

ACTINIDE SOLUBILITY CONTROLS IN
PERFORMANCE ASSESSMENT OF NUCLEAR WASTE REPOSITORIES

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ABSTRACT

The importance of solubility control of radionuclide concentrations in repository groundwaters is discussed. Such control allows readily defensible estimation of the maximum concentrations of some actinide radionuclides in groundwaters. Estimates from currently available data indicate a number of cases where such maximum concentrations will be near or below the concentrations that are permissible, without the benefit of other processes that will lower the concentrations even more. Available information is briefly summarized and further research needs, which are not overly extensive, are discussed.

INTRODUCTION

Licensing requirements for any candidate site for a nuclear waste repository will most likely include a performance assessment incorporating credible long-term (>1000 year) predictive capability. Such long-term extrapolation of relatively short-term radioactive waste-form leaching and radionuclide migration data requires that the processes studied be essentially time-independent or that the mechanisms be understood. In addition, The Nuclear Waste Policy Act of 1982 provides site characterization and selection target dates that necessitate assessment methods which will provide defensible predictions in a timely manner.

The primary means of radionuclide mobilization and migration is groundwater transport. The geochemical behavior of radionuclides, in this case, will involve precipitation/dissolution and adsorption/desorption mechanisms in both near- and far-field conditions. Knowledge of the relevant chemical species present in solution and the solubility of radioactive solid phases can be used to set upper limits on the concentrations of radionuclides available for transport under different geologic conditions. The purpose of this paper is to discuss the solubility control approach and to present some supporting data for its application in assessing maximum source-term and groundwater actinide concentrations in solutions.

SOLUBILITY CONTROL

If a discrete solid phase containing a radionuclide is present in a repository or if the concentration of an element in the groundwater is such that a radioactive solid phase can precipitate, the equilibrium concentration of the radionuclide will be determined by the solubility of that solid phase (Fig. 1). Of course, adsorption/desorption of the radionuclide by the material in a repository and along the groundwater path would also occur. However, as long as the solid phase is in contact with the groundwater, the equilibrium concentration of that radionuclide would be controlled by the solubility of the solid phase. In the absence of a solubility controlling solid phase, the radionuclide concentration would depend on adsorption reactions (Fig. 1).

The precipitation/dissolution and adsorption/desorption mechanisms also control the chemical

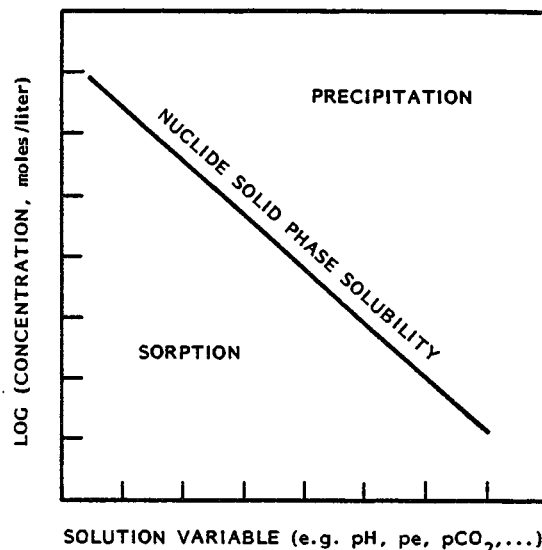


Fig. 1. Schematic Diagram of Processes that Control Solution Concentrations. Above the solubility line, a solid can precipitate. In the presence of a solid phase, the equilibrium concentration will be along the solubility line. In the absence of a solid phase, the equilibrium solution will be controlled by adsorption/desorption.

composition of the groundwater entering a waste package system (the waste package system is defined here as including the waste form, canister, backfill and near-field host rock). In the waste package system, the heat, ionizing radiation, and waste package chemistry will alter the groundwater compositions. Changes in groundwater composition and subsequent dissolution and precipitation of various waste package components and the resultant solution speciation define the source term for each radioactive element.

Away from the near-field, dissolution/precipitation reactions in the aquifer, also involving the non-radioactive species leached from the waste package, will affect radionuclide solution concentrations. Changes in aqueous speciation will depend on changes in pH, Eh (especially for redox-sensitive elements), or ligand concentrations.

In a thermodynamic approach, equilibrium conditions are assumed to exist along the flow path. The equilibrium assumption is reasonable if the concentration controlling reactions are limited to kinetically rapid precipitation, hydrolysis, and redox reactions. However, equilibrium may not exist at the waste form/groundwater interface, although under such non-equilibrium conditions, radionuclide concentrations will be less than predicted at equilibrium. If precipitation of more stable and complex phases incorporating the radioisotopes occurs over a longer time scale, the solubility-controlled radionuclide concentrations would be further reduced.

APPLICATION OF SOLUBILITY CONTROL APPROACH

If the thermodynamic data for all the solution species and solid phases were available, predictions of maximum solution concentrations would be possible. If these predicted concentrations were near or below the acceptable limits, then it could be defensibly shown that radioactive wastes could be safely disposed in the geologic environments.

The concentrations deduced from the thermodynamic data are the maximum possible for the given solid phases and groundwater compositions. Slow dissolution of waste forms can result in concentrations that increase with time, but only up to the solubility-limited concentration. Data illustrating this were obtained in a study by Rai et al.¹ using aqueous suspensions of Np-doped borosilicate glass (a potential waste form). Neptunium solution concentrations were observed to increase initially with time (Fig. 2). However, within 300 days the Np concentrations were essentially the same as the concentrations observed from the solubility measurements² of NpO₂.

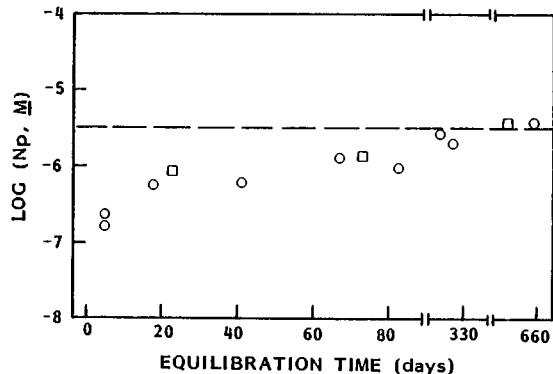


Fig. 2. Concentration of Np in Solutions ($6 < \text{pH} < 7$) Contacting Np-Doped Glass (○) and Np-Doped Glass Plus NpO₂ (□) as a Function of Time. Average NpO₂ solubility (dashed line) estimated from experimented data obtained under similar conditions as Np-doped glass.

The stable solid phases of pure actinide oxides may, in a repository environment, be converted gradually to solid phases having even lower free energy (and hence lower solubilities). The result of such a conversion would be to lower even more the maximum concentration of actinide ions that may exist in a groundwater. Therefore, the method still provides a conservative limit to long-term predictions of maximum concentrations.

However, accurate thermodynamic data for all solid phases and solution species are neither available nor essential for making predictions. The data are only needed for predominant nuclear waste isotopes having very long half lives such as Tc, Pu, Np, Am, and I.

The concentrations of many ligands ($\text{NO}_3^- = \text{Cl}^- = \text{SO}_4^{2-} = 10^{-3} \text{ M}$; $\text{H}_2\text{PO}_4^- = \text{F}^- = 10^{-5}$) in most groundwaters and their formation constants with key radionuclides (such as Pu, Am, U, Np) are such that the complexed species are not expected to contribute significantly to the total soluble radionuclide concentration and hence can be ignored³. However, groundwaters from specific locations⁴ may be high in some of the ligands such that their complexed species may contribute significantly to the total soluble radionuclide (e.g., salt waters are high in SO_4^{2-} and Cl^- ; basalt waters are relatively high in F^-). Hydroxo and carbonate ligands do form very strong complexes with many of the important radionuclides and hence need to be considered. Unfortunately, reliable thermodynamic data for these complexes for most of the radionuclides of concern are not available. As one example, until recently⁵ the values of hydrolysis constants of trivalent actinides were primarily estimated. Use of such values in making predictions would have resulted in up to nearly 5 orders of magnitude difference in predicted concentrations, hardly acceptable for safety assessment calculations (Fig. 3). As another example, uranium (IV) hydrolysis constants have been estimated from a few measurements by Gayer and Leider⁹ and have been used for predicting behavior of other tetravalent actinides. Recently Ryan and Rai¹⁰ have shown from measurements of uranium (IV) hydrous oxide under anoxic, reducing conditions that the U(IV) hydrolysis constants are, in fact, at least four orders of magnitude lower than estimated by Baes and Mesmer¹¹ from the Gayer and Leider data.

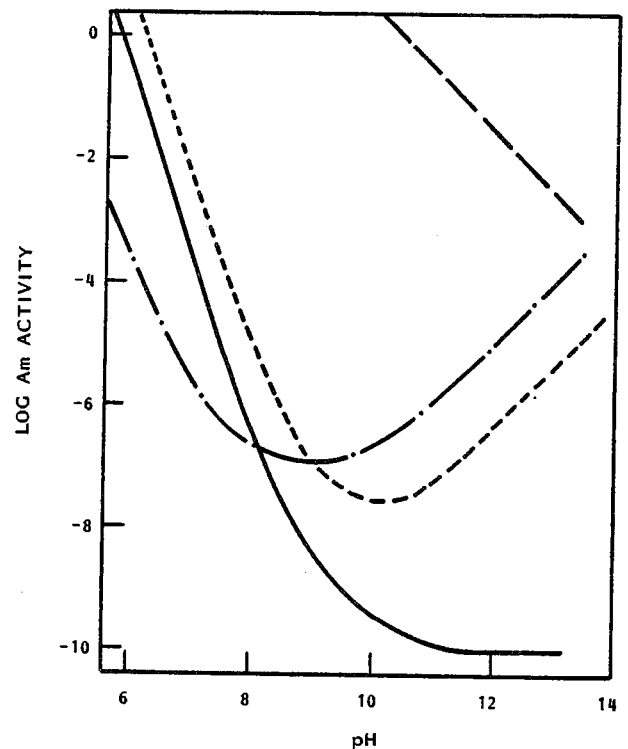


Fig. 3. Estimated and Experimentally Determined Solubility of $\text{Am}(\text{OH})_3(\text{am})$ as a Function of pH. Based on estimated thermodynamic data reported by Phillips⁶ (-----) and Allard et al.⁷ (— · —), the experimental data of Rai et al.⁵ (—), the experimental solubility product of Rai et al.⁹ combined with the hydrolysis constant of Shelinets and Stepanov⁸ (— — —).

Accurate thermodynamic data are also needed for those solid phases which are expected to be present in the wastes, have fast precipitation kinetics, are thermodynamically most stable, and can form in the geologic environment. The most stable solid phases can be chosen by comparing relative solubilities of solids based upon reliable thermodynamic data. As an example, the relative solubilities of Pu solid phases, for which thermodynamic data are available, are shown in Fig. 4. One concludes from this figure that PuO_2 is the most stable compound under oxidizing conditions and an environmental range of pH values. Similar conclusions are drawn for reducing conditions as well¹².

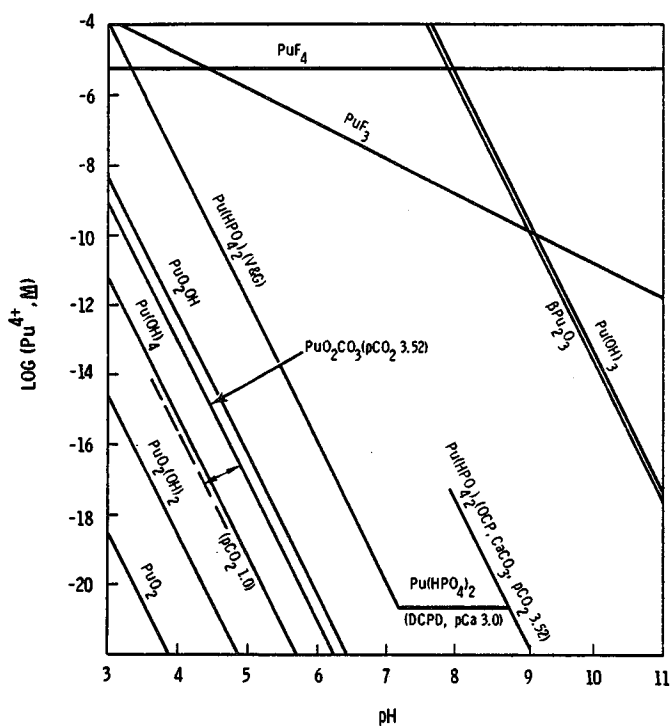


Fig. 4. Relative Stabilities of Pu Solids Under Oxidizing Conditions (from Rai and Serne¹²)

From independent information it is known that the precipitation kinetics of Pu(IV) hydrous oxide are very rapid. PuO_2 and Pu(IV) hydrous oxide, therefore, are important solid phases for which accurate data will be needed and other solid phases such as PuO_2OH , $\text{Pu}(\text{HPO}_4)_2$, and Pu_2O_3 can be ignored. Although PuO_2 is predicted to be the most stable phase of the compounds considered, and was found to be controlling Pu concentrations in Pu-contaminated sediments¹³ and Pu-doped glass¹⁴, more stable phases could form in a repository environment. The formation of such phases could further increase the safety margin.

Solubilities of selected solid phases of important actinides (U, Pu, Np, Am) in low ionic strength solutions under oxidizing conditions and pH regimes representative of most geologic environments have recently been summarized³. These results show that:

- 1) the concentrations of Pu in equilibrium with Pu contaminated sediments and Pu-doped glasses were similar to these in equilibrium with discrete PuO_2 solid,
- 2) the maximum concentrations of Np in solutions contacting Np-doped glass were similar to those in solutions contacting NpO_2 particles, and

- 3) the concentrations of Am in sediments appeared to be controlled by Am-soil solid (although the identity of Am-soil solid is not known, its solubility over a broad pH range is known)¹⁵.

It is also known that while UO_2 is the stable uranium solid under reducing conditions, $\text{UO}_2(\text{OH})_2$ has fast precipitation kinetics and under oxidizing conditions can be used to set upper limits on the uranium solubility. Using experimentally determined solubilities of these solids (PuO_2 , NpO_2 , UO_2 , $\text{UO}_2(\text{OH})_2$, Am-soil solid), which are expected to control actinide activities near the waste package, and using the available thermodynamic data to extrapolate results from oxidizing to reducing conditions, Wood and Rai³ predicted actinide concentrations in equilibrium with these selected actinide solids under assumed conditions [25°C, 1 atm, pH=7, Eh=0.29 V (oxidizing) and Eh=-0.27 V (reducing)]. Their results showed that actinide solubilities will be very low under these conditions and that the solubility controlled concentrations may be near or below maximum permissible concentrations.

The above discussion strongly affirms the fact that the solubility of radioactive solids that may be present in the wastes or form in the geologic environments can be used to defensibly predict maximum concentrations of radionuclides. The determined solubilities will be independent of the release scenarios or hydrologic properties of the repository site, and of time. Thus, long-term predictions are possible.

However, the maximum concentrations predicted so far have largely ignored two effects (heat and radiation) that will be very important in the near field. While the same approach is valid, more data are necessary before the magnitude of these effects can be properly evaluated. Limited data are available on the solubilities of actinide solids at high temperatures and under repository pH and Eh conditions. UO_2 solubility was not observed¹⁶ to increase at temperatures of up to 300°C. Similar results have been obtained from calculations based upon the thermodynamic data¹⁷ for UO_2 and U(IV) solution species.

Radiation can cause changes in both the solution composition and the nature of the solid phases. Radiolysis of dissolved N_2 in air-equilibrated suspensions of Pu compounds in dilute salt solutions was observed to produce nitric acid¹⁸. The rate of H^+ formation was observed to be proportional to the H^+ activity of the solution from approximately pH 8 to pH 3 (Fig. 5). Although the solubility of PuO_2 was observed to increase with time (Fig. 6) as a result of HNO_3 production, the Pu concentrations followed the PuO_2 solubility pattern¹³. Radiolysis can also affect the crystallinity of the solid phases. Rai and Ryan¹⁹ showed that $^{238}\text{PuO}_2(\text{c})$ becomes amorphous as a result of radiolytic effects. However, the Pu solution concentrations are still predictable if the solubility of the resulting solid phase were known, as was the case in the study of Rai and Ryan. Overall, very little information is known on the possible effects of high radiation on the pH, Eh, and resulting solid phases.

FURTHER RESEARCH NEEDS

At the outset, it may appear that even for the actinides, a herculean effort would be required for measuring all possible solid phases and complexing species. However, a rather limited number of solid phases and complexing species would provide the essential information needed on the actinide elements of primary interest under most expected geologic conditions. Careful determination of hydroxo and carbonate complexes of reduced oxidation states of Pu, Np, U is

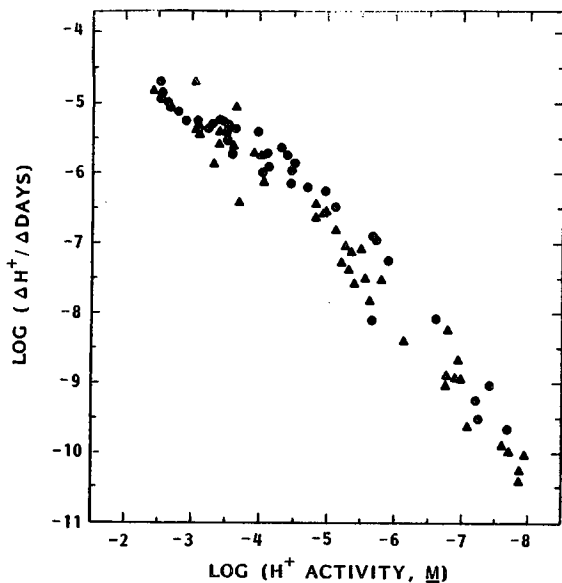


Fig. 5. Measured Rate of Change of H^+ Activity Versus Average H^+ Activity for Air-Equilibrated Solutions Contacting PuO_2 (●) or $Pu(IV)$ Hydroxide (▲) (from Rai et al.¹⁸).

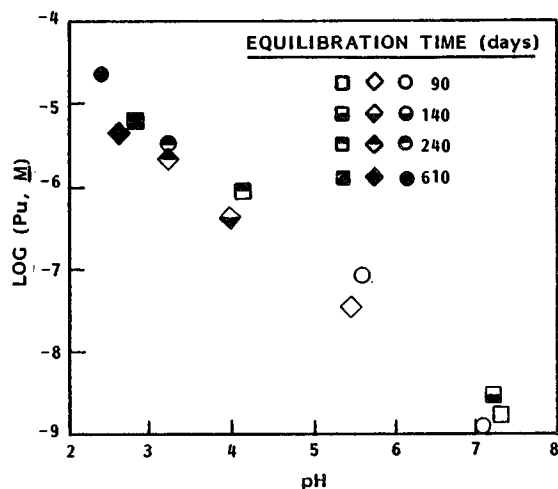


Fig. 6. The Effect of Plutonium Concentrations in Filtered (0.1 μm) Aliquots of Three, Separate PuO_2 Suspensions (Symbolized by Circles, Squares and Diamonds).

needed. Complexation constants with ligands that may be important at different repository sites also need to be measured. Although all possible actinide solid phases cannot be studied, the solubility of selected phases can be compared to the solubilities determined in solutions contacting candidate waste forms.

Especially near the waste form, higher temperatures and radiation will be important factors affecting solubility. Appropriate methods should be developed for measuring the solubility of actinide solid phases at higher temperatures and in the presence of radiolytically produced chemical species in the groundwater solution.

No single approach to the nuclear waste assessment will provide a complete panacea for all radionuclides. The solubility-control approach can provide defensible experimental data on the maximum concentration limits for those radionuclides that form

sparingly soluble solids. The preliminary results do indicate that actinides and many fission products fall into this category.

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