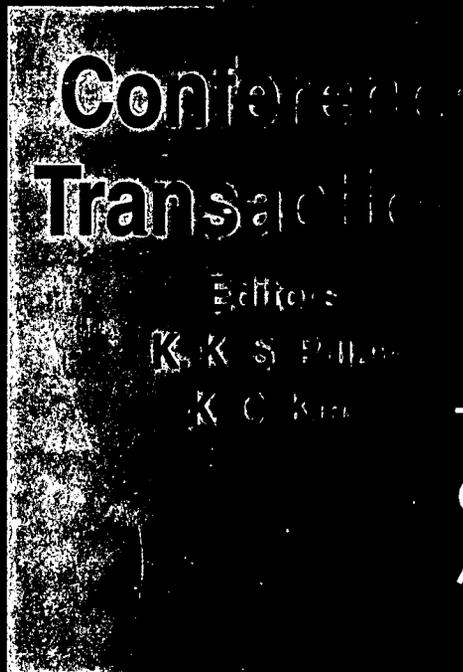


# PLUTONIUM FUTURES —THE SCIENCE



TOPICAL CONFERENCE  
ON PLUTONIUM  
AND ACTINIDES

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## Aquatic Chemistry of Actinides: Is a Thermodynamic Approach Appropriate to Describe Natural Dynamic Systems?

The worldwide civilian use of nuclear energy generates yearly about 11,000 tons of spent-fuel from 433 nuclear power plants (NPP) in operation for the moment with an installed capacity of approximately 350 GWe (36 NPP are being under construction). This contributes to the world electricity production about 17%. The hitherto discharged spent-fuel is estimated to be around 220,000 tons, which contain about 1,400 tons of plutonium and a considerable amount of minor actinides and fission products. The total quantity of long-lived radioactive elements, mostly actinides, increases steadily. The foreseeable solution for their isolation from the biosphere is a geological disposal with safe confinement. The long-term safety assessment of such containment entails well-founded knowledge on the aquatic chemistry of actinides, most of all, their thermodynamic properties in the geochemical environment.

A thermodynamic approach is indispensable for the appraisal of the chemical behavior of actinides in natural aquatic systems. However, the real natural systems are dynamic and "open" for a variety of geochemical reactions. Actinide ions exposed once to natural dynamic systems undergo a multiplicity of nanoscopic chemical reactions, in which individual processes may not be equilibrated or may appear irreversible. For the assessment of such complexities, a challenging question arises indubitably: "Is a thermodynamic approach capable of describing the actinide behavior in natural dynamic systems?"

Actinides to be disposed of are immobilized in different solid phases, called engineered barriers, which are then contained by back-fills known as geo-engineered barriers and further by natural geological barriers. Whatever the perceived scenarios are to come after disposal, the long-term performance assessment of such a multi-barrier system necessitates the quantification of the geochemical behavior of individual actinides in the environment of each barrier. The two characteristics are recognized for actinides in aquifer systems: the oxidation state specific chemical behavior, namely M(III), M(IV), M(V), and M(VI), on the one hand and the chemical reactions governed by the effective charge of individual ions on the other hand. These characteristics can be followed as a primary guide for understanding their general chemical behavior in both laboratory and natural systems. Under reducing conditions, which are mostly the case for deep aquifers, actinides of M(V) and M(VI) become reduced to M(III) or M(IV). Actinides of M(III) and M(IV) are sparingly soluble in water at neutral pH, and these particular chemical properties lead to their strong tendency toward the so-called pseudo-colloid formation. How can such processes be quantified? Can it be delivered by a thermodynamic approach?

Whatever the engineered barriers are made of, they are thermodynamically unstable in the near-field environment once water comes in contact with them and they undergo a variety of geochemical reactions. Solid phases of waste are first subject to corrosion, leaching and dissolution of individual components, the processes of which generate the *new* secondary solid phases that appear to be stable thermodynamically as compared to the primary solid phases in the near-field environment. Upon the phase conversion of engineered barriers, the actinides dissolved are submitted to hydrolysis, complexation, redox-reaction and

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colloid generation, and largely immobilized by incorporation into the secondary solid phases that are partially equilibrated in the new environment. Under these conditions the chemistry of actinides in the aqueous phase is submerged into the geochemical condition evolved from water interactions with waste, backfill and surrounding geological matrices. Taking into account these conditions the source terms of individual actinides are to be quantified. How far is a thermodynamic approach capable for such quantification?

The so-called "Kd-concept" is often used to calculate the migration behavior of individual actinides in a given aquifer system. Since Kd is a simple operational parameter, which depends on various unknown geochemical effects involved, it has no solid thermodynamic foundation, and its applicability to the long-term performance assessment has become the subject of controversial debate. An alternative to the Kd-concept is to evaluate thermodynamic parameters for the complexation of individual radionuclides onto the surface of geo-matrices. This can be realized by the study of solid-water interface reactions for a given actinide ion on a number of single minerals and thereafter by a combination of the results proportionally into a composite model. The development of such a surface complexation model is in progress in a number of laboratories worldwide. Is such a model conceived for actinides applicable to natural dynamic systems?

The paper summarizes the present state of available thermodynamic approaches that can be applicable for the performance assessment of multi-barrier systems. Limitations of the approaches, as perceived for the moment, are to come into view simply as repercussions of the present discussion. To provide an overview on a multiplicity of convoluted chemical reactions in natural systems, the present discussion is separated into the following three areas:

- Laboratory systems (closed system),
- Natural dynamic systems (open systems),
- Applicability of laboratory knowledge to natural systems.

Along these subject areas, detailed discussion is further directed to the speciation of actinides in solution, in solid phase and in solid-water interface interaction for laboratory systems, and additionally to the quantification of source terms in the near-field and the migration behavior in the far-field.

## Plutonium in the Environment: Speciation, Solubility, and the Relevance of Pu(VI)

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The critical role of plutonium in long-term and interim storage of nuclear waste attracts great attention to its fate under environmental conditions. The unique feature of plutonium, the ability to occur in multiple oxidation states simultaneously, complicates its geochemistry. For decades  $\text{PuO}_2$  has been considered the most stable form of Pu with the lowest solubility and lowest mobility among the actinide oxides/hydroxides. However, recent reports have raised concern on the stability of  $\text{PuO}_2$ . Colloidal transport of Pu at the Nevada Test Site and absorption of oxygen in the presence of water to form a higher oxide,  $\text{PuO}_{2+x}$ , indicated the potential implications for the long-term storage of plutonium. In specific, the formation of a "superoxide" in which more than 25% of the Pu(IV) is oxidized to soluble Pu(VI) raised concerns regarding the safety of underground storage facilities.

We combined fundamental chemical studies, site-specific investigations, and geochemical modelling to evaluate the understanding of the environmental behavior of plutonium. Solubility studies were conducted in J-13 water from the Yucca Mountain site representing the range of natural waters of low ionic strength. In these waters, amorphous plutonium oxide/hydroxide and/or colloidal Pu(IV) dominated the solubility-controlling solid. X-ray absorption spectroscopy studies revealed the +IV oxidation state to be prevalent. Geochemical modelling showed that at neutral pH, the Pu solubility is controlled by the solubility of the Pu(IV) solid at Eh (the redox potential of the solution) < 300 mV. Increasing Eh results in the stabilization of Pu(V). Maintaining the high Eh and increasing pH results in the stabilization of Pu(VI). While Pu(V) is the most stable oxidation state at neutral pH, the formation of Pu(VI) causes a significant increase in Pu solubility due to the formation of highly soluble anionic Pu(VI) carbonate complexes. The stability of these complexes increase with carbonate concentrations. At the carbonate concentrations common for natural waters, Pu(VI) is calculated to be stable only at pH above 9 (Figure 1).

The stability of Pu(VI) was tested at varying pH and NaCl concentrations. At low pH and chloride concentration Pu(VI) is unstable towards reduction and green Pu(IV) solid precipitates from oversaturation. Increase in chloride and pH stabilizes Pu(VI), most likely due to radiolysis and complexation reactions. Radiolytic formation of oxidizing species, such as  $\text{ClO}^\cdot$ , at  $[\text{NaCl}] > 2 \text{ M}$  may create an oxidizing system and Pu(IV) is oxidized to Pu(VI). In the presence of reductive agents, such as Fe, Pu(VI) rapidly reduces to lower oxidation states, Pu(V) and Pu(IV).

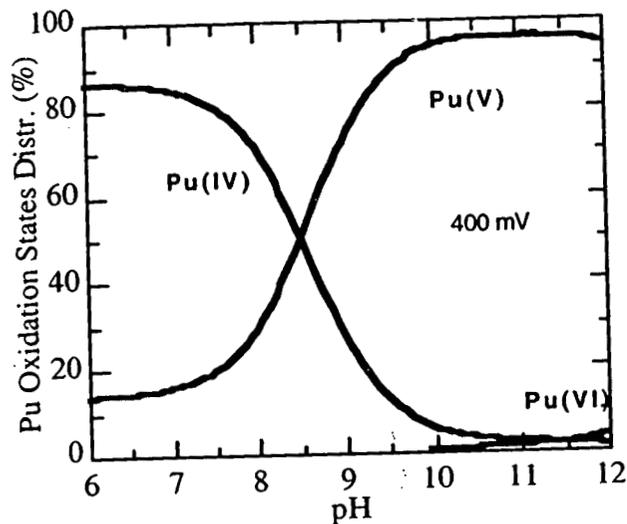


Figure 1. Pu oxidation state distribution at 400 mV and 500 mV. The carbonate concentration was maintained at 1 millimolar.

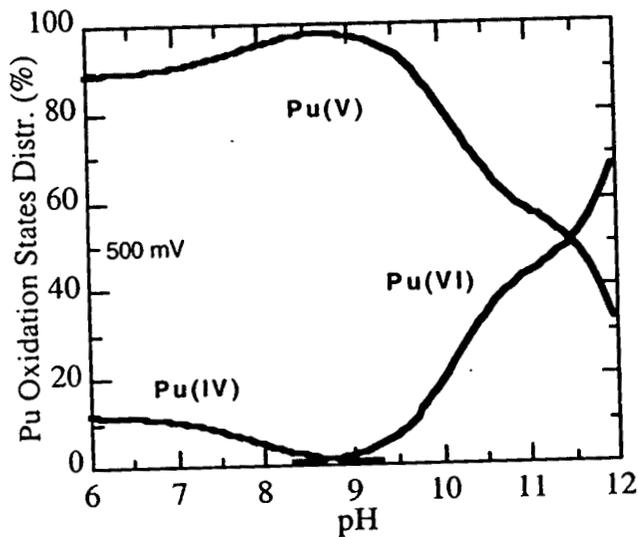


Figure 2. Pu oxidation state distribution at 400 mV and 500 mV. The carbonate concentration was maintained at 1 millimolar.

Geochemical modelling predicts Pu(IV) in its low soluble solid oxide/hydroxide form that predominates over most natural conditions. We studied the speciation of Pu in contaminated soil from the Rocky Flats Environmental Test Site (RFETS). X-ray absorbance data on soil samples from the RFETS indicate the Pu present is tetravalent and structurally similar to the highly stable and immobile PuO<sub>2</sub>. Dissolution reactions are ongoing to determine the release rate and Pu concentration boundaries. Here we evaluate the present understanding of plutonium environmental chemistry and discuss how solid phase stability, solution speciation, and redox potential interact and influence the solubility of plutonium in natural systems.

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