered around 10^{-10} M (*Radiochim. Acta* 1999, 86, 101) in water, at neutral pH, even after equilibration over a period of years. Dozens of measurements, performed all over the world, over a period of many decades inherently include the influence of this higher oxide (if it is present) on the solubility.

Particles, Colloids, and Kersting's *Nature* Article. At this point it is worth recalling the original premise of the AME group that the fate and transport of Pu is governed by the solubility of its compounds in groundwater and surface waters, the tendency of Pu compounds to be adsorbed onto mineral phases in soil particles, and by the probability that the colloidal forms of Pu are removed through filtration by the soil or rock matrices, or adsorb or precipitate during transport. Indeed, much of the original AME effort was focused on examination of the solubility of Pu and identification of its chemical form as previously discussed. However, the fact that Pu is insoluble does not mean that Pu is immobile in the environment. It appears as though Dr. Moore, like many other stakeholders, has intertwined the concept of insolubility with that of immobility. We reiterate that the key to understanding Pu mobility lies in the role of particles and colloids as a transport pathway.

Kersting and coworkers published their observation (*Nature*, 1999, 397, 56) of colloid-associated Pu at the Nevada Test Site (NTS), and the recognition that Pu transport occurred to a point 1.3 km from the underground blast source cavity. The Pu concentrations were exceedingly low at 10^{-14} M, and the results were consistent with Pu migrating as colloidal material from an underground detonation source term. Dr. Moore claims that no one has explained how Pu could possibly move 1.3 km at NTS. This claim is mystifying in light of the clearly stated conclusion of Kersting's study that Pu mobility likely occurred through movement of colloidal particles. The role of colloidal particles has also been under investigation at RFETS, where we know that the colloid loads are very small, and we have inferential evidence (Honeyman's early work and Santschi's more recent studies at RFETS) that RFETS colloids may be comprised of either inorganic or organic varieties. The important question is not about the "rate of movement" as Honeyman once suggested at a public meeting, but whether colloids represent a significant exposure pathway. Honeyman also pointed out (*Nature*, 1999, 397, 23) that the very properties of compounds that make them good candidates for colloidal transport - low solubility and high particle reactivity - limit the amount of contaminants that can be transported by colloids. Indeed, as suggested by Honeyman (*Nature*, 1999, 397, 23), colloids are both the means and the bottleneck.

Unfortunately, Dr. Moore is trying to link Haschke's unsupported and erroneous claim of an oxidation state change with Kersting's observation of colloid transport. This is a serious error for the reasons outlined above. All the data accumulated so far indicates that Pu is insoluble, and that the insoluble Pu can associate with particles and colloids as a transport pathway for Pu in soils at RFETS. The fact that the *Nature* article concludes that any transport model for Pu migration "must take colloids into account" in fact agrees with our current approach to develop erosion/sediment transport models to predict actinide migration at the Site.

Environmental Behavior of Pu/Am at RFETS. The data amassed during AME studies is consistent with our expectations of Pu and Am chemical behavior in the environment. The data indicate that Pu and Am in the dissolved fraction of RFETS surface waters have extremely low concentrations in the femtomolar (10^{-15} M) range, similar to global fallout. Site-specific studies indicate that reducing conditions do not remobilize Pu by solubility mechanisms, and that the bulk of Pu and Am is associated with particles that settle in ponded water, and small ($< 2\mu\text{m}$) colloidal particles that won't settle, but can be filtered out by soil and rock matrices. These results are consistent with the known chemical behavior of Pu(IV) and Am(III). X-ray Absorption Fine Structure (XAFS) studies show unambiguously that Pu in soils taken from the 903 Pad is in oxidation state (IV), in the chemical form (speciation) of very insoluble PuO_2 . The identification of Pu(IV) in the chemical form of PuO_2 is consistent with the observed insolubility of Pu in Site-specific waters.

The data from AME studies clearly indicate that physical (particulate) transport is the dominant mechanism for Pu migration in soils and surface waters at RFETS. Most important is the recognition that the insolubility of Pu does not equate to immobility. The association of Pu with small particles and colloids is the key to understanding, and ultimately predicting and controlling the migration of Pu and Am in RFETS soils and waters.

We hope that the level of detail provided above has offered sufficient answers to Dr. Moore's questions. We all agree that such dialogue is important, and it helps the advisors refine complex scientific data, concepts, and models into a form that is useful to the Site managers, the Regulators, and the

7/7