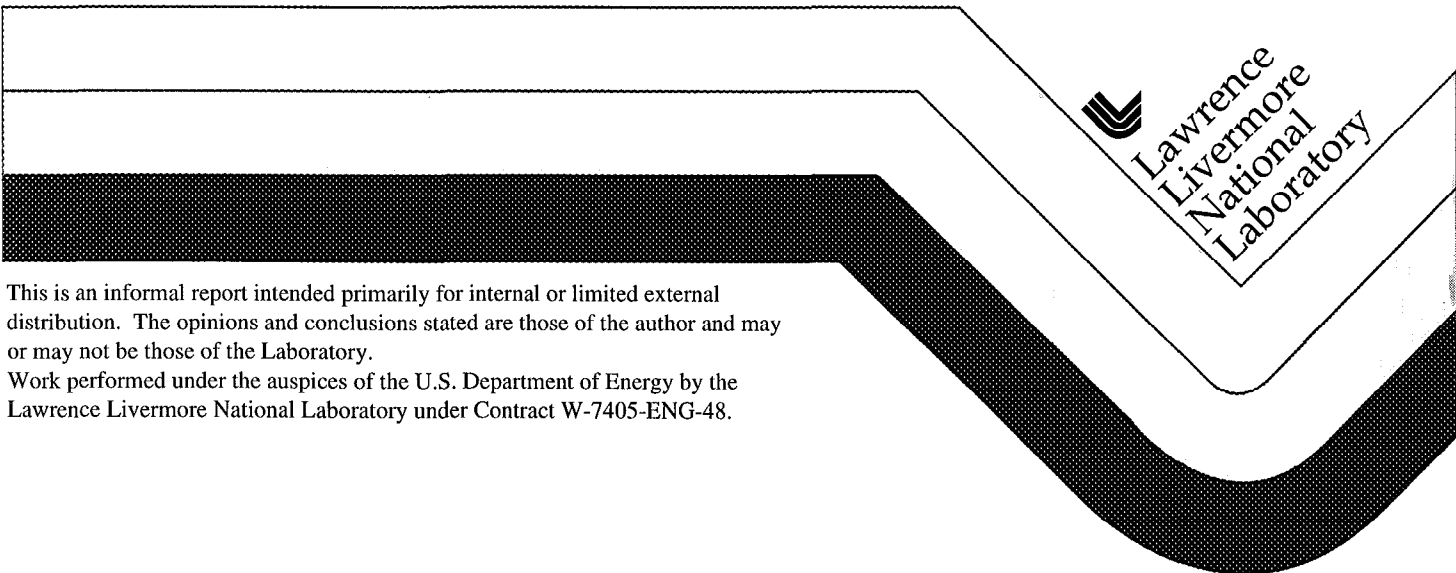


Potential for Radionuclide Immobilization in the EBS/NFE: Solubility Limiting Phases for Neptunium, Plutonium, and Uranium

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Potential for Radionuclide Immobilization in the EBS/NFE: Solubility
Limiting Phases for Neptunium, Plutonium, and Uranium

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Retardation and dispersion in the far field of radionuclides released from the engineered barrier system/near field environment (EBS/NFE) may not be sufficient to prevent regulatory limits being exceeded at the accessible environment. Hence, a greater emphasis must be placed on retardation and/or immobilization of radionuclides in the EBS/NFE. The present document represents a survey of radionuclide-bearing solid phases that could potentially form in the EBS/NFE and immobilize radionuclides released from the waste package and significantly reduce the source term. A detailed literature search was undertaken for experimental solubilities of the oxides, hydroxides, and various salts of neptunium, plutonium, and uranium in aqueous solutions as functions of pH, temperature, and the concentrations of added electrolytes. Numerous solubility studies and reviews were identified and copies of most of the articles were acquired. However, this project was only two months in duration, and copies of some the identified solubility studies could not be obtained at short notice.

The results of this survey are intended to be used to assess whether a more detailed study of identified low-solubility phase(s) is warranted, and not as a data base suitable for predicting radionuclide solubility. The results of this survey may also prove useful in a preliminary evaluation of the efficacy of incorporating chemical additives to the EBS/NFE that will enhance radionuclide immobilization.

1. Neptunium

Speciation diagram calculations [Allard, Kipatsi, and Liljezin, 1980; Eriksen, Ndalamba, et al., 1993; Kim, 1986; Martinot, 1978; Rees, 1985] using then available thermodynamic data bases indicate that dissolved species of Np(III), Np(IV), Np(V), Np(VI), and Np(VII) can form in aqueous solutions. However, Np(III) can exist only under very reducing conditions and at acidic pHs, and it is unlikely to be present in significant amounts under environmental conditions. Similarly, Np(VI), which is present as the $\text{NpO}_2^{2+}(\text{aq})$ ion and its various hydrolyzed and complexed species in aqueous solutions, and Np(VII), which may exist as $\text{NpO}_3^+(\text{aq})$ {and possibly as $\text{NpO}_5^{3-}(\text{aq})$ in concentrated sodium hydroxide [Martinot, 1978]}, occur only under oxidizing conditions. Above a pH of 8 or 9 the formation of $\text{NpO}_2^{2+}(\text{aq})$ ion is more favored, especially when carbonate is present [Newton and Sullivan, 1985]. The formal potential of the $\text{NpO}_3^+(\text{aq})/\text{NpO}_2^{2+}(\text{aq})$ redox couple in 1 molar acid occurs around 2.0 V [Martinot, 1978; Martinot and Fuger, 1985], which is above the water stability field and thus Np(VII) will be reduced by water. Some solubility studies are available for Np(VI) [Kato, Kimura, et al., 1996; Moskvina, 1971; Novak, Nitsche, et al., 1996] but the conditions required to prepare these solutions, i.e., oxidation with ozone [Kato, Kimura, et al., 1996] or electrochemical oxidation [Novak, Nitsche, et al., 1996], indicate that Np(VI) species will also not form in significant amounts for aqueous solutions at equilibrium under environmental conditions.

Published speciation calculations using available thermodynamic data bases indicate that aqueous solutions and solid compounds of Np(V) will be present under most typical environmental conditions, and that Np(IV) will be more important under fairly reducing conditions especially at low values of the pH [Allard, Kipatsi, and Liljezin, 1980; Eriksen, Ndalamba, et al., 1993; Kim, 1986; Martinot, 1978]. Long-term solubility studies seem to confirm this conclusion. For example, solutions of Np(V) at pH = 6 and at 8.5 with an atmosphere of Ar-CO₂ mixtures, equilibrated at 298 and 333 K with solid crystalline phase(s) of uncertain composition, contained 100 % Np(V) in the solution phase at equilibrium [Nitsche, 1987]. Similar solubility experiments with solutions initially containing Np(IV) and Np(V), but involving an atmosphere of CO₂-free Ar and 5.3 molar NaCl, were performed for periods ranging up to 2500 days [Silber, Nitsche, et al., 1994] yielded solubilities at

alkaline pHs that were converging at long equilibration times. According to the authors, this probably indicates that radiolysis products in the Np(IV) solutions are gradually converting the solutions of Np(IV) to Np(V). In moderately to very concentrated high-chloride synthetic brines [Novak, Nitsche, et al., 1996] at nearly neutral pH, electrolytically-generated solutions of Np(VI) underwent < 7 % reduction to Np(V) but still contained mainly Np(VI) even after solubility experiments lasting 734 days. These solutions were maintained in an atmosphere of Ar-O₂-CO₂ mixtures containing about 21 % O₂(g). The solid phase observed at the end of these solubility experiments was KNpO₂CO₃·xH₂O(s) which contains Np(V). However, in that same study and under similar experimental conditions, solutions of Np(V) equilibrated with a solid phase of KNpO₂CO₃·xH₂O(s) contained only Np(V) in the solution phase after equilibrations ranging from 543 to 763 days, which implies that Np(V) is not oxidized to Np(VI) in these oxygen-saturated solutions. The conclusion of Andersson [Andersson, 1989] that Np(OH)₄(s) is the solubility limiting phase under both oxidizing and reducing conditions probably resulted from use of an incomplete thermodynamic data base.

The studies described in the preceding paragraph imply that aqueous solutions, initially containing Np(IV) and Np(V), will contain predominantly or entirely Np(V) after long-term equilibrations with hydrous oxides or neptunium carbonate phases when these equilibrations are performed in an essentially oxygen-free non-reducing atmosphere or with an oxygen-rich oxidizing atmosphere. There is no observed significant oxidation of Np(V) to Np(VI), but if Np(VI) is generated by electrolytic or chemical oxidation, it can persist for long periods in the presence of oxygen or ozone.

Solubility studies have been performed for the hydrous oxide of Np(IV), which we shall write as NpO₂·xH₂O(s). References for these solubility studies are [Eriksen, Ndalamba, et al., 1993; Ewart, 1985; Krupka, Rai, et al., 1985; Moskvina, 1971b; Nakayama, Yamaguchi, and Sekine, 1996; Pratopo, Moriyama, and Higashi, 1990; Rai and Ryan, 1985; Rai, Swanson, and Ryan, 1987]. Neptunium was maintained as Np(IV) by addition of strong reducing agents to the solution, or by equilibrating them against a solid reducing agent. For example, Eriksen, Ndalamba, et al. [1993] used the aqueous redox buffers S₂O₄²⁻/SO₃²⁻ and S₄O₆²⁻/S₂O₃²⁻, Moskvina [1971b] used hydrazine nitrate, Nakayama, Yamaguchi, and Sekine [1996] used copper metal or Na₂S₂O₄ (i.e., the S₂O₄²⁻/SO₃²⁻ redox buffer), Pratopo, Moriyama, and Higashi [1990] used

hydrazine chloride, and Rai and co-workers [Krupka, Rai, et al., 1985; Rai and Ryan, 1985] used $\text{Na}_2\text{S}_2\text{O}_4$, metallic iron, or metallic zinc. All of the above reducing agents were quite effective in maintaining neptunium as Np(IV). However, Rai and Ryan [1985] found that metallic lead and metallic nickel were not sufficiently strong reducing agents to perform this reduction, and Rai, Swanson, and Ryan [1987] found that the Cu(I)/Cu(II) redox buffer yielded a mixture of Np(IV) and Np(V) at equilibrium. Any reducing agent or redox buffer that produces solutions with $E_h < -0.3$ V should be satisfactory for keeping Np present in the +4 valence state.

Solubilities of $\text{NpO}_2\text{OH}(s)$ have been reported as a function of pH in several studies [Moskvin, 1971b; Roberts, Silber, et al., 1996; Sevost'yanova and Khalturin, 1976; Silber, Nitsche, et al., 1994]. No reducing agents or redox buffers were added to these solutions to control the oxidation of the neptunium during the solubility experiments. These solutions are slow to reach equilibrium at alkaline pHs, presumably due to slow hydrolysis reactions in the aqueous phase [Silber, Nitsche, et al., 1994]. Long term solubility experiments [Roberts, Silber, et al., 1996; Silber, Nitsche, et al., 1994] indicate an equilibrium or steady state concentration of Np(V) of about 10^{-6} to 10^{-5} molar for pH = 9 to 13 and about 10^{-2} molar at pH = 7.

A much greater number of studies have been performed of the solubility of Np(V) in the presence of carbonate [Lemire, Boyer, and Campbell, 1993; Marx and Keiling, 1989; Maya, 1983; Neck, Runde, et al., 1994; Nitsche, 1987; Nitsche, 1991; Novak, Nitsche, et al., 1996; Simakin, 1977; Ueno and Sato, 1975; Visyashcheva, Volkov, et al., 1974]. No reducing agents or redox buffers were added to these solutions to control the oxidation state of the neptunium during the solubility experiments. At low carbonate concentrations the solid phase remains $\text{NpO}_2\text{OH}(s)$, but at high carbonate concentrations solid phases such as $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(s)$ [Lemire, Boyer, and Campbell, 1993; Maya, 1983; Neck, Runde, et al., 1994; Ueno and Sato, 1975], $\text{KNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(s)$ [Novak, Nitsche, et al., 1996], $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(s)$ [Lemire, Boyer, and Campbell, 1993; Simakin, 1977] and $\text{K}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(s)$ [Visyashcheva, Volkov, et al., 1974] were formed. A variety of mixed oxy- or hydroxycarbonate complexes of neptunium form in these saturated solutions, and their stability constants have been summarized in several reviews [Clark, Hobart, and Neu, 1995; Kim, 1986; Neck, Runde, et al., 1994; Newton and Sullivan, 1985]. Addition of carbonate at concentrations of up to about 10^{-4} molar cause the solubility of

Np(V) to decrease to a minimum solubility, but at higher carbonate concentrations there is a rapid increase in solubility with increasing carbonate concentration [Lemire, Boyer, and Campbell, 1993; Maya, 1983; Neck, Runde, et al., 1994; Ueno and Sato, 1975]. These solubility changes with carbonate concentration are due to changes in aqueous speciation and the switch over in the equilibrium solid phase from $\text{NpO}_2\text{OH}(\text{s})$ to other phases such as $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$. Minimum solubilities are also observed at pHs around 7 at high electrolyte concentrations [Neck, Runde, et al., 1994].

The solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ in carbonate-free water or at very low carbonate concentrations in the presence of reducing agents is about 10^{-8} molar and is independent of pH from about pH = 6 to 13 [Eriksen, Ndalamba, et al., 1993; Ewart, 1985; Krupka, Rai, et al., 1985; Nakayama, Yamaguchi, and Sekine, 1996; Rai and Ryan, 1985]. However, the solubility is much higher at lower pHs: 1.2×10^{-2} at pH = 3.00 to 4.2×10^{-2} at pH = 1.20 [Moskvin, 1971]. Carbonate complexes in neutral to alkaline solutions increase the solubility of $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ by one to two orders of magnitude [Eriksen, Ndalamba, et al., 1993; Pratopo, Moriyama, and Higashi, 1990], depending on pH and carbonate concentration, owing to the formation of mixed hydroxycarbonate complexes.

There are very few studies that report solubilities for solutions of Np(VI). Solubilities of "neptunyl hydroxide" were reported that range from 2.3×10^{-2} to 6.3×10^{-4} molar over the pH range of 3.5 to 8.5 [Moskvin, 1971] and of $\text{NpO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ were reported graphically to be about 10^{-2} to 10^{-3} molar from pH \approx 4.2 to 4.5 at low carbonate concentrations [Kato, Kimura, et al., 1996]. Solubilities of Np(VI) in the presence of the solid phase $\text{KNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$, formed by partial reduction of Np(VI), were from 3.2×10^{-4} to 8.3×10^{-4} molar for pHs of 7.1 to 7.5 in high-chloride concentrated brines containing carbonate [Novak, Nitsche, et al., 1996]. In the presence of an atmosphere of 80 % CO_2 /20 % O_2 , $\text{NpO}_2\text{CO}_2(\text{s})$ was observed to be the solubility limiting phase [Kato, Kimura, 1996]. These solubilities are about 4 to 6 orders of magnitude larger than those of Np(IV) under comparable conditions.

No solubilities were located for neptunium silicates. However, based on analogies with uranyl silicates [Moll, Geipel., et al., 1996; Nguyen, Silva, et al., 1992; Puidgomènech and Bruno, 1988] we expect $(\text{NpO}_2)_2\text{SiO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ to be comparable in solubility to $\text{NpO}_3 \cdot x\text{H}_2\text{O}(\text{s})$. Andersson [Andersson, 1989] cited values for the solubility product of $\text{NpO}_2(\text{HPO}_4)(\text{s})$, $K = 10^{-13}$, and of $(\text{NpO}_2)_3(\text{PO}_4)(\text{s})$, $K = 10^{-50}$. It is likely that the second formula is a misprint for

$(\text{NpO}_2)_3(\text{PO}_4)_2(\text{s})$, in which case these solubility products for the plutonium phosphates are nearly identical to those given for their uranium analogues. These solubility products for the neptunyl phosphates may simply be estimates based on the uranyl phosphate data. The first solubility product indicates that $\text{NpO}_2(\text{HPO}_4)(\text{s})$ should be quite soluble. Stability constants [Patil, Ramakrishna, and Ramaniah, 1978; Moskvina and Peretrukhin, 1964] and Gibbs energies of formation [Lemire and Garisto, 1989] have been reported for various HPO_4^{2-} and H_2PO_4^- complexes of neptunium, and indicate that the presence of these complexes should considerably enhance the solubility of neptunium.

Examination of the solubility and redox information summarized in the preceding paragraphs indicates that minimum solubilities for neptunium are favored by $\text{pH} \approx 6$ to 13, by very low carbonate concentrations, and by reducing conditions with $\text{Eh} < -0.3$ V. Less reducing conditions and acidic pHs favor increased solubility, as do alkaline conditions when high concentrations of carbonate are present.

It is suggested that two of the three conditions for lower solubilities of neptunium in a repository can be met by adding materials that compete for carbonate from infiltrating groundwater, by forming sparingly soluble carbonate precipitates, and which increase the alkalinity. One possibility is to add mixtures of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4) and lime (CaO). These would raise the pH into a favorable range as these materials dissolve, and would provide sources of calcium ions to precipitate most of the dissolved carbonate/bicarbonate as calcite (CaCO_3). Jackson [Jackson, 1996] has proposed the use of MgO (periclase) for a similar function. The calcium sources could also give precipitation of hydroxy apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, or calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, to help sequester the phosphate from the groundwater. Solubilities of Np(IV) of about 10^{-8} molar and lower have been observed in cement-equilibrated waters, which indicates that this alkaline system would also be satisfactory for controlling pH [Ewart, Gore, and Williams, 1985; Ewart, Howse, et al., 1986].

Reducing conditions with $\text{Eh} < -0.3$ V are even more critical for lowering the solubility of neptunium by formation of Np(IV) solutions and solid phases. Some of the methods described above for reducing the dissolved Np(V) to Np(IV) and keeping it in that valence state involved use of hydrazine or the $\text{S}_2\text{O}_4^{2-}/\text{SO}_3^{2-}$ and $\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}$ redox buffers. It would be very

difficult to control the concentrations of these chemical species for long periods of time (and thus the Eh of these solutions) in a repository situation due to their high solubilities in water and the complicated chemistry of the sulfur-oxygen-water system with its numerous redox couples. Use of one of the metal powders described above (Fe, Zn, or Cu), added in large excess to the backfill material, could produce the desired highly reducing conditions. Corrosion of the waste canister overpack would also contribute to the desired reducing environment close to the waste canister. However, generation of $H_2(g)$ upon overpack or metal powder dissolution at acidic or alkaline pHs could be a problem in certain waste repository configurations. Another possibility would be to make use of the I^-/I_3^- redox buffer for which $E \approx -0.5$ V; this would avoid problems with gas generation since this involves a pH-independent redox reaction. A sparingly soluble salt such as CuI might make a suitable additive for slow release of iodide, although considerable amounts may be required to maintain reducing conditions for long periods of time.

2. Plutonium

Speciation diagram calculations [Allard, Kipatsi, and Liljezin, 1980; 1993 Kim, 1986; Martinot, 1978; Puigdomènech and Bruno, 1991; Rai, Serne, and Swanson, 1980; Yamaguchi, Sakamoto, and Ohnuki, 1994] using then available thermodynamic data bases indicate that dissolved species of Pu(III), Pu(IV), Pu(V), and Pu(VI) can form in aqueous solutions. All of these valence states can occur in the Eh, pH range of natural waters [Kim, 1986] and thus solutions of all of these ions are important for controlling solubilities. The valence state Pu(VII) is also known in aqueous solution, but it forms only under very oxidizing conditions [Delegard, 1987, Martinot and Fuger, 1985] and is reduced by water to Pu(VI).

Long-term solubility studies are consistent with this conclusion. Nitsche [Nitsche, 1987] found that for solutions equilibrated at pH = 6 with a precipitated solid phase, Pu(V) predominated at "equilibrium" with slightly smaller amounts of Pu(VI) being present, but at pH = 8.5 Pu(IV) predominated over Pu(V) in the solutions. These experiments were done at 298 and 333 K with 120 ppm carbonate in the solutions, and the solid phase was reported to be $PuO_2 \cdot xH_2O(s)$ or a Pu(IV) colloid. In "J-13" groundwater [Nitsche, 1991], solutions equilibrated for lengthy periods at 298, 333, and 363 K yielded solid phases of "polymeric Pu(IV) and plutonium carbonates." The

solution phases contained predominantly Pu(V), with major amounts of Pu(VI) and lesser amounts of Pu(III) and Pu(IV). Solutions equilibrated with a solid phase of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ at $295 \pm 2 \text{ K}$ [Rai, 1984] were analyzed after being equilibrated for 5 days and after 83 days. After 5 days, Pu(III) + Pu(IV) predominated for $0.55 \leq \text{pH} \leq 1.20$ but for $1.50 \leq \text{pH} \leq 4.30$ Pu(V) + Pu(VI) were the predominant valence states. For the 83 day equilibration, Pu(IV), Pu(V), and Pu(VI) were detected at most pHs. For $0.50 \leq \text{pH} \leq 1.00$ Pu(IV) predominated, for $1.20 \leq \text{pH} \leq 2.00$ Pu(V) predominated, but for $2.30 \leq \text{pH} \leq 3.40$ Pu(V) and Pu(VI) were present in comparable amounts. At higher pHs of $3.70 \leq \text{pH} \leq 4.90$, Pu(V) predominated over Pu(IV) but the amount present as Pu(VI) was not determined. Solubility experiments for $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in 1 molar $\text{HClO}_4(\text{aq})$ at $293 \pm 1 \text{ K}$ contained mainly Pu(IV) colloid and monomer after 45 days, along with small amounts of Pu(VI) [Kim and Kanellakopoulos, 1989]. In that same study solutions equilibrated with $\text{PuO}_2(\text{cr})$ contained mainly Pu(III) with lesser amounts of monomeric Pu(IV) and a trace of Pu(VI).

Solubility experiments were also done with "H-17" brine [Nitsche, Roberts, et al., 1994], which is a predominantly a NaCl brine with $\text{pH} \approx 7.1$. In these experiments, the plutonium was added to separate samples of the brine as Pu(III), as monomeric Pu(IV), as polymeric Pu(IV), as Pu(V), or as Pu(VI). The solutions were saturated with a gas mixture containing $\text{Ar-O}_2\text{-CO}_2$. The various saturated solutions equilibrated in contact with the precipitated solid phase(s) for 328 to 342 days contained from 69 to 96 % Pu(VI), from 2 to 27 % Pu(V), small amounts of monomeric Pu(IV), and very small amounts of Pu(III) and polymeric Pu(IV). The solid phases formed in contact with the solutions that were prepared from Pu(III) and monomeric Pu(IV) were crystalline but were not identified, whereas the solid phase that formed when Pu(V) or Pu(VI) were used to prepare the initial solution was probably $\text{NaPuO}_2\text{CO}_3(\text{s})$. Solubility experiments were reported [Felmy, Rai, et al., 1989] in which the solid phase was controlled to be $\text{Pu}(\text{OH})_3(\text{s})$ by addition of iron powder. This is the only one of the cited solubility studies for plutonium in which a reducing agent was used to control the valence of plutonium. These experiments were performed in an atmosphere of purified argon in solutions of distilled water and two types of brines. Values of Eh for these solutions ranged from -0.25 to -0.37 V . The pHs were adjusted by use of HCl and carbonate-free NaOH. Solubilities were consistently higher in the brines than

in the distilled water. The solubility of $\text{Pu}(\text{OH})_3(\text{s})$ was $\leq 1 \times 10^{-9}$ molar for $\text{pH} \approx 9$ to 13, but increased rapidly at lower pHs, reaching a value of about 1×10^{-4} molar at $\text{pH} = 7$ in distilled water.

Rai and Ryan [Rai and Ryan, 1982] studied the solubilities of $^{238}\text{PuO}_2(\text{cr})$, of $^{239}\text{PuO}_2(\text{cr})$, and of $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in aqueous solutions for up to 1300 days. The solubilities of the two materials containing ^{239}Pu seemed to approach each other after long equilibrations, which indicated that the crystalline material slowly converted (because of reaction with the radiolysis products of water) to a less-crystalline or amorphous material. In contrast, the $^{238}\text{PuO}_2(\text{cr})$ was converted into a colloidal hydrous oxide. The solubility of the polymeric Pu(IV) is intermediate between that of $\text{PuO}_2(\text{cr})$ and $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ [Puigdomènech and Bruno, 1991].

Clearly, in the absence of a redox potential control, solutions of plutonium in equilibrium with a solid plutonium hydrous oxide or carbonate phase will exist as mixture of various valence states, whose proportions will change with time, pH, and carbonate concentration. Crystalline $\text{PuO}_2(\text{cr})$ evolves into $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ due to radiolytic effects, which is in opposition to the Ostwald step rule [Rard, 1989] which predicts changes from an amorphous to a crystalline material.

Owing to difficulties described above, it is quite difficult to interpret some of the published solubility studies. These difficulties include the multiplicity of valence states of plutonium present in its saturated aqueous solutions, the fact that equilibrium is not achieved in many cases even after allowing considerable time for the saturated solutions to equilibrate with the solid phase, the incomplete characterization of solid phases in contact with saturated solutions, the formation of colloids under certain conditions, and the effect of radiolysis on the crystallinity of solid phases. The following discussion is based mainly on the critical analysis of solubility by Puigdomènech and Bruno [Puigdomènech and Bruno, 1991] who compared some of the solubility data graphically. However, a few other experimental studies are also described.

Weigel et al. [Weigel, Katz, and Seaborg, 1986] have summarized solubility data (presumably at "room temperature") for a number of plutonium salts, mostly salts and double salts containing Pu(IV). However, a few salts of Pu(VI), Pu(V), and Pu(III) were included, as were a few solubility studies for " $\text{Pu}(\text{OH})_3 \cdot x\text{H}_2\text{O}(\text{s})$ " and " $\text{Pu}(\text{OH})_4 \cdot x\text{H}_2\text{O}(\text{s})$." These were not critically assessed

values, but are useful for qualitative comparisons. By far the most soluble plutonium salts were salts containing Pu(VI): $\text{PuO}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ in dilute HCl and $\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in HNO_3 , followed by $\text{Pu}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ in 0.1 molar H_2SO_4 . The double salt $(\text{NH}_4)_4\text{Pu}(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$ is also quite soluble [Anderson, 1949]. However, the solubility of $\text{Pu}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ is reduced considerably in the presence of fluoride salts [Deichman and Tananaev, 1962]. Plutonium(IV) hydroxynitrates have also been reported to be very soluble at $\text{pH} < 2$ [Schmidt, Andryushin, et al., 1981]. The least soluble plutonium compounds considered by Weigel et al. were " $\text{Pu}(\text{OH})_4 \cdot x\text{H}_2\text{O}(\text{s})$ " and Pu(IV) peroxides in concentrated acidic aqueous hydrogen peroxide.

A number of studies report solubilities of various oxides, hydroxides, and hydrous oxides of plutonium in the absence of carbonate, phosphate, or other strongly complexing ligands [Davydov, 1967; Moskvina and Zaitseva, 1962; Felmy, Rai, et al., 1989; Kim and Kanellakopoulos, 1989; Musante and Porthaulte, 1973; Pérez-Bustamante, 1965; Rai, 1984; Rai and Ryan, 1982; Rai, Serne, and Swanson, 1980] and a few other studies have been cited by Puigdomènech and Bruno [Puigdomènech and Bruno, 1991]. The assessed solubilities of Puigdomènech and Bruno indicate that $\text{PuO}_2(\text{OH})_2(\text{cr})$ has a minimum solubility of about 10^{-8} molar at pH around 10 to 11, but becomes more soluble as the pH decreases, ca. 10^{-2} molar at low pHs. The assessed solubilities of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ have a minimum of about 10^{-10} to 10^{-9} molar for pHs of about 8 to 12. $\text{Pu}(\text{OH})_3(\text{s})$ has a minimum solubility of $\leq 1 \times 10^{-9}$ molar for $\text{pH} \approx 9$ to 13, but it increases rapidly at lower pHs, reaching a value of about 1×10^{-4} molar at $\text{pH} = 7$ [Felmy, Rai, et al., 1989]. Crystalline PuO_2 is expected to have lower solubilities than $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$, but radiolysis products gradually convert it into the more soluble $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ [Rai and Ryan, 1982].

Numerous studies have been performed of plutonium solubilities in carbonate solutions, e.g., see references [Gel'man, Moskvina, and Zaitseva, 1962; Nitsche, 1987; Nitsche, Roberts, et al., 1994; Pashalidis, Runde, and Kim, 1993; Robuch and Vitorge, 1987; Yamaguchi, Sakamoto, and Ohnuki, 1994] and additional studies cited by Puigdomènech and Bruno [Puigdomènech and Bruno, 1991] and [Clark, Hobart, and Neu, 1995]. Critically assessed stability constants of the plutonium carbonates and hydroxy carbonates have been reported [Clark, Hobart, and Neu, 1995; Kim, 1986; Newton and Sullivan, 1985]. Solubilities of $\text{PuO}_2(\text{cr})$ and $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in solutions containing

carbonate have a minimum solubility of about 10^{-8} molar from about $7.5 \leq \text{pH} \leq 9.6$ but the solubilities increase considerably at higher and lower pHs. The solubility of Pu(VI) in carbonate solutions reaches a minimum of about 2.5×10^{-5} molar for carbonate concentrations of about 10^{-8} to 3×10^{-6} molar, but is considerably higher at higher and lower carbonate concentrations because of changes in the aqueous complexes and changes in the solid phase. These solid phases include $\text{PuO}_2\text{CO}_3(\text{s})$ [Pashalidis, Runde, and Kim, 1993; Robuch and Vitorge, 1987], possibly $\text{NaPuO}_2\text{CO}_3(\text{s})$ [Nitsche, Roberts, et al., 1994], and $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3(\text{s})$ [Gel'man, Moskvina, and Zaitseva, 1962].

Solubilities of Pu(IV) in phosphoric acid and acidic phosphate solutions [Denotkina and Shevchenko, 1967a, 1967b; Denotkina, Moskvina, and Shevchenko, 1960; King, 1949; Moskvina, 1971a; Puigdomènech and Bruno, 1991] have been reported. The assessment of Puigdomènech and Bruno indicates that $\text{PuPO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ has a minimum solubility of about 10^{-5} molar for $\text{pH} > 3.5$, $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ has solubilities of about 10^{-4} to 10^{-3} molar for wide ranges of concentration of added acid, and that $\text{PuO}_2(\text{HPO}_4) \cdot 4\text{H}_2\text{O}(\text{s})$ has a solubility of about 2×10^{-5} molar in water but which increases to about 10^{-3} molar in excess $\text{H}_3\text{PO}_4(\text{aq})$. Stability constants for the HPO_4^{2-} and H_2PO_4^- complexes of plutonium have been tabulated [Andersson, 1989; Lemire and Tremaine, 1980] as have Gibbs energies of formation of these complexes [Lemire and Garisto, 1989].

No solubilities were located for plutonium silicates. However, based on analogies with uranyl silicates [Moll, Geipel., et al., 1996; Nguyen, Silva, et al., 1992; Puigdomènech and Bruno, 1988] we expect $(\text{PuO}_2)_2\text{SiO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ to be comparable in solubility to $\text{PuO}_2(\text{OH})_2(\text{s})$.

Examination of the solubility and redox information summarized in the preceding paragraphs indicates that minimum solubilities for plutonium are favored by $\text{pH} \approx 8$ or 9 to 13, by very low carbonate concentrations, by very low concentrations of phosphate (especially when the solutions are acidic), and by slightly reducing conditions. Oxidizing conditions and acidic pHs favor increased solubility, as do alkaline conditions when high concentrations of carbonate are present.

It was suggested in the discussion for neptunium that two of the three conditions needed to lower solubilities could be met by adding materials that compete for carbonate and phosphate from infiltrating groundwater, by forming sparingly soluble carbonate and phosphate precipitates, and which

increase the alkalinity. A suggested possibility was to add mixtures of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4) and lime (CaO) to raise the pH into a favorable range as these materials dissolve, and which would provide sources of calcium ions to precipitate most of the dissolved carbonate/bicarbonate as calcite (CaCO_3). Precipitation of hydroxy apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, or calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, would help to sequester the phosphate. Thus the suggested additives would also be beneficial for reducing the solubility of plutonium. Use of MgO (periclase) may also be satisfactory [Jackson, 1996]. Solubilities of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ of about 10^{-10} molar have been observed in cement-equilibrated waters [Ewart, House, et al., 1986], which indicates that this system would also be satisfactory.

The solubility data discussed above indicate that $\text{PuO}_2(\text{OH})_2(\text{cr})$ and other Pu(VI) compounds should be avoided as the solid phase since they are more soluble than the oxides, hydroxides, and hydrous oxides of Pu(IV) and Pu(III). $\text{PuO}_2(\text{cr})$ is probably the least soluble of all of these compounds, but available evidence suggests that radiolysis products will convert it to poorly crystalline or amorphous $\text{PuO}_2(\text{s})$ or $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$. These other two Pu(IV) materials have solubilities similar to those of $\text{Pu}(\text{OH})_3(\text{s})$, and any of them should be about equally satisfactory for reducing the solubility of plutonium. Reducing conditions with $E_h < -0.2$ V should be adequate for maintaining $\text{Pu}(\text{OH})_3(\text{s})$ as the solid phase. Using the Γ/Γ_3 redox buffer or certain metal powders, as suggested for neptunium, should be more than adequate to form and preserve $\text{Pu}(\text{OH})_3(\text{s})$. A sparingly soluble salt such as CuI might make a suitable additive for slow release of iodide. Corrosion of the overpack would also contribute to the desired reducing environment close to the waste canister.

3. Uranium

Speciation diagram calculations [Allard, Kipatsi, and Liljezin, 1980; Grenthe, Fuger, et al., 1992; Langmuir, 1978; Lemire and Garisto, 1989; Martinot, 1978] and potential diagrams [Martinot and Fuger, 1985] using available thermodynamic data bases indicate that dissolved species of U(III), U(IV), U(V), and U(VI) can be present in aqueous solutions. However, U(III) can form only under extremely reducing conditions and at acidic pHs, and its standard reduction potential of $E^\circ = -0.55$ V [Grenthe, Fuger, et al., 1992] indicates that it will readily reduce water. Thus it is absent under

environmental conditions. The dominant valence state of uranium in water under oxidizing conditions is U(VI) in the form of the uranyl ion $\text{UO}_2^{2+}(\text{aq})$ and its various hydrolyzed forms and complexes. The standard potential for the reduction of $\text{UO}_2^{2+}(\text{aq})$ to $\text{U}^{4+}(\text{aq})$, $E^\circ = 0.27 \text{ V}$ [Grenthe, Fuger, et al., 1992] indicates that U(IV) will be important in deoxygenated systems and under reducing conditions. Electrolytic reduction of $\text{UO}_2^{2+}(\text{aq})$ yields $\text{UO}_2^+(\text{aq})$, but U(V) species predominate over U(IV) and U(VI) species only over very narrow conditions of pH and Eh. Thus, for most practical purposes, the aqueous chemistry of uranium is dominated by U(VI) and U(IV).

In this section a large number of aqueous studies for uranium compounds and salts are described. The published literature for uranium is so extensive that many more references could have been included. However, many of these have been included in the recent Nuclear Energy Agency (NEA) review of uranium thermodynamics [Grenthe, Fuger, et al., 1992], and solubilities of uranium oxides, hydroxides, and carbonates were reviewed in an SKB report [Puigdomènech and Bruno, 1988; also see Bruno and Puigdomènech, 1989]. Extensive listings of older solubility data can be found in the book by Linke [Linke, W. F., 1965]. These three reviews should be used as sources for references to numerous additional solubility studies. Gibbs energies of formation of various solid compounds, aqueous ions, and complexes of uranium have been reviewed critically [Grenthe, Fuger, et al., 1992; Langmuir, 1978; Lemire and Tremain, 1980]. Langmuir [Langmuir, 1978] discussed the uranium solution solid equilibria relevant to the formation of sedimentary ore deposits.

Many of the uranyl salts with common inorganic anions are extremely soluble. For example, the solubility of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$ is 3.21 molal at 298 K and 6.17 molal at 328 K [Cohen-Adad, Lorimer, et al., 1995]. The solubility of $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$ is about 4 molal at 298 K and about 7 molal at 425 K [Secoy, 1948]. Above about 594 K two separate liquid phases are observed [Secoy, 1950]. The uranyl halides are also quite soluble, especially $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ [Linke, 1965], as is $\text{UO}_2(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ [Goldberg, 1979].

Uranium(VI) can form a variety of anhydrous and hydrated oxides. The oxide $\text{UO}_3(\text{s})$ can exist in at least five different crystalline forms, denoted as α , β , γ , δ , and ϵ , along with an amorphous material. The hydrated oxides include $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, two or three forms of $\text{UO}_3 \cdot \text{H}_2\text{O}(\text{cr})$, some substoichiometric hydrates of the type $\text{UO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ where $x = 0.8$ or 0.9 , and a lower hydrate

sometimes claimed to be $\text{UO}_3 \cdot 0.5\text{H}_2\text{O}(\text{s})$. This $\beta\text{-UO}_3 \cdot \text{H}_2\text{O}(\text{cr})$ is also frequently written as $\beta\text{-UO}_2(\text{OH})_2(\text{cr})$. See the discussions in the NEA thermodynamic review [Grenthe, Fuger, et al., 1992] and the article by O'Hare et al. [O'Hare, Lewis, and Nguyen, 1988]. The mineral schoepite, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{cr})$ or $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, widely known in geological situations, is believed to form during the weathering of uraninite (UO_2) under oxidizing conditions. It has also been observed to form in long-term leaching studies of spent nuclear fuel under oxidizing conditions [Bruno and Sandino, 1989]. The most important of these oxides, hydroxides, and hydrous oxides from the viewpoint of disposal of nuclear waste is schoepite, and it is the only one that will be discussed in more detail. However the NEA review [Grenthe, Fuger, et al., 1992] gives a detailed discussion and critical review of the available thermodynamic information, and their critically assessed values could be used to predict the solubilities of the other phases.

Numerous studies have been reported of the solubility of schoepite in waters of various compositions and pHs [Babko and Kodenskaya, 1960; Brusilovskii, 1958; Bruno and Sandino, 1989; Gayer and Leider, 1955; Gryzin and Koryttsev, 1967; Kim, Choi, et al., 1994; Krupka, Rai, et al., 1985] and a few other studies were cited by Puigdomènech and Bruno [Puigdomènech and Bruno, 1988]. Most of these data are for the crystalline material, and the majority of these studies are in reasonable agreement. The analysis by Puigdomènech and Bruno indicates that the solubility at 298 K is at a minimum from $\text{pH} = 8$ to 9 , at about 2.5×10^{-6} to 6×10^{-5} molar. However, it increases rapidly with pH at both higher and lower pH s, and solubilities of about 10^{-1} molar are observed by $\text{pH} = 4$. Bruno and Sandino [Bruno and Sandino, 1989] found that the solubility of amorphous schoepite was about 10 to 30 times more soluble than microcrystalline material for the same pH range.

Formation constants for the uranyl carbonates and mixed hydroxycarbonates are fairly large [Clarke, Hobart, and Neu, 1995; Grenthe, Fuger, et al., 1992; Newton and Sullivan, 1985] and indicate that the presence of carbonate will considerably enhance the solubility of schoepite.

The solubility of sodium uranate $\text{Na}_2\text{U}_2\text{O}_7(\text{s})$ was reported to be 2.05×10^{-5} molar in cement-equilibrated water saturated with NaCl [Marx and Keiling, 1989]; the pH of this solution was presumably about 11. Solubilities of a uranium(VI) sodium uranate, presumably also $\text{Na}_2\text{U}_2\text{O}_7(\text{s})$, in cement-

equilibrated water were reported graphically for $\text{pH} \approx 3.5$ to 13 [Brownsword, Buchan, et al., 1989]. The solubility had a rather broad minimum of from 10^{-6} to 10^{-5} molar for $\text{pH} = 6$ to 13, but showed a rapid increase in solubility at lower pHs.

A number of solubility studies have been reported for the uranyl carbonate rutherfordinide, $\text{UO}_2\text{CO}_3(\text{cr})$. See, for example, the studies [Grenthe, Ferri, et al., 1984; Sergeyeva, Nikitin, et al., 1972] and also other reports referenced by Puigdomènech and Bruno [Puigdomènech and Bruno, 1988]. It has been reported that to synthesize this material from aqueous solutions requires a partial pressure of $\text{CO}_2(\text{g})$ that is $> 3 \times 10^{-4}$ atm [Grenthe, Ferri, et al., 1984; Sergeyeva, Nikitin, et al., 1972], whereas Babko and Kodenskaya claim that a molar concentration of dissolved CO_2 of > 0.6 molar is required [Babko and Kodenskaya, 1960]. The solubility minimum for uranyl carbonate of about 2×10^{-5} to 10^{-4} molar occurs around $\text{pH} \approx 5$, with rapid increases in solubility at higher and lower pHs. The existence of numerous uranyl carbonate, hydroxycarbonate, and possibly a hydroxyb carbonate complex in the solution phases gives rise to this strong variation of solubility with pH [Clark, Hobart, and Neu, 1995; Grenthe, Fuger, et al., 1992; Lemire and Garisto, 1989; Lemire and Tremaine, 1980; Newton and Sullivan, 1985]. Its solubility varies little with temperature [Puigdomènech and Bruno, 1988; Sergeyeva, Nikitin, et al., 1972].

Solubilities have been reported for the uranyl phosphates $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$, $\text{UO}_2(\text{HPO}_4) \cdot 4\text{H}_2\text{O}(\text{s})$, $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{s})$, and $\text{UO}_2(\text{HPO}_4)(\text{s})$ and their mixtures with H_3PO_4 [Karpov, 1961; Marković and Pavković, 1983; Moskvina, Shelyakina, and Perminov, 1967; Schreyer and Baes, 1954; Veselý, Pekárek, and Abbrent, 1965]. The reported solubility of $\text{UO}_2(\text{HPO}_4) \cdot 4\text{H}_2\text{O}(\text{s})$ in water at 298.15 K is 6×10^{-5} molar [Moskvina, Shelyakina, and Perminov, 1967], although Schreyer and Baes reported that this solid phase only formed when the total phosphate concentration in the solution was between 0.014 and 6.1 molar [Schreyer and Baes, 1954]. At higher phosphate concentrations $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{s})$ becomes the precipitating phase. These phase studies were done in solutions of H_3PO_4 , so high acidities were also involved. Concentrations of uranyl as high as 0.2 molar in solutions could be obtained at high concentrations of H_3PO_4 . Evaluated solubility products are 8×10^{-13} for $\text{UO}_2(\text{HPO}_4)(\text{s})$, 2×10^{-24} for " $(\text{UO}_2)_2(\text{HPO}_4)_2(\text{s})$," and 1×10^{-49} for $(\text{UO}_2)_3(\text{PO}_4)_2(\text{s})$ [Anderson, 1989]. The

second of these formulas is equivalent to $\text{UO}_2(\text{HPO}_4)(\text{s})$. Presumably, these solubility products actually refer to the hydrated solids. The NEA review of uranium thermodynamics [Grenthe, Fuger, et al., 1992] reports a value of the thermodynamic solubility product of 5×10^{-54} for $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{cr})$ from an unpublished dissertation. They attributed this smaller value to use of material with greater crystallinity than in the earlier studies, although differences in the number of waters of hydration may also have been present. Numerous complexes of the uranyl ion with HPO_4^{2-} , H_2PO_4^- , and H_3PO_4 have been reported [Grenthe, Fuger, et al., 1992; Lemire and Garisto, 1989], and their formation is responsible for the rapid increase in solubility of the phosphates with increasing acidity. Evidence for additional hydrates of the uranyl phosphates are summarized in the NEA review [Grenthe, Fuger, et al., 1992].

Solubilities have also been reported for various alkali metal and ammonium uranyl phosphates: $\text{LiUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{NaUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{KUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{RbUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{CsUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, and $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ [Chukhlantsev and Stepanov, 1956; Moskvina, Shelyakina, and Perminov, 1967; Murav'eva, Zaborenko, et al., 1964; Veselý, Pekárek, and Abbrent, 1965]. These solid phases form from solutions of alkali metal or ammonium salts in the presence of phosphoric acid. Evaluated solubility products at 293 K [Veselý, Pekárek, and Abbrent, 1965] are: 6×10^{-25} for $\text{NaUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, 3×10^{-26} for $\text{KUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, 2×10^{-26} for $\text{RbUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, 4×10^{-26} for $\text{CsUO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, and 6×10^{-27} for $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}(\text{s})$. These double salts are significantly more soluble than $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$.

As noted earlier, $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$ is very soluble in water. However, various divalent metal mixed hydroxysulfates (zippeïtes) are known with the general formula $\text{M}(\text{II})_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot x\text{H}_2\text{O}(\text{s})$, and which are much less soluble [Haacke and Williams, 1979]. Reported solubility products at 298 K are: 8×10^{-147} for $\text{Mg}_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot x\text{H}_2\text{O}(\text{s})$, 1×10^{-146} for $\text{Co}_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot x\text{H}_2\text{O}(\text{s})$, 3×10^{-146} for $\text{Ni}_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot x\text{H}_2\text{O}(\text{s})$, and 1×10^{-153} for $\text{Zn}_2(\text{UO}_2)_6(\text{SO}_4)_3(\text{OH})_{10} \cdot x\text{H}_2\text{O}(\text{s})$. These extremely small values occur because they represent complete dissociation to form M^{2+} , UO_2^{2+} , SO_4^{2-} , and OH^- . The actual total concentration of UO_2^{2+} is about $\approx 10^{-5}$ molar in these solutions at $\text{pH} \approx 5$. These solubility products are not very certain since the solubilities were measured at a single pH.

The uranium silicate mineral soddyite, $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$, is well known and is a possible solubility limiting phase under oxidizing conditions for uranium solutions containing dissolved silica [Moll, Geipel, et al., 1996; Nguyen, Silva, et al., 1992]. Its solubilities have been determined at 303 K [Nguyen, Silva, et al., 1992] and 298 K [Moll, Geipel, et al., 1996]. In both studies it required about 60 to 100 days to reach saturation equilibrium (or a steady state). A minimum solubility of about 10^{-5} molar is observed at $\text{pH} \approx 6$, but higher solubilities are observed both at lower and higher pH. Solubilities greater than 10^{-2} molar occur at $\text{pH} = 3$. Nguyen et al. [Nguyen, Silva, et al., 1992] also determined solubilities of synthetic uranophane, $\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{cr})$, synthetic sodium boltwoodite, $\text{Na}(\text{H}_3\text{O})(\text{UO}_2)\text{SiO}_4 \cdot \text{H}_2\text{O}(\text{cr})$, and synthetic sodium weeksite, $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 7\text{H}_2\text{O}(\text{cr})$. Lengthy equilibrations were also required for these systems. The solubility of these three uranyl silicates were slightly lower than that of soddyite, but no detailed comparison is possible since the solubility experiments were performed at a single pH.

Potential-pH diagrams using the critically assessed NEA thermodynamic data base [Grenthe, Fuger, et al., 1992] indicates that in the uranium/oxygen/water phase system at room temperature, schoepite $\{\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{cr}) \text{ or } \text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})\}$ should be the solubility-limiting phase under more oxidizing conditions. However, as the solution becomes less oxidizing the solubility-limiting phase should switch to $\text{U}_3\text{O}_8(\text{cr})$ {equivalent to $\text{UO}_{2.6667}(\text{cr})$ }, then to $\beta\text{-U}_3\text{O}_7(\text{cr})$ {equivalent to $\text{UO}_{2.3333}(\text{cr})$ }, to $\beta\text{-U}_4\text{O}_9(\text{cr})$ {equivalent to $\text{UO}_{2.25}(\text{cr})$ }, and finally to uraninite $\text{UO}_2(\text{cr})$.

This predicted precipitation series is based on critically assessed calorimetric data in most cases, because detailed solubility studies are available only for the two homovalent end members schoepite and uraninite. There are no obviously reliable solubility data for the mixed-valence uranium oxides according to the NEA review [Grenthe, Fuger, et al., 1992]. Ollila et al. [Ollila, Olin, and Lipponen, 1996] studied the dissolution behavior of polycrystalline UO_2 pellets in distilled water and in several synthetic groundwaters containing bicarbonate, with all dissolution experiments performed in nitrogen atmospheres. The fraction of dissolved uranium present as U(VI) varied from 91.4 to 99.0 % in their experiments. They measured solubilities at $\text{pH} = 7.0$ and at 8.9-9.1 that were essentially identical to those predicted for $\beta\text{-U}_4\text{O}_9(\text{cr})$ using the NEA data base with $\text{Eh} = -0.3 \text{ V}$. They suggested that the

surface layer of their $\text{UO}_2(\text{cr})$ could have been more highly oxidized due to radiolysis. However, the value of $E_h = -0.3 \text{ V}$ used in their modeling calculations was assumed rather than measured (their measured values of E_h ranged between $+0.15$ and 0.18 V), and the composition of the solid phase was not analyzed after the solubility experiments were performed. Thus the actually solubility-limiting phase in these experiments is unknown.

It is far from certain that all of these mixed-valence oxides can form by precipitation from aqueous solutions, or by aging of the initial precipitates, or by changing the E_h value of an aqueous solution with which they are in contact. However, mixed valence oxides of uranium do occur as natural minerals, e.g., the mineral ianthinite $\text{UO}_{2.833} \cdot 1.76\text{H}_2\text{O}(\text{s})$ [Grenthe, Fuger, et al., 1992].

The solubility of amorphous or precipitated UO_2 has been reported in numerous studies [Bruno, Casas, et al., 1987; Bruno, Ferri, et al., 1986; Galkin and Stepanov, 1960; Gayer and Leider, 1957; Rai, Felmy, and Ryan, 1990; Ryan and Rai, 1983]. This material has been described in the various studies as $\text{UO}_2(\text{am})$, $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{U}(\text{OH})_4(\text{s})$, etc. For the present discussion we will denote this material as $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$, although, depending on the precipitation conditions and aging of the solid, its composition could vary from truly amorphous to microcrystalline material and the degree of hydration may vary.

Solubilities reported in three of these studies [Bruno, Casas, et al., 1987; Gayer and Leider, 1957; Galkin and Stepanov, 1960] are fairly consistent with each other [Puigdomènech and Bruno, 1988], and show a minimum solubility of about 3×10^{-5} molar between pHs of about 6 to 13. In contrast, the solubilities measured by the group at PNL [Rai, Felmy, and Ryan, 1990; Ryan and Rai, 1983] have considerably lower solubilities, about 10^{-8} to 10^{-7} molar for pHs from 6 to 14. In two of these studies [Gayer and Leider, 1957; Galkin and Stepanov, 1960] no attempt was made to control the E_h of the solution, whereas Bruno et al. [Bruno, Casas, et al., 1987] reduced the U(VI) in their solution to U(IV) by using hydrogen gas, but then replaced the H_2 with N_2 for the solubility experiments. Ryan and Rai [Ryan and Rai, 1983] used $\text{Na}_2\text{S}_2\text{O}_4(\text{aq})$ or zinc metal to provide reducing environments in the solubility experiments, whereas Rai et al. [Rai, Felmy, and Ryan, 1990] used iron powder or $\text{Eu}^{2+}(\text{aq})$ as reducing agents. Bruno et al. [Bruno, Casas, et al., 1987] attributed this solubility difference to possibly a greater degree of crystallinity

in the PNL study [Ryan and Rai, 1983]. Rai et al. [Rai, Felmy, and Ryan, 1990], however, reported X-ray diffraction patterns that were very similar to those reported by Bruno et al., so crystallinity differences can not account for the different solubilities. Rai et al. noted that solubilities of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ reported in the other three studies [Bruno, Casas, et al., 1987; Gayer and Leider, 1957; Galkin and Stepanov, 1960] were essentially identical to those of $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{cr})$ or $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})$, and thus they attributed the solubility differences to partial oxidation of U(IV) to U(VI). Furthermore, Tremaine et al. [Tremaine, Chen, et al., 1981] found that $\text{UO}_2(\text{cr})$ in contact with an aqueous solution at $\text{pH} = 12.5$ had slightly more than half of the surface layer oxidized to U(VI) at 298 K even though the solutions had been purged with H_2 . Partial oxidation of the surface of UO_2 in the other studies [Bruno, Casas, et al., 1987; Gayer and Leider, 1957; Galkin and Stepanov, 1960] seems to be a plausible explanation, and we tentatively accept the results from the PNL studies [Rai, Felmy, and Ryan, 1990; Ryan and Rai, 1983].

Solubilities have also been reported for uraninite, $\text{UO}_2(\text{cr})$, in this case from 298 to 873 K [Ollila, Olin, and Lipponen, 1996; Parks and Pohl, 1988; Red'kin, Ivanov, and Omel'yanenko, 1988; Tremaine, Chen., et al., 1981]. The solubilities of Ollila et al. appear to be high, and they suggested that surface oxidation may have occurred on their $\text{UO}_2(\text{cr})$. Tremaine et al. did report surface oxidation of their $\text{UO}_2(\text{cr})$, and thus their solubilities are also likely to be high by about a factor of about 10^2 . The results of Parks and Pohl are probably more reliable, and their solubilities of $\text{UO}_2(\text{cr})$ in water only vary from 10^{-9} to 10^{-10} molar from 373 to 473 K for pHs of 2 or 3 to 10. Their results suggest that a solubility of 10^{-9} to 10^{-10} molar should be about right for the solubility of uraninite in water at 298.15 K under reducing conditions.

Stability constants have been reported for the tetra and penta carbonate complexes of U(IV) [Clarke, Hobart, and Neu, 1995; Grenthe, Fuger, et al., 1992; Newton and Sullivan, 1985]. Since these complexes are fairly strong, the presence of carbonate in the aqueous phase will increase the solubility of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{UO}_2(\text{cr})$ significantly.

The uranium(IV) phosphate $\text{U}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ has been reported [Schreyer, 1955] to form when the total concentration of phosphate was between 1.5 and 9.8 molar. Solubilities were determined in solutions of H_3PO_4 but results were only presented graphically. An attempt to determine its solubility in water apparently yielded a partially hydrolyzed product of

uncertain composition. Grenthe et al. [Grenthe, Fuger, et al., 1992] cited a solubility product (corrected to infinite dilution by them) of 3×10^{-31} for $U(HPO_4)_2 \cdot 4H_2O(s)$, but without making any corrections for phosphate or hydroxyphosphate complexes owing to a lack of reliable experimental values. Thus this solubility product is highly questionable.

Merkusheva et al. [Merkusheva, Skorik, et al., 1967] studied the solubility of $U(P_2O_7) \cdot 20H_2O(s)$ at 298 K in dilute $HClO_4$ at an ionic strength of 0.1 molar. The solubility varied from 3.2×10^{-6} molar at $pH = 1.00$ to 1.2×10^{-6} molar at $pH = 2.68$. As noted by Grenthe et al. [Grenthe, Fuger, et al., 1992] the solubility product reported by Merkusheva is questionable because of an inadequate knowledge of the aqueous speciation under their experimental conditions.

Several studies report the solubilities of $U(SO_4)_2 \cdot 8H_2O(s)$ and $U(SO_4)_2 \cdot 4H_2O(s)$ and these solubilities are tabulated by Linke [Linke, 1965]. Solubilities of these salts in water are probably not meaningful owing to gradual "clouding" of the solutions and precipitation of hydrolyzed solids. The reported solubility of $U(SO_4)_2 \cdot 8H_2O(s)$ at 298 K in 0.05 molar H_2SO_4 is about 0.29 molal. Stepanov and Galkin [Stepanov and Galkin, 1962] studied the pH conditions for precipitation as a function of the concentration of $U(SO_4)_2(aq)$. From that information they deduced that the basic sulfate formed was $U(OH)_2(SO_4)(s)$ and that its solubility product (presumably at room temperature) was 7×10^{-32} . Given that their solubilities refer to fresh precipitates, they are probably much greater than the corresponding equilibrium solubilities.

Examination of the solubility and redox information summarized in the preceding paragraphs indicates that minimum solubilities for uranium are favored by $pH \approx 6$ to 12 or 13, by very low carbonate concentrations, by very low concentrations of phosphate (especially when the solutions are acidic), and by very reducing conditions. Oxidizing conditions and acidic pHs favor increase solubility, as do alkaline conditions when high concentrations of carbonate are present.

It was suggested in the discussion for neptunium and plutonium that two of the three conditions needed to lower solubilities could be met by adding materials that remove carbonate and phosphate from infiltrating groundwater, by forming sparingly soluble precipitates, and which increase the alkalinity. A suggested possibility was to add mixtures of gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4) and lime (CaO) to raise the pH into a favorable range as these materials dissolve, and which would provide sources of calcium ions to precipitate most of the dissolved carbonate/bicarbonate as calcite (CaCO_3) and dissolved phosphate as hydroxy apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, or calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. These same additives would also be beneficial for reducing the solubility of uranium. Use of MgO (periclase) [Jackson, 1996] or cement-equilibrated waters may also be satisfactory.

The solubility data discussed above indicate that schoepite and other U(VI) compounds should be avoided as the solid phase since they are considerably more soluble than the oxides, hydroxides, and hydrous oxides of U(IV). $\text{UO}_2(\text{cr})$ is probably the least soluble of all of these compounds, but $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ also appears to have very low solubilities. However, the surface layer of $\text{UO}_2(\text{cr})$ and $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ is extremely sensitive to the presence of oxygen and even a brief exposure can oxidize the surface partially to U(VI). These more highly oxidized surface layers appear to have solubilities greater by factors of 10^2 to 10^3 than those of the corresponding unoxidized materials. Highly reducing conditions with $E_h < -0.3$ V are essential for maintaining $\text{UO}_2(\text{cr})$ or $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ as the solid phase. Using the Γ/Γ_3 redox buffer or certain metal powders, as suggested for neptunium and plutonium, should be adequate. A sparingly soluble salt such as CuI might make a suitable additive for slow release of iodide. Corrosion of the overpack would also contribute to the desired reducing environment close to the waste canister.

4. Additional Comments About the Literature Search

There is a recent review of the aqueous solubilities of the actinide nitrates: IUPAC Solubility Data Series, Vol. 55, Actinide Nitrates, S. Siekierski and S. L. Phillips editors, Oxford University Press, Oxford, 1994. The subscription to the IUPAC Solubility Data Series in the library at Lawrence Livermore National Laboratory is complete through volume 53 but was then terminated. There were also several articles in published conference proceedings or books that were sought and which were once available in the library at LLNL, but which are no longer available since they were removed from the "stacks" to make space for newer reports. Some of the journal subscriptions (e.g., the Soviet Journal of Radiochemistry) did not extend far enough back in time to include issues reporting some of the early solubility studies.

In spite of this difficulty, a considerable number of reports on the aqueous solubilities of these three actinides were acquired, including the majority of those studies that were published as journal articles, and including the majority of the recent reports. We believe that solubility values contained in those reports that were unobtainable on short notice will merely confirm the conclusions contained in the present report.

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