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PRELIMINARY CONSIDERATIONS CONCERNING ACTINIDE SOLUBILITIES

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ABSTRACT

Work at LASL on the fundamental solution chemistry of the actinides has thus far been confined to preliminary considerations of the problems involved in developing an understanding of the precipitation and dissolution behavior of actinide compounds under environmental conditions. Attempts have been made to calculate solubility as a function of Eh and pH using the appropriate thermodynamic data; results have been presented in terms of "contour maps" showing lines of constant solubility as a function of Eh and pH. Possible methods of control of the redox potential of rock-groundwater systems by the use of Eh buffers (redox couples) is presented.

INTRODUCTION

The principal practical reason for studying the near-neutral solution chemistry of the lighter actinides is to provide quantitative information for input to models being developed for prediction of the transport of these elements by groundwater. Information is needed on the oxidation states, actual species present, and maximum concentration, governed by solubility. Additional important uses for this information are the interpretation of the results of laboratory and field studies of the sorptive behavior of geologic media and the design of meaningful studies of their partioning between rock and groundwater.

DISCUSSION

During the past year work on fundamental solution chemistry pertinent to the WRIT project (Erdal 1980-1, 1980-2, 1980-3, Daniels 1980) has been initiated. Thus far, work has been confined to preliminary considerations of the problems involved in developing an understanding of the precipitation/dissolution behavior of actinide compounds under environmental conditions. For the first step in gaining this understanding the considerations have been restricted to equilibrium solubilities in the absence of complexing agents and for actinide oxides and hydrated oxides, or hydroxides.

In order to get a preliminary idea of the solubility behavior, attempts to calculate solubility as a function of Eh and pH using the appropriate thermodynamic data have been made. The solubility of a substance is the sum of the concentrations of all the species that are in equilibrium with it; for an actinide oxide or hydrous oxide these will be all the hydrolyzed forms of the usual four oxidation states (the +7 states of Np and Pu can safely be ignored). For each oxidation state the concentrations of these hydrolyzed species depend on the hydrolysis constants and the concentration of the unhydrolyzed species (see the Appendix for the relevant equations). When the solid phase is the +4 oxide or hydrous oxide, the concentration of the unhydrolyzed species (An^{+4}) is determined by the value of the solubility product and the pH. The concentrations of the other three unhydrolyzed species will depend on the Eh, the pH, and the standard oxidation potentials in accord with the Nernst equation. Thus, if the solubility products, hydrolysis constants, and oxidation potentials are available, the solubilities can be calculated in a direct way. Unfortunately, almost none of the required data have been accurately determined, so recently published estimates (Allard _et al._, 1980) have been used. The results are presented in terms of "contour maps" showing lines of constant solubility as a function of Eh and pH. Calculations have been made for the +4 oxides and hydrous oxides of uranium, neptunium, and plutonium. As an example, the results for $PuO_2 \cdot nH_2O$ are shown in Figure 1. The diagrams were constructed under the assumption that conversions of the hydrated oxides to the more stable crystalline oxides are slow compared with the establishment of the solubility equilibria. In spite of the uncertainty in the input data the results are very instructive; they show that the Eh and pH dependences are certainly quite complex. In addition, these results will be of value in planning solubility experiments and in interpreting the data.

The solubility diagram for $PuO_2 \cdot nH_2O$ (Figure 1) is divided into two regions by a solid diagonal line; below this line the solid phase is the

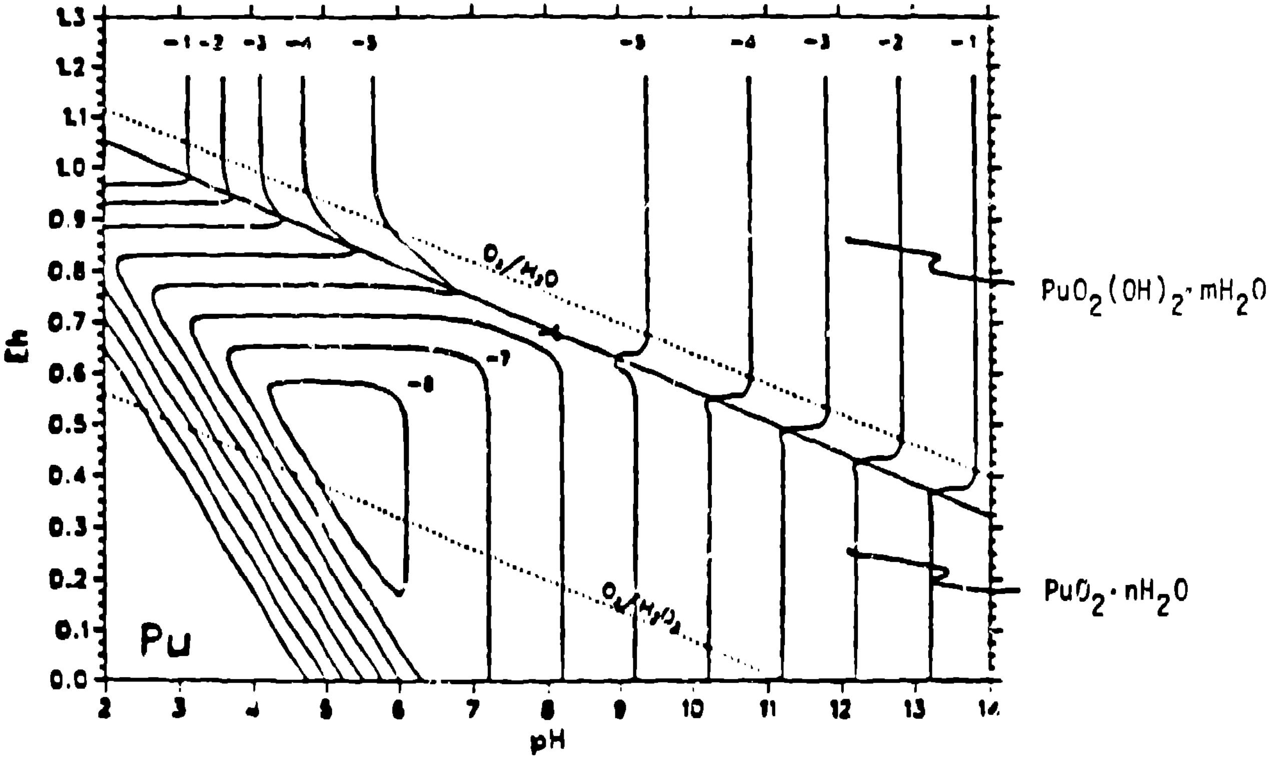

FIGURE 1. Lines of constant log(solubility) vs. Eh and pH for plutonium hydrous oxides

+4 hydrated oxide, while above the line the +6 hydroxide is stable. It is not surprising that rather abrupt changes in solubility occur when crossing this line. The upper dotted line on the diagram represents the potential of the water/oxygen couple: $2H_2O = O_2 + 4H^+ + 4e^-$; systems with apparent Eh values below this line are thermodynamically unstable in the presence of one atmosphere of oxygen. Reactions involving this couple are usually very slow, so the potential for the more rapid H_2O_2/O_2 couple, $H_2O_2 = O_2 + 2H^+ + 2e^-$, is also shown. Systems with potentials below this line are expected to react reasonably rapidly with oxygen.

The diagram shows that the calculated minimum solubility occurs at the bottom of a basin with approximately triangular contours. Three distinct principal solubility equilibria are associated with the regions showing diagonal, horizontal, and vertical contour lines, respectively. In the lower left of the diagram the contour lines show a slope of about -4 x 0.059, and the plutonium half-reaction for the principal equilibrium is

$$PuO_2 \cdot nH_2O + 4H^+ + e^- = Pu^{3+} + (2 + n)H_2O. \qquad (1)$$

Further up on the diagram where the contours are horizontal, the half-reaction is

$$PuO_2 \cdot nH_2O = PuO_2^+ + nH_2O + e^-. \qquad (2)$$

This result is consistent with the observations of Rai and coworkers at Battelle Pacific Northwest Laboratory (PNL), who showed that where Pu(V) is the principal solution species in contact with $PuO_2 \cdot nH_2O$, the solubility depends on the Eh but is essentially independent of pH. In the lower part of the diagram where the contours are vertical, the solubility is independent of Eh, and the principal equilibrium is

$$PuO_2 \cdot nH_2O + OH^- = Pu(OH)_5^- + (n - 2)H_2O. \qquad (3)$$

This analysis shows that if the input for the calculations is reasonably correct, the only parameters that contribute significantly to the solubility of $PuO_2 \cdot nH_2O$ are: (a) the solubility product, (b) the Pu^{3+}-Pu^{4+}

standard potential, (c) the Pu^{4+}-PuO_2^+ standard potential, and (d) the fifth hydrolysis constant for Pu^{4+}.

This discussion indicates that only a limited number of properly chosen experiments are required to predict the solubility of $PuO_2 \cdot nH_2O$ over the whole range of Eh and pH. Since there is a fairly reliable value for the Pu^{3+}-Pu^{4+} standard potential (Fuger and Oetting, 1976), the solubility product could be determined from a set of solubility measurements in the $3 \leq pH \leq 4$ and $0.5 \leq Eh \leq 0.6$ V range where (1) is the principal equilibrium. Careful measurements in the $3.5 \leq pH \leq 6$ range where (2) is the principal equilibrium could be used for an independent determination of the solubility product with the difficulty that the estimated uncertainty in the required potential for the Pu^{4+}-PuO_2^+ couple is quite large (Fuger and Oetting, 1976). The equilibrium constant for (3) could be determined in any convenient region with $pH \geq 7$ or 8 and $Eh \lesssim 0.5$ V.

The diagram shows that careful measurement and control of the Eh will be required for meaningful solubility determinations in regions where (1) and (2) are the principal equilibria. A good way of doing this is probably to use Eh moderators or buffers together with a potentiostat. The requirements for such a moderator for use in actinide solubility studies are:

(1) Formal potentials in the range -0.5 to 0.9 V, approximately.

(2) Stable for many days with respect to decomposition in either the oxidized or reduced forms in the pH range from about 2 to about 9.

(3) Relatively rapid redox reactions with actinide species, but no other reactions such as precipitation or complexation.

(4) Reversible redox reactions at the working electrode of a potentiostat.

Bondietti and Lee at Oak Ridge National Laboratory have used redox indicators as Eh buffers in their work on technetium. They report that Nile Blue, Thionine, and 2,6-dichloroindophenol (DCIP) at concentrations of 10^{-6} M gave Eh values in agreement with the theoretical ones within 10 to 20 mV at a pH of about 8.25. The reported potentials (Ottaway, 1972) for Thionine and DCIP are such that they might be useful for $PuO_2 \cdot nH_2O$ solubility studies in the regions where (1) and (2) are the principal equilibria, and for $NpO_2 \cdot nH_2O$ where equilibria analogous to (2) and (3) are predominant. However, DCIP probably would not be ideal for the present purposes since it is insoluble in acid solutions, unstable in strongly alkaline solutions, and decomposes slowly even in neutral solutions (Ottaway, 1972). In addition, it forms anions that might complex actinide species. Other dyes should be considered, e.g., Bindschedler's Green forms cations, shows Eh versus pH similar to that for DCIP, is useful in the $2 \leq pH \leq 9.5$ range, and shows instability only at the extremes of pH. In addition, it shows evidence for semiquinone formation, which may facilitate the one-electron steps required in the redox reactions of the actinides.

A preliminary list of possible Eh moderators is given in Table 1, together with the formal potential at pH 7 (E_m^7) and the pH range under which they can be investigated.

TABLE 1. Possible Eh Moderators

	E_m^7 (V)	pH range
Os(II) - Os(III) couples		
tris (1,10-phenonthroline)	0.88	
2,2′-bipyridine	0.88	
dicyano-bis-(2,2′-bipyridine)	0.78	
4,7-dimethylphenanthroline	0.68-0.73	
3,4,7,8-tetramethylphenanthroline	0.68-0.73	
Co(II) - Co(III) sepulchrate	-0.3	
Organic couples[a]		
Bindschedler's Green	0.224	2 - 9.5
Induline Scarlet	-0.299	3.0 - 8.6
Rosinduline 2G	-0.281	4.8 - 11.4
Lissamine Blue BF	-0.253	1 - 11
N,N′-dimethyl Viologens	-0.446[b]	8.4 - 13
Indigo Carmine	-0.125	<9[c]
Pyocyanine	-0.034	1 - 12

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[a] Data taken from Ottaway, 1972.

[b] Potentials of substituted violegens are independent of pH and follow the simple Nernst equation $Eh = E_o + \frac{RT}{F} \ell n \frac{Co}{Cr}$.

[c] Semiquinone is formed above pH 9.

Rai and Strickert (PNL) have used quinhydrone as an Eh buffer in their study of $NpO_2(c)$ solubility. Quinhydrone has an Eh-pH dependence that suggests its use in the region where (1) is the principal $PuO_2 \cdot nH_2O$ equilibrium. The rate of reaction between Pu(IV) and hydroquinone has previously been studied (Newton, 1974), so it is possible to get an idea of how well the hydroquinone-quinone couple (quinhydrone) meets requirement (3) above.

The observed (Newton, 1974) rate law in solutions with $0.2 \leq (H^+) \leq 1$ M indicates that the most important steps in the mechanism are

$$Pu^{4+} + H_2Q = Pu^{3+} + HQ\cdot + H^+ \qquad k_1 \text{ forward, } k_2 \text{ reverse}$$

and

$$Pu^{4+} + HQ\cdot = Pu^{3+} + Q + H^+ \qquad k_3 \text{ forward, } k_4 \text{ reverse,}$$

where H_2Q, $HQ\cdot$, and Q represent hydroquinone, the semiquinone radical, and quinone, respectively. The rate constants k_1 and (k_2/k_3) were measured in the experiments, and the overall equilibrium constant K is known from the potentials. The rate of approach to equilibrium for small displacements from equilibrium can be determined from these data; the half-time is estimated to be about 100 seconds for 10^{-4} M quinhydrone (see Appendix). Thus, the rate of reaction of quinhydrone with Pu^{3+} or Pu^{4+} is rapid enough to make it a satisfactory buffer for plutonium.

Inorganic couples also should be considered for use as redox buffers or moderators. Professor Henry Taube at Stanford University, who has had considerable experience with a wide variety of inorganic complexes, suggests that although many ruthenium complex couples have desirable potentials, they are probably not stable enough. Certain osmium complexes are much more stable, and Taube suggests that the II-III couples such as $Os(bipyridyl)_3$ and $Os(bipyridyl)_2(CN)_2$ should be tried.

CONCLUSIONS

The preliminary conclusions discussed here are sufficient to indicate some important experimental work that should be done. Solubility and distribution studies require control of Eh, so for this purpose various redox couples should be tested for stability and for rapidity of reaction with actinide species of trace concentrations.

APPENDIX

Solubility Calculations

The solubility, S, of an actinide oxide or hydrated oxide is given by the expression

$$S = \sum_{x=3}^{6} \left((M_x) + \sum_{ij} iK_{xij}(M_x)^i \, (OH^-)^j \right),$$

where x is the oxidation state, $M_x = An^{x+}$ for x = 3 or 4, and $M_x = AnO_2^{(x-4)+}$ for x = 5 or 6. K_{xij} are the hydrolysis constants

$$K_{xij} = \frac{((M_x)_i(OH)_j)}{(M_x)^i \, (OH^-)^j} \qquad \text{(charges omitted for clarity).}$$

K_{xs} are the solubility products, e.g., $K_{4s} = (An^{4+})(OH^-)^4$ or $\log(M_4) = \log K_{4s} - 4 \log K_w - 4\,pH$.

From the Nernst equation,

$$\begin{aligned} \log(M_5) &= (Eh - E^\circ_{45})/\alpha + \log(M_4) + 4\,pH \\ &= (Eh - E^\circ_{45})/\alpha + \log K_{4s} - 4 \log K_w, \\ \log(M_6) &= 2(Eh - E^\circ_{46})/\alpha + \log K_{4s} - 4 \log K_w, \\ \log(M_3) &= (E^\circ_{34} - Eh)/\alpha + \log K_{4s} - 4 \log K_w - 4\,pH, \end{aligned}$$

where $\alpha = (\ell n 10)RT/F = 0.05916$ V at 25°C, $K_w = (H^+)(OH^-)$, the dissociation constant for water, and the E°'s are the indicated standard potentials (for unit activity of H^+). The values for (M_x) calculated in this way are substituted into the above equation for S.

Estimate of the Half-time for Approach to Equilibrium in the Quinhydrone Pu(III-IV) SYSTEM

The equilibrium constant for the reaction is given by

$$K = \frac{(Pu^{3+})^2(Q)(H^+)^2}{(Pu^{4+})^2(H_2Q)}$$

Its value at zero ionic strength, calculated from the potentials, is 3.7 x 10^{10} M^2, within a factor of about 1.5. This uncertainty is caused by the difference in the suggested values for the Pu^{3+} - Pu^{4+} potentials (Allard et al., 1980, Fuger and Oetting, 1976). The rate constants k_1 and (k_2/k_3) were reported to be 9.6 x 10^4 $M^{-1}sec^{-1}$ and 0.24 (H^+) at 25°C and unit ionic strength (Newton, 1974). Terms k_1 and k_3 should be essentially independent of ionic strength, but it is reasonable to expect k_2 to decrease by a factor of about 8 on going from unit to zero ionic strength.

Extending a published derivation (King, 1979), it can be shown that the reciprocal of the life-time for equilibration after a small displacement form equilibrium is given by

$$\tau^{-1} = \frac{k_1(H_2Q)(4 + 4/\sqrt{K(H_2Q)/(Q)/(H^+)^2}\,)}{1 + (k_2/k_3)\sqrt{K(H_2Q)/(Q)}} \quad .$$

Substituting values that might correspond to those in a typical experiment: $(H_2Q) = (Q) = 10^{-4}M$, $(H^+) = 10^{-3}$ M, and the values given above for K, k_1, and (k_2/k_3), we find $\tau^{-1} = 6.6 \times 10^{-3}$ seconds or $t_{1/2}$ = 104 seconds. This estimate is probably good within a factor of 2 or 3.

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