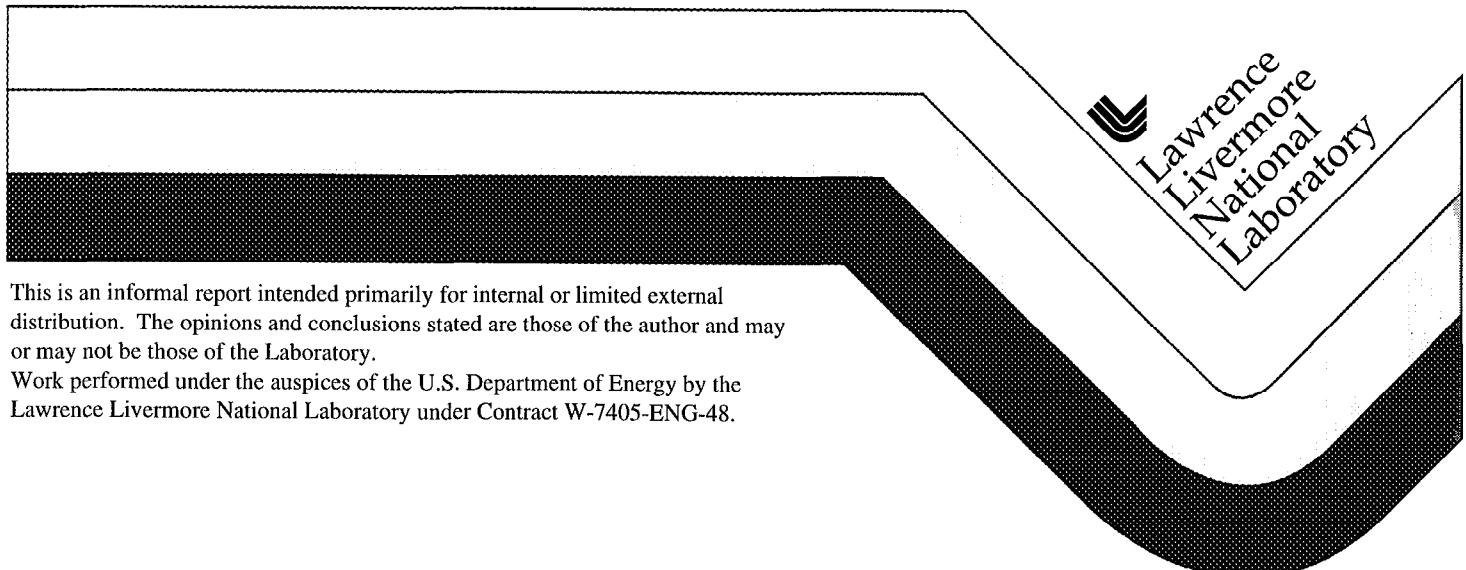


Status of Solubility Data for Selected Elements (U, Np, Pu, Am, Tc, Ni, and Zr)

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September 8, 1997



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**Status of Solubility Data for Selected Elements
(U, Np, Pu, Am, Tc, Ni, and Zr)**

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1. Introduction

This report is an evaluation of solubility data for U, Np, Pu, Am, Tc, Ni and Zr compounds at ambient and elevated temperatures. We review the status of such data in light of the most recently reported experimental results. The focus is on the solid phases that may control solubilities under expected conditions in and near a potential nuclear waste repository at Yucca Mountain, Nevada. Solubility data or reliable predictions over the temperature range 20 to 150°C will be used in geochemical modeling studies of the Yucca Mountain Project [96PAL].

The geochemistry of U, Np, Pu, Am and Tc with respect to a geological repository has recently been discussed in [97LAN]. Aqueous transport is considered the most likely scenario for migration of nonvolatile radionuclides from a repository to the accessible environment [95SIL1]. Solubility studies using groundwater samples from the region can indicate conservative upper limits on the individual radioelement concentrations in the waters, and the solubility experiments can provide initial radioelement concentrations for following work such as sorption studies. Solubility data are important for multi-parameter transport models and allow a conservative source term evaluation for the selected element in natural systems. Thermodynamic solubility products are required as input to geochemical codes such as EQ3/6 [92WOL].

Well-defined solubility studies should satisfy the following criteria: solution equilibrium conditions, accurate solution concentrations, a well-defined solid phase and knowledge of the soluble species distribution [91NIT]. Ideally, the measurements should be carried out from both oversaturation and undersaturation in order to demonstrate that equilibrium was attained. For unknown solubility systems, oversaturation experiments can reveal the solubility-controlling solid under steady-state conditions. Experiments are also possible from the undersaturation approach if the solid phase can be identified and synthesized.

The solubility of a given element in an aqueous system depends on several parameters, including the Eh of the system and redox chemistry of the element, the nature and concentration of ions and complexing ligands present, the pH, temperature, and ionic strength of the system and the nature of the solid phases in contact with the aqueous phase. In dilute groundwaters and simulated groundwaters, solubility experiments with U(VI), Np(V), Pu(IV) and Am(III) have indicated that oxide, hydroxide, carbonate or mixed hydroxycarbonate compounds are the dominant solid phases, but solubility data for U, Np, Pu and Am in all possible oxidation states and under all possible environmental conditions are not currently available [95SIL1]. Model calculations have indicated that some radionuclides (e.g., Pu, Am) are highly insoluble in the proposed repository environment at near-neutral pH and both oxidizing and reducing conditions [97LAN]. Other radionuclides (e.g., Tc, U, Np) are insoluble in a low Eh environment but may be quite soluble at high Eh values. The formation of silicate and/or phosphate complexes of Tc, Np, Pu and other radionuclides could increase the computed solubilities of their (IV) metal oxides, hydroxides, and other solids by orders of magnitudes. Little or no data is available on this issue [97LAN].

Solubility and speciation measurements have been made from oversaturation for Np, Pu, and Am in Yucca Mountain region well waters (J-13 and UE-25p#1) at temperatures in the range 25 to 90°C [93NIT, 94NIT, 95NIT]. In a number of cases of interest, there is little data available or accurate solubility products cannot be determined from the published data. Further experiments to obtain some of the missing data are suggested in the section for each element in the present report.

2. Reference groundwater

The chemical composition of groundwater samples from the Yucca Mountain region has been discussed in [96PAL]. The water from well J-13 is thought to be representative of interstitial and fracture waters in the Yucca Mountain region and is used as a reference water in this report. The effect of temperature on the composition of J-13 water in contact with Yucca Mountain tuff has been investigated in a number of studies [84KNA, 85KNA1, 85KNA2, 85OVE, 86KNA, 87KNA]. There are only minor changes in solution composition over the temperature range 25 to 150°C. As the temperature is raised, there is an increase in the dissolved Si concentration and slight decreases in the dissolved Mg, Ca, and carbonate concentrations. The J-13 water composition at 25°C and suggested maximum concentrations in interstitial and fracture waters at elevated temperatures [86GLA] are summarized in Tables 1 and 2.

Table 1: Cation concentrations (mM) in the reference water.

	Li	Na	K	Mg	Ca	Al	Si	Mn	Fe	pH
J-13	0.009	1.96	0.136	0.072	0.29	0.001	0.92	0.00002	0.0008	6.9
high T	-	< 2.8	<0.38	<0.21	<0.37	<0.19	<5.7	-	-	6.9-7.6

Table 2: Anion concentrations (mM) in the reference water.

	F ⁻	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	O ₂
J-13	0.11	0.18	0.16	2.34	0.19	0.18
high T	<0.26	<0.28	<0.24	<2.30	<0.26	-

3. Temperature extrapolations

Knowledge of the solubility-controlling solid phases is an important step in understanding the geochemical behavior of an element. Initially, relevant solids may be identified through solubility experiments conducted from oversaturation. This approach will not always be successful; for example, it may be difficult to identify the solid due to the presence of amorphous or mixed phases, or the time to reach equilibrium may be very long. Even

when solubility-controlling solids can be identified through oversaturation experiments, one generally has data at one or a few fixed temperatures. In order to model equilibrium reactions at an arbitrary temperature, the equilibrium constants must be extrapolated to the temperature of interest.

Temperature extrapolations of chemical equilibrium data, including solubility products, are described in detail in [97PUI, 97LAN]. It is rare to have complete information on the temperature dependence of thermodynamic functions for the reactions of interest, thus approximation methods must be used to predict the equilibrium constants, such as solubility products and complex stability constants, over the temperature intervals of interest. The integrated van't Hoff equation is useful over small temperature ranges (about 10 K or less):

$$\log K^0(T) = \log K^0(T_0) + \frac{\Delta H^0(T_0)}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \quad (1)$$

Here R is the ideal gas constant 8.3145 J mol⁻¹ K⁻¹. Included in Eq. (1) is the assumption that the enthalpy of reaction ΔH^0 is constant over the temperature range, and there is no change in heat capacity. Eq. (1) is applicable over a larger temperature range, approximately 20 to 200°C, when the reaction is isoelectric, that is, the sum of positive charges among the reactants equals the sum of positive charges among the products and the sum of negative charges among the reactants equals the sum of negative charges among the products [97PUI].

If the change in heat capacity ΔC_p^0 is assumed to be a nonzero constant over the temperature range T_0 to T, the equation for the equilibrium constant becomes:

$$\log K^0(T) = \log K^0(T_0) + \frac{\Delta H^0(T_0)}{2.303R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta C_p^0}{2.303R} \left(\frac{T_0}{T} - 1 + \ln \frac{T}{T_0} \right) \quad (2)$$

In the next level of approximation, an empirical expression is used to describe the temperature dependence of ΔC_p^0 . However, such expressions are rarely available for the reactions of interest. Values of ΔH^0 and ΔC_p^0 can be determined by calorimetric measurements at two or more temperatures or by direct measurements of the equilibrium constant at several temperatures.

4. Uranium

The estimated U solubility in J-13 water at 25°C is about 10⁻⁴ M [84KER] and the principal aqueous species are $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and UO_2CO_3^0 [92PAL]. Potential solubility-controlling solids include schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$ or $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) rutherfordine (UO_2CO_3), the sodium uranates and $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$. Uranyl silicate ($(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$) and mixed uranyl silicate phases ($\text{Na}(\text{H}_3\text{O})(\text{UO}_2)\text{SiO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 7\text{H}_2\text{O}$) may also be significant due to the high Si concentrations present in J-13 and other waters of the Yucca Mountain region. Under reducing conditions,

important solid phases may include uraninite (UO_2), oxide phases UO_x with $2 < x < 3$, and the crystalline and amorphous forms of USiO_4 .

The OECD Nuclear Energy Agency Thermochemical Data Base Project (NEA-TDB) has completed a critical review of thermodynamic data for U compounds and species [92GRE, 95GRE]. Solubility reactions for schoepite, the uranium oxides and UO_2CO_3 are relatively well-understood over the temperature range of interest. A detailed discussion of original publications and data selection for these phases is available in the NEA-TDB review and will not be repeated here.

In a review of experimental data up to 1980, thermodynamic functions were calculated for several U species and compounds over the temperature range 25 to 200°C [80LEM]. The Atomic Energy of Canada Limited (AECL) thermodynamic database used for geochemical modeling of U is derived from [80LEM] and subsequent revisions [89LEM, 92LEM]. A comparison of the NEA-TDB and AECL databases has indicated there are only minor differences in predicted U solubilities based on the two databases [97MCM].

The dependence of U solubility on ligand concentrations in groundwaters has been discussed [93MIY]. The NEA-TDB data [92GRE] was used for the evaluation. The U concentration in solution increases very sensitively with increasing carbonate concentration. The temperature dependence was not considered.

Solubility data for uranyl orthosilicate and mixed uranyl silicate solids are available at 25°C [92NGU, 94CAS, 96MOL]. In a review of thermodynamic data for uranyl silicate minerals to 1995, a plan was outlined for the study of uranophane ($\text{Ca}(\text{UO}_2)_2[\text{SiO}_3(\text{OH})]_2 \cdot 5\text{H}_2\text{O}$), soddyite ($(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$), and schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$ or $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) solubilities at 25, 60, and 90°C [95MUR]. However, no data was found for the elevated temperature solubility behavior of uranium silicates and mixed silicates.

Although phosphate concentrations are low in J-13, uranyl phosphate solids have low solubilities and may be significant [92GRE, 92SAN, 95DAC]. No data was found for the elevated temperature solubility behavior of uranium phosphates.

Solubility of the UO_2 matrix is an important parameter for predicting the stability of spent nuclear fuel under disposal conditions. The dissolution process is dependent on the redox conditions in the repository. Solubility experiments have been conducted using unirradiated UO_2 pellets under anoxic conditions [96OLL]. Steady-state results obtained at pH 9.0 and a temperature of 27 to 30°C are listed in Table 3. Based on the NEA-TDB data [92GRE], it was determined that U_4O_9 ($\text{UO}_{2.25}$) was the solubility-controlling solid phase.

Table 3: Steady-state results from [96OLL].

[U], M	Medium
$6\text{-}9 \cdot 10^{-9}$	deionized water
$2 \cdot 10^{-8}$	$[\text{CO}_3^{2-}]$: 60-275 ppm
$4 \cdot 10^{-8}$	$[\text{CO}_3^{2-}]$: 600 ppm
$2.0\text{-}2.5 \cdot 10^{-8}$	synthetic groundwaters

The dissolution mechanism of spent UO_2 fuel under oxic conditions has also been reported [90GRA]. A three-phase model was proposed: (1) the UO_2 matrix, (2) an oxidized surface such as U_3O_7 , and (3) a U(VI)-containing solid alteration product (schoepite in deionized water).

The solubility of amorphous $\text{UO}_2\text{-xH}_2\text{O}$ has been studied at room temperature in the pH range 2 to 12 [90RAI]. The amorphous solid is expected to be metastable with respect to crystalline UO_2 , but the transformation kinetics may be slow.

The solubility of schoepite, uranium oxides and UO_2CO_3 are relatively well-understood under expected repository conditions. There is little or no data on the high temperature solubility behavior of uranium silicates, uranium phosphates, sodium uranates and mixed sodium uranium carbonates. Schoepite is generally assumed to be the solubility-controlling phase in systems in equilibrium with atmospheric CO_2 at 25°C and pH 7, but the carbonate and silicate phases also have low solubilities and may become solubility-controlling at elevated temperatures. Cristobalite in the tuff could be a major source of SiO_2 for the formation of uranium silicates. U solubility experiments could be performed from oversaturation in reference waters in contact with tuff at elevated temperatures. Such experiments may help bound the maximum U concentrations at elevated temperatures, and solubility-controlling solid phases may also be identified.

5. Neptunium

The solubility and speciation of Np in J-13 and UE-25p#1 waters has been investigated in a series of experiments [91NIT, 93NIT, 94NIT, 95NIT]. The experiments were conducted from oversaturation and some of them were also conducted from undersaturation at pH 5.9 to 8.5 and temperatures in the range 25 to 90°C. Np was introduced as NpO_2^+ . At steady-state, NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$ were the principal aqueous Np species. At all temperatures investigated, NpO_2^+ was the main species near pH 6, and $\text{NpO}_2\text{CO}_3^-$ was the dominant species near pH 8.5.

Steady-state Np concentrations were in the 10^{-5} to 10^{-3} M range and decreased as the pH increased. Reported solid phases are listed in Table 4. The solubility-controlling solid changed from a mixed sodium Np(V) carbonate to Np_2O_5 at high temperature and low pH values, but the steady-state Np concentrations showed little temperature dependence.

Table 4. Solubility-controlling solids from [91NIT, 93NIT, 94NIT, 95NIT].

pH	25°C	60°C	90°C
5.9	$\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}\cdot\text{H}_2\text{O}$	$\text{Na}_{2n-1}\text{NpO}_2(\text{CO}_3)_n\cdot x\text{H}_2\text{O}$	Np_2O_5
7.1	$\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}\cdot 2.5\text{H}_2\text{O}$	$\text{Na}_{2n-1}\text{NpO}_2(\text{CO}_3)_n\cdot x\text{H}_2\text{O}$	Np_2O_5
8.5	$\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}\cdot 2.5\text{H}_2\text{O}$	$\text{Na}_{2n-1}\text{NpO}_2(\text{CO}_3)_n\cdot x\text{H}_2\text{O}$	$\text{Na}_{2n-1}\text{NpO}_2(\text{CO}_3)_n\cdot x\text{H}_2\text{O}$

The relatively high solubility of Np(V) solids is an important issue for geological disposal of spent nuclear fuel. If risk calculations are made using the most conservative assumption, i.e., that the Np(V) solids control the long-term Np concentrations, then calculated dose values exceed proposed regulatory levels [95WOL]. Under reducing conditions, the Np solubility is several orders of magnitude smaller and is controlled by $\text{NpO}_2\cdot x\text{H}_2\text{O}$ ($x < 2$) or Np(OH)_4 , as shown in waste form leaching experiments [82RAI, 90WIL]. It is thought that the Np(V) phases observed in the oversaturation experiments under oxidizing conditions are metastable with respect to NpO_2 , a Np(IV) phase. A better understanding is needed of the Np(V)/Np(IV) transformation kinetics involving the solid phases [95WOL].

The solubility of mixed sodium Np(V) carbonates has been investigated at 30, 50 and 75°C [93LEM]. Solid-state conversions such as $\text{NaNpO}_2\text{CO}_3 \rightarrow \text{Na}_3\text{NpO}_2(\text{CO}_3)_2$ occurred very slowly, were difficult to detect and complicated the data analysis. The results were analyzed using two models. In one model, it was assumed that $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ was the only equilibrium solid. In the other model, an equilibrium was assumed to occur between $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2\cdot y\text{H}_2\text{O}$. The results suggested the product $[\text{NpO}_2^+][\text{CO}_3^{2-}]$ decreases as the temperature is raised at a fixed Na concentration.

Experimental and predicted Np(V) solubilities have been reported for concentrated NaCl solutions at 25°C in [96RUN] and in salt solutions at ionic strength usually less than one [92NEC, 94NEC1]. The solubility-controlling solids were identified as $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ for $[\text{CO}_3^{2-}] < 10^{-3}$ M and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2\cdot y\text{H}_2\text{O}$ for $[\text{CO}_3^{2-}] > 10^{-3}$ M.

The solubility of amorphous NpO_2OH has been investigated at room temperature [92ITA, 96ROB]. The results of the two studies are in agreement. The solubility product constant $\log K^\circ([\text{NpO}_2^+][\text{OH}^-])$ was determined to be -8.68 ± 0.26 and -8.79 ± 0.12 .

The solubility and speciation of Np(V) and Np(IV) in brine solutions has been investigated in long-term experiments (>2000 days) [94SIL]. The steady-state Np concentrations were 10^{-5} to 10^{-6} M in the pH range 8 to 13. Radiolysis effects caused the oxidation of Np(IV) to Np(V) and increased the apparent Np solubility with time.

The dissolution of NpO_2 has been investigated over a range of pH values (2 to 6), ionic strength (0.001 and 0.1 m) and temperatures (30 to 90°C) in NaClO_4 solutions [91NAK].

Measured dissolution rates decreased as the pH increased and increased as the temperature increased. Solubility equilibria were not reached in all runs.

Solubility studies of Np(IV) hydrous oxide in water and 0.1 M NaClO₄ have been reported [96NAK]. Measurements were carried out from over- and undersaturation directions at 25°C and a pH range of 5.3 to 13.7 in the presence of reducing agents (Na₂S₂O₄, Fe and Cu). Steady-state Np concentrations were in the range 10⁻⁷ to 10⁻⁸ M. Very little information was given about the precipitates, but based on the analogous Pu(IV) system, the results are consistent with formation of Np(IV) hydrous oxides.

The NEA-TDB review of chemical thermodynamics of Np and Pu is in preparation.

The solubility of Np under expected repository conditions is reasonably well-understood for reducing conditions and over short time scales (a few months to 1 year). As discussed above, a better understanding of the Np(V)/Np(IV) solids is critically needed. Some experimental work is in progress [97PAL], but considering the importance of the Np(V)/Np(IV) issue, more work should be done in this area. Additional experiments of lower priority could include investigations of long-term radiolysis effects and calorimetric measurements of the heats of dissolution of the Np(V) solids.

6. Plutonium

The solubility and speciation of Pu in J-13 and UE-25p#1 waters has been investigated in a series of experiments [91NIT, 93NIT, 94NIT, 95NIT]. Experiments were conducted from oversaturation and undersaturation at several pH values and temperatures. Pu was added as Pu⁴⁺. At steady-state the major oxidation state in solution was Pu(V). The Pu concentration decreased from about 2·10⁻⁷ M at 25°C to about 8·10⁻⁹ M at 90°C. No significant influence of the pH was observed. The precipitates were identified as mixtures of Pu(IV) hydrous oxide and Pu carbonates. It was not possible to further identify the solid phases, and therefore solubility product constants were not determined.

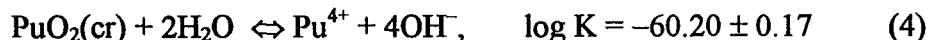
It is likely that slow transformations of the Pu solids were significant in the experiments. The observed decrease in Pu concentrations with increasing temperature may have resulted from the temperature dependence of the reaction rates rather than the temperature dependence of solubility products. Due to the kinetics problem it may be impossible to uniquely identify the solubility-controlling solid phase. However, this is probably not necessary for repository performance assessment, because maximum Pu concentrations will differ by many orders of magnitude depending on whether Pu(V) or Pu(IV) solids are solubility-controlling. The measured Pu concentrations were inconsistent with Pu(V) solids such as NaPuO₂CO₃ or PuO₂OH.

The solubility and speciation of Pu introduced as Pu⁴⁺, PuO₂⁺ and PuO₂²⁺ has been investigated in J-13 water at 25°C [85NIT] and dilute carbonic acid solutions at pH 6, 0.057 atm CO₂ partial pressure and 30°C [93NEU]. The experiments were monitored for

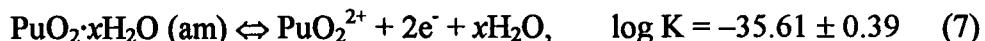
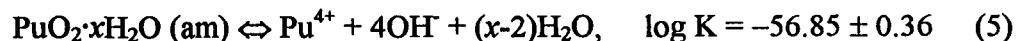
25 to 150 days. When Pu was introduced as Pu^{4+} , the Pu concentrations rapidly decreased to about 10^{-6} M. When Pu was introduced as PuO_2^+ or PuO_2^{2+} , steady-state Pu concentrations on the order of 10^{-5} M were reported. However, the oxidation state distribution of the dissolved Pu was dependent on the initial Pu oxidation state, so it is likely that the results do not reflect true equilibrium conditions. When Pu is introduced as PuO_2^+ or PuO_2^{2+} , kinetic considerations may cause the initial precipitation of metastable $\text{NaPuO}_2\text{CO}_3$ hydrate followed by slow conversion to a less-soluble Pu(IV) hydrous oxide. Disproportionation of Pu(V) is very slow under the conditions investigated in [85NIT] and [93NEU], but studies of Pu(V) in near-neutral solutions at 75°C have indicated the Pu concentration decreases to 10^{-6} M in less than 18 hours in the presence of carbonate [96WRU].

Solubility studies have been reported for Pu introduced as Pu^{3+} , Pu^{4+} , Pu(IV) polymer, PuO_2^+ and PuO_2^{2+} in a synthetic brine solution under oxic conditions [94NIT2]. The experiments were performed at room temperature. Steady-state Pu concentrations were in the range $3 \cdot 10^{-8}$ to $8 \cdot 10^{-7}$ M. At steady-state the major Pu oxidation state in solution was Pu(VI). The following solid phases were observed: for Pu(IV)-polymer, Pu(IV) hydrous oxide; for Pu^{3+} and Pu^{4+} , crystalline unidentified compounds; for PuO_2^+ and PuO_2^{2+} , $\text{NaPuO}_2\text{CO}_3$.

Pu(IV) polymer (colloidal Pu(IV) hydrous oxide) is formed during the neutralization of acidic Pu(IV) solutions. The solubility behavior of Pu(IV) polymer has been described as intermediate between that of amorphous $\text{Pu}(\text{OH})_4$ and crystalline PuO_2 [81RAI]. The solubility products of amorphous $\text{Pu}(\text{OH})_4$ and crystalline PuO_2 at 20°C have been determined as follows [89KIM]:



The solubility of amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, with x near 2, has been investigated at room temperature [84RAI]. The analysis included the Pu redox equilibria in solution. The solubility product results were as follows:



There is a large spread (3 to 4 orders of magnitude) in the solubility of amorphous $\text{PuO}_2 \cdot x\text{H}_2\text{O}$, colloidal Pu(IV) hydrous oxide and crystalline PuO_2 at room temperature. The differences in solubility may be related to differences in particle size and degree of hydration, similar to the situation for various forms of silica [79ILE]. Experiments using carefully prepared and characterized Pu(IV) colloid could investigate particle size effects.

Also, experiments at various temperatures could be performed to see if increasing the temperature destabilizes the more hydrated, higher solubility forms of Pu(IV) polymer.

The effect of complexation on the solubility of Pu(IV) in the aqueous carbonate system has been investigated at room temperature [94YAM]. The solubility-controlling solid was identified as $\text{PuO}_2 \cdot x\text{H}_2\text{O}$.

Ground and surface waters which contain Fe powder can maintain Pu in the Pu(III) oxidation state. The solubility of $\text{Pu}(\text{OH})_3$ has been studied from both oversaturation and undersaturation at 23°C [89FEL]. The solubility product constant was determined to be $\log K_{\text{sp}}^{\circ} ([\text{Pu}^{3+}][\text{OH}^-]^3) = -26.2 \pm 0.8$.

In a review of experimental data to 1980, equilibrium constants were estimated for the dissolution of several Pu oxide, fluoride and phosphate compounds over the temperature range 25 to 200°C [80LEM].

The NEA-TDB review of chemical thermodynamics of Np and Pu is in preparation.

The solubility behavior of Pu under expected conditions is reasonably well-understood. Solid phases were not precisely determined in the oversaturation experiments, so model assumptions concerning the solid phases are required for geochemical modeling. The Pu(V) solids do not appear to be significant under expected repository conditions. Solubility models based on $\text{Pu}(\text{OH})_4$ or $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ should include the Pu redox equilibrium in the solution phase under expected repository conditions.

7. Americium

The solubility of Am in J-13 and UE-25p#1 waters was investigated in a series of experiments [91NIT, 93NIT, 94NIT, 95NIT]. Experiments were conducted from oversaturation and undersaturation with Am added as Am^{3+} . No clear solubility trend was found with temperature (25, 60 and 90°C) and pH (6, 7 and 8.4). Steady-state Am concentrations ranged from roughly 10^{-10} to 10^{-6} M. The solubility-controlling solid phase was orthorhombic AmCO_3OH under J-13 conditions and a mixture of $\text{Am}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ and orthorhombic AmCO_3OH under UE-25p#1 conditions. Different solids were observed because the carbonate concentration is higher by about a factor of 6 in UE-25p#1 water.

The NEA-TDB project has completed the critical review of thermodynamic data for Am compounds and species [95SIL2]. A detailed discussion of original publications and the data selection process is available in the NEA-TDB review, so only a brief summary will be presented here.

AmCO_3OH has two structural forms, orthorhombic and hexagonal. Solubility studies have been made only for the orthorhombic form. At 25°C, the equilibrium between AmCO_3OH (orthorhombic) and $\text{Am}_2(\text{CO}_3)_3(\text{cr})$ occurs at a CO_2 equilibrium partial pressure of approximately 0.1 bar. Solubility product constants for AmCO_3OH

(orthorhombic) and $\text{Am}_2(\text{CO}_3)_3$ are well-known near room temperature, but elevated temperature solubility data, aside from the results of Nitsche et al. discussed above, are not available.

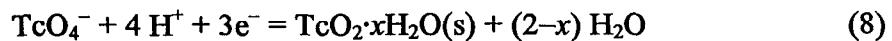
$\text{Am}(\text{OH})_3$ may be significant in waters with very low carbonate concentrations. Both crystalline and amorphous forms of $\text{Am}(\text{OH})_3$ have been identified, and they have similar solubilities in aqueous media. At 25°C, the equilibrium between $\text{Am}(\text{OH})_3(\text{cr})$ and orthorhombic AmCO_3OH occurs at a CO_2 equilibrium partial pressure of about 10^{-4} bar. Solubility product constants for the $\text{Am}(\text{OH})_3$ solids are reasonably well-known near room temperature, but elevated temperature solubility data is not available.

The identity of Am solubility-limiting solids for expected Yucca Mountain repository conditions is known, and the solubility product constants at 25°C are relatively well-understood. Detailed solubility behavior of the solid phases at elevated temperatures is not known. Thermodynamic functions for AmCO_3OH , $\text{Am}_2(\text{CO}_3)_3$ and $\text{Am}(\text{OH})_3$ solids could be determined by calorimetric measurements or solubility experiments at elevated temperatures.

8. Technetium

The $\text{Tc}(\text{VII})/\text{Tc}(\text{IV})$ redox equilibrium has a critical effect on Tc solubility under expected repository conditions [96PAL]. At 25°C and reducing conditions, the Tc concentration is limited to $< 10^{-7}$ M by the $\text{TcO}_2\text{xH}_2\text{O}$ solid phase. Under oxic conditions Tc is very soluble as TcO_4^- [84KER].

The $\text{Tc}(\text{VII})/\text{Tc}(\text{IV})$ redox equilibrium has been investigated by emf measurements on $\text{TcO}_2\text{xH}_2\text{O}$ ($x = 1.63 \pm 0.28$) electrodes in contact with TcO_4^- solutions at 24-25°C [53COB, 55CAR, 75LIE, 91MEY]. The reaction can be written as



The Nernst equation for reaction (12) is

$$E = E^0 + \frac{2.303RT}{3F} (\log a(\text{TcO}_4^-) - 4pH) \quad (9)$$

Here E is the potential, R is the gas constant, F is the Faraday constant, and $a(\text{TcO}_4^-)$ denotes the TcO_4^- activity. The standard potential E^0 is 0.75 ± 0.02 V [91MEY]. The Nernstian behavior has been verified as a function of pH and TcO_4^- activity, but not temperature.

The solubility of $\text{TcO}_2\text{xH}_2\text{O}$ has been investigated in aqueous solutions at room temperature in the pH range 6 to 12 and under constant pCO_2 conditions [92ERI]. The results were described by four different equilibrium expressions to take into account the principal aqueous species in each case (CO₂-free solutions with pH 6 to 9.5, CO₂-free

solutions with pH 11 to 12, carbonate-containing solutions with pH 6 to 9.5 and carbonate-containing solutions with pH 11 to 12).

Tc solubility experiments have been conducted under ambient-temperature conditions relevant to a proposed radioactive waste repository in the UK [90PIL]. The waste is stored in steel containers which are surrounded by a cementitious grout. This results in a pH above 10.5 and reducing conditions ($Eh = -400$ mV). Ammonium pertechnetate solution or solid hydrated technetium dioxide was added to cement-equilibrated waters. The experiments were equilibrated for only 6-7 weeks. No accurate statements were given concerning the solubility-controlling solids formed during the oversaturation experiments. The measured Tc concentration in solution was about 10^7 M. The authors observed an increasing Tc solubility by a factor of 10 if organic degradation products were present.

The NEA-TDB review of thermodynamic data for Tc compounds and species is in preparation.

There is little or no data available on the temperature dependence of the solubility of Tc compounds. However, the Tc(VII)/Tc(IV) redox equilibrium has a strong effect on the Tc solubility and is the critical issue for Tc in a repository. The Tc(VII)/Tc(IV) redox behavior is relatively well-understood at 25°C. The validity of temperature extrapolations using the Nernst equation could be verified by emf measurements on $TcO_2 \cdot xH_2O$ electrodes at a number of temperatures. High carbonate or Si concentrations may alter the $TcO_2 \cdot xH_2O$ surface and this could be checked by measurements in various electrolyte solutions. A small number of Tc solubility experiments in reference waters could also help verify the expected behavior. For performance assessment of a repository it is probably not necessary to have a detailed understanding of the solubility behavior of individual Tc compounds, and undersaturation experiments with Tc compounds should be given relatively low priority.

9. Nickel

If $Ni(OH)_2$ is assumed to be the solubility-controlling solid, then Ni is relatively soluble (to about 0.1 m) in J-13 water at 25°C [97WRU]. The main aqueous species is Ni^{2+} , and a small amount of $NiSO_4^0$ is also present.

The solubility of nickel oxocompounds has been reported by various authors at ambient temperatures [49GAY, 56JEN, 72PAV, 73NOV, 77DIB, 93BAL]. A few papers are also available on the solubility of nickel oxocompounds at elevated temperatures [80TRE, 80CHI, 93DIN]. A brief summary will be presented here.

The solubility of $Ni(OH)_2$ has been investigated at room temperature [49GAY, 56JEN, 73NOV]. The various solubility products reported for reaction (10) are not consistent (Table 5).

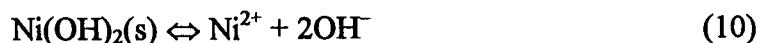


Table 5: Summary of solubility product constants for Ni(OH)₂ (reaction (10)).

Ionic Medium	T(°C)	log K	Reference
HCl/NaOH	25	-17.2	49GAY
HCl/CH ₃ COOH/NaCH ₃ COO	28-30	-16.0	53JEN
0.55M NaCl/1M NaClO ₄	25	-15.2	73NOV

A reason for the different values obtained could be the preparation method and the age of the nickel hydroxide as well as the different electrolyte systems used.

The solubility of Ni(OH)₂ has also been investigated up to 40°C [80CHI]. Dissolution of Ni(OH)₂ is an endothermic process, i.e., the solubility product determined for reaction (10) increased with increasing temperature. The experiments were only conducted over a time period of about 10 hours.

Thermodynamic values ($\Delta_f H^\circ$, $\Delta_f G^\circ$, S° at 298 K) for the system Ni/aqueous solution are available in [72PAV, 77DIB, 93BAL].

The solubility of NiO in pure water has been investigated over the temperature range 373 to 523K in a special batch autoclave system [93DIN]. The Ni solubility from NiO decreased with increasing temperature (at 373K [Ni]: 2.099 $\mu\text{M}/\text{kg}$ and at 573 [Ni]: 0.769 $\mu\text{M}/\text{kg}$). The formation of Ni(OH)⁺, Ni(OH)₂ (aq) and Ni(OH)₃⁻ influences the dissolution of NiO. The data reported in [93DIN] are consistent with the data of [80TRE]. The dissolution process of NiO is described by the following reaction:



The solubility product constant for reaction (11) decreased from $\log K$ [kg/mol] = 12.16 at 298K to about 3.11 at 573K. The same trend was observed for Ni and β -Ni(OH)₂.

The solubility of nickel ferrite NiFe₂O₄ at high temperatures (273 to 623K) is reported in [96HAN, 90CHU]. This compound may be relevant due to the use of stainless steel alloys in the waste containers. Thermodynamic calculations were also described for predicting equilibrium phenomena at high temperatures in water-cooled nuclear reactors [90CHU].

Although sulfate concentrations are low in J-13, nickel sulfate and mixed nickel hydroxide sulfate solids have low solubilities and may possibly be significant [54DOB]. No data was found for the elevated temperature solubility behavior of nickel sulfates.

The solubility of NiO and Ni(OH)₂ are relatively well-understood under expected repository conditions. There is little or no data on the high temperature solubility behavior of Ni silicates, Ni carbonates and Ni sulfates. NiO and/or Ni(OH)₂ are generally assumed to be solubility-controlling in equilibrium with atmospheric CO₂ at 25°C and pH 7, but the increase in carbonate [87EMA] and silicate concentrations with temperature may result in a change in the solubility-controlling solid at elevated temperatures. A small number of Ni

solubility experiments in reference waters could help verify the expected behavior. If the limiting Ni concentrations are high (for example, as calculated when NiO or Ni(OH)₂ is assumed to be the solubility-controlling solid) it may not be necessary to have a detailed understanding of the solubility behavior of individual Ni compounds.

10. Zirconium

The maximum Zr concentration in J-13 water at 25°C is estimated to be less than 10⁻¹⁰ M and limited by the Zr(OH)₄ solid phase [61KOV]. Zr(OH)₄⁰ and Zr(OH)₅⁻ are expected to be the primary solution species for a pH range of 6 to 9.

The solubilities of Zr(OH)₄ and ZrO₂ have been investigated at room temperature [61KOV, 66BIL, 81BAE]. Very little data is available for the solubility of these solid phases at elevated temperatures [66BIL1]. The dissolution reactions were given as:



The reported solubility products are summarized in Table 6.

Table 6: Solubility products for Zr(OH)₄ and ZrO₂.

Method	Ionic medium	compound	T (°C)	log K	Reference
solubility	0 corr	Zr(OH) ₄	19	2.04	[61KOV]
tyndallometric method	1 M NaClO ₄	Zr(OH) ₄	20	≈ 3.8	[66BIL1]
tyndallometric method	dilute	Zr(OH) ₄	20	≈ 4.6	[66BIL1]
tyndallometric method	dilute	Zr(OH) ₄	40	5.05±0.18	[66BIL1]
tyndallometric method	1 M NaClO ₄	Zr(OH) ₄	20	(-4.36±0.05)*	[66BIL1]
tyndallometric method	sea water	Zr(OH) ₄	20	(-4.60)*	[66BIL]
solubility	NaOH: 1 to 18.4 M	Zr(OH) ₄	25	(-3.98) [#]	[60SHE]
solubility	dilute	ZrO ₂	25	-1.9	[81BAE]

* for reaction: $\text{Zr(OH)}_4(\text{s}) \leftrightarrow \text{Zr(OH)}_4(\text{aq})$

[#] for reaction: $\text{Zr(OH)}_4(\text{s}) + \text{OH}^- \leftrightarrow \text{Zr(OH)}_5^-$

In [61KOV] the solubility of freshly prepared $\text{Zr}(\text{OH})_4$ was measured in the pH range 1.54 to 2.02 at a temperature of 19°C. The Zr concentration in solution was detected via a colorimetric method over a period of 24 hours. The solubility product constant determined in these experiments appears to be reliable.

In [66BIL, 66BIL1] the solubility of $\text{Zr}(\text{OH})_4$ was characterized using a tyndallometer. The turbidity of the solution was measured in order to determine whether precipitation of the assumed solid $\text{Zr}(\text{OH})_4$ had occurred. The solubilities determined in these experiments are much larger than the solubility determined in [61KOV]. The authors admit that the precipitate is hard to detect by the tyndallometric method at low Zr concentration (below about 10^{-6} M). Also, the nature of the solution species and the solid phases were not determined and the ionic strength was not always well-defined during the tyndallometric studies. Therefore, the solubility products reported in [66BIL, 66BIL1] are unreliable.

The dissolution of $\text{Zr}(\text{OH})_4$ in different NaOH solutions ranging from 1 to 18.4 M was investigated in [60SHE]. The authors measured a linear relationship between the Zr concentration in solution and the NaOH concentration in the range of 1 to 8 M. They assume from the slope of one the solubility reaction $\text{Zr}(\text{OH})_4(\text{s}) + \text{OH}^- \leftrightarrow \text{Zr}(\text{OH})_5^-$ for zirconium hydroxide in highly concentrated NaOH solutions.

There is little or no data on the high temperature solubility behavior of ZrSiO_4 . The silicate phase has a low solubility at room temperature and may become solubility-controlling at elevated temperatures. Thermodynamic data for Zr have been tabulated in [82WAG].

Phosphate concentrations are low in J-13, but Zr phosphates have low solubilities and may become significant. Thermodynamic data is available for $\text{Zr}(\text{HPO}_4)_2$ [79ALL].

A review of the chemical thermodynamics of Ni and Zr is currently being conducted by the Yucca Mountain Project, and will result in a database for Ni and Zr which is internally consistent with the NEA-TDB thermodynamic data for Tc, U [92GRE], Np, Pu, and Am [95SIL].

Little or no data is available on the temperature dependence of the solubility of $\text{Zr}(\text{OH})_4$, ZrO_2 and ZrSiO_4 . More reliable values for the solubility product constants of these compounds are needed to provide confidence in modeling calculations of zirconium solubilities. Solubility experiments could be performed from oversaturation in reference waters and from undersaturation at ambient and elevated temperatures. Such experiments could help bound the maximum Zr concentrations at ambient and elevated temperatures, and solubility-controlling solid phases may also be identified. However, detailed experimental investigations of Zr solubilities are not of the highest priority because the Zr solubility is expected to remain low as the temperature increases.

11. Concluding Remarks

The goal of this review has been to present a summary of recent literature on the solubility behavior of selected elements (U, Np, Pu, Am, Tc, Ni and Zr) with a focus on solubility-controlling solids for expected conditions at Yucca Mountain, Nevada. An overview of likely solubility-controlling solid phases is given in Table 7. The solubilities of the uranium oxides, schoepite, UO_2CO_3 , PuO_2 and the Ni and Zr phases can be reliably predicted over the temperature range 20 to 150°C. For the other phases there is little or no experimental data on the temperature dependence, and solubilities must be estimated at temperatures above 25°C.

Table 7.: Summary of expected solubility-controlling solids.

	Low Eh conditions	High Eh conditions
U	UO_2 UO_x , $2 < x < 3$ USiO_4 (cr, am)	UO_2CO_3 $\text{UO}_3 \cdot 2\text{H}_2\text{O} / \text{UO}_2(\text{OH})_2$ $\text{Na}_2\text{U}_2\text{O}_7$ $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ $\text{Na}(\text{H}_3\text{O})(\text{UO}_2)\text{SiO}_4 \cdot \text{H}_2\text{O}$ $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 7\text{H}_2\text{O}$
Np	NpO_2 (cr) $\text{Np}(\text{OH})_4$ (am)	$\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ Np_2O_5
Pu	PuO_2 $\text{Pu}(\text{OH})_4$ (am) $\text{Pu}(\text{IV})$ polymer	same as low Eh, but metastable phases (amorphous solids, $\text{NaPuO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$) are more prevalent
Am	AmOHCO_3 $\text{Am}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$ $\text{Am}_2(\text{CO}_3)_3$ $\text{NaAm}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ $\text{Am}(\text{OH})_3$	same as low Eh
Tc	TcO_2 $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ ($x = 1-2$)	NaTcO_4
Ni	NiO $\text{Ni}(\text{OH})_2$	same as low Eh
Zr	ZrO_2 $\text{Zr}(\text{OH})_4$ ZrSiO_4	same as low Eh

Specific recommendations for further work have been made in the section for each element in this report. The relative need for further solubility experiments is roughly in the order Np > U > Pu > Am > Zr > Tc > Ni. The kinetics of precipitation and transformation of the solid phases are particularly important for Np and Pu. An additional area for further

experimental work is the possibility of mixed actinide solids. For example, if Np and Pu are both present, does formation of a mixed Np-Pu solid result in lower solution concentrations than would be predicted based on individual Np and Pu solids?

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