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The Aqueous Geochemistry of Neptunium: Dynamic Control of Soluble Concentrations with Applications to Nuclear Waste Disposal

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The valence state of neptunium, one of the most important radionuclides of concern for long-term emplacement of nuclear waste, primarily defines its geochemical reactions and migration behavior. We evaluate how redox potential and solid-phase stability interact and influence neptunium solubility and aqueous speciation in natural systems. Neptunium thermodynamic data for the most important valence states for natural waters, +IV and +V, are updated to correct database inconsistencies. The most significant changes are as follows: (1) Np_2O_5(cr) is 2 orders of magnitude more stable than reported previously, (2) the stability of NpO_2OH(aq) is reduced, (3) $NpO_2(OH)_2^-$ and mixed Np(V) hydroxo-carbonato species become important at high pH, and (4) $Np(OH)_5^-$ is disregarded as a valid species. As a result, Np_2O_5 and $Np(OH)_4$(am) are the stable solids in aquifers of low ionic strength, neptunium solubility decreases in the pH range 10−12 and increases at pH above 12, and both redox potential and $Np(OH)_4$(am) solubility product control soluble neptunium concentrations at neutral pH and Eh between −0.2 and 0.3. These relationships are important for effective nuclear waste package design, such as including cement as an engineered barrier and evaluating impacts of discharged solutions on natural waters in release scenarios at nuclear waste storage facilities.

Introduction

Neptunium is an important constituent in nuclear waste and one of the most problematic actinides for long-term storage of nuclear waste. While the initial neptunium concentration in spent nuclear fuel is relatively small (0.03%), its concentration increases with time due to the radioactive decay of ^{241}Am ($t_{1/2}$ = 432.7 years). Because of its long half-life (2.14 × 10^6 years), ^{237}Np will become the major contributor to the radiation inventory of nuclear waste repositories after about 100 000 years. The critical role of neptunium in nuclear waste disposal and risk assessments attracts great attention to its geochemical behavior.

The valence state of redox-sensitive radionuclides, such as neptunium, primarily defines the geochemical reactions of these elements. Solubility-limited concentrations, complexation reactions in solutions, sorption onto minerals, and colloid formation differ considerably among the oxidation states. Neptunium ions may exist in the III, IV, V, VI, and even VII valence states (*1*), but only the IV, V, and VI states are relevant for natural environments (*1*−*3*). Aqueous neptunium speciation is dominated by the pentavalent cation, NpO_2^+, under a wide range of environmental conditions. Since Np(V) solid phases are relatively soluble and Np(V) aqueous species do not easily sorb on common minerals, Np(V) is very mobile in the environment. Tetravalent neptunium exists under reducing conditions such as those expected at some nuclear waste disposal sites. Np(IV) solids are less soluble than those of Np(V), and the high tendency for Np(IV) to form aqueous complexes produces strong interactions with the geomatrix. Np(VI) is not important under most environmental conditions and is stable only in highly oxidizing solutions.

Accurate thermodynamic data are key to reliable modeling of the geochemistry of natural aqueous systems. Despite numerous reviews of actinide chemistry and their thermodynamics (*2*−*13*), few studies focus on neptunium geochemistry (*14*−*18*) and the relevant thermodynamic data (*3, 14, 17*). The thermodynamic data compilation of Lemire (*14*) is widely used to model neptunium geochemistry and is, for example, resident in databases used by geochemical codes such as EQ3NR (*19*) and The Geochemist's Workbench (*20*). Many of these thermodynamic data (*14*) are based on extrapolation and estimation and include species which have not been verified to exist in aqueous systems. In addition, experimental data published in the previous 15 years have superseded much of the data in Lemire (*14*). We assemble a thermodynamic model for the dynamic control of soluble neptunium concentrations by solid phase solubility and system redox potential that incorporates recent advances in neptunium chemistry. The updated model focuses on the IV and V states, the two most important valence states for neptunium in natural aqueous systems. We then apply this revised model to environmental issues of neptunium geochemistry and nuclear waste storage and disposal facilities, including radionuclide mobility and design of nuclear waste packages.

Analysis of Thermodynamic Data

The neptunium species most relevant to natural waters of low to moderate ionic strength are the aqueous ions and oxide, hydroxide, and carbonate compounds in solution and solid state (*2*). Sulfate, phosphate, fluoride, chloride, and nitrate solid phases and solution complexes are generally not important in these natural waters (*2, 3, 21, 22*). In this paper, we compile thermodynamic data for the aqueous ions, oxides, hydroxides, and carbonates and calculate the Gibbs free energy of formation, $\Delta_f G°_{298}$, from data corrected for ionic strength at standard conditions. The results are summarized in Table 1. A detailed discussion of the thermodynamic data is attached as Supporting Information. Only data published in peer-reviewed journals are used. We use the specific ion-interaction theory (S.I.T.) (*23*) to correct ion activity coefficients for ionic strength since few Pitzer parameters are available for the Np(IV) species. The available S.I.T. and Pitzer ion-interaction parameters are listed in the Supporting Information.

Neptunium Aquo Ions. The $\Delta_f G°_{298}$ of NpO_2^+ is calculated from the standard potential for the NpO_2^+/NpO_2^{2+} couple and the $\Delta_f G°_{298}$ of NpO_2^{2+} (*5*). We averaged S.I.T.-corrected standard potentials for the NpO_2^+/NpO_2^{2+} couple (*24, 25*) to obtain a standard potential of 1.161 ± 0.014 V (V) and used this value to derive $\Delta_f G°_{298}$ for NpO_2^+ (Table 1). The $\Delta_f G°_{298}$

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TABLE 1. Thermodynamic Stability Constants and $\Delta_f G°_{298}$ Values (Species in Bold) for Environmentally Relevant Np(IV) and Np(V) Compounds[a]

reaction	log $K°$ or log $\beta°$	$\Delta_f G°_{298}$ (kJ mol^{-1})	source
Aqueous Species			
NpO_2^{2+}		-795.8 ± 5.4	(*5*)
NpO_2^{+}		-907.9 ± 5.8	(*24, 25*)
Np^{4+}		-491.1 ± 9.5	(*26, 27*)
$NpO_2^+ + 3H^+ = Np^{4+} + 0.25O_2(g) + 1.5H_2O(l)$	-10.7 ± 2.0		
$NpO_2^+ + OH^- =$ **$NpO_2OH(aq)$**	2.7 ± 0.2	-1080.6 ± 5.9	(*33*)
$NpO_2^+ + 2OH^- =$ **$NpO_2(OH)_2^-$**	4.35 ± 0.15	-1247.3 ± 5.8	(*33*)
$NpO_2^+ + 2OH^- + CO_3^{2-} =$ **$NpO_2(OH)_2(CO_3)^{3-}$**	7.1 ± 0.8	-1791.0 ± 7.4	(*46, 53*)
$NpO_2^+ + OH^- + 2CO_3^{2-} =$ **$NpO_2(OH)(CO_3)_2^{4-}$**	6.0 ± 0.6	-2155.4 ± 6.7	(*46, 53*)
$NpO_2^+ + CO_3^{2-} =$ **$NpO_2CO_3^-$**	4.81 ± 0.15	-1463.3 ± 5.8	(*46*)
$NpO_2^+ + 2CO_3^{2-} =$ **$NpO_2(CO_3)_2^{3-}$**	6.55 ± 0.23	-2001.3 ± 5.9	(*46*)
$NpO_2^+ + 3CO_3^{2-} =$ **$NpO_2(CO_3)_3^{5-}$**	5.54 ± 0.19	-2523.5 ± 5.9	(*46*)
$Np^{4+} + H_2O =$ **$NpOH^{3+}$** $+ H^+$	-0.4 ± 0.7	-726.0 ± 10.3	(*36, 37*)
$Np^{4+} + 4H_2O =$ **$Np(OH)_4(aq)$** $+ 4H^+$	-10 ± 1	-1382.7 ± 11.1	(*35*)
$Np^{4+} + 5CO_3^{2-} =$ **$Np(CO_3)_5^{6-}$**	33.9 ± 2.6	-3324.6 ± 11.3	(*23*)
$Np^{4+} + 4CO_3^{2-} =$ **$Np(CO_3)_4^{4-}$**	35.1 ± 2.6	-2803.1 ± 11.4	(*23, 47*)
Solid Phases			
$NpO_2(OH)$ (am) $= NpO_2^+ + OH^-$	-8.77 ± 0.09	-1115.3 ± 5.8	(*33, 59, 60*)
$NpO_2(OH)$ (cr) $= NpO_2^+ + OH^-$	-9.48 ± 0.16	-1119.3 ± 5.8	(*33, 59, 60*)
Np_2O_5 (s) $+ 2H^+ = 2NpO_2^+ + H_2O$	5.2 ± 0.8	-2023.3 ± 12.4	(*55*)
$NaNpO_2CO_3 \cdot 3.5H_2O$(s) $= Na^+ + NpO_2^+ + CO_3^{2-}$	-11.06 ± 0.17	-2591.0 ± 5.9	(*59, 60*)
$Na_3NpO_2(CO_3)_2$(s) $= 3Na^+ + NpO_2^+ + 2CO_3^{2-}$	-14.28 ± 0.24	-2831.0 ± 5.9	(*59, 60*)
$KNpO_2CO_3$(s) $= K^+ + NpO_2^+ + CO_3^{2-}$	-13.6 ± 0.7	-1796.0 ± 7.1	(*57*)
$K_3NpO_2(CO_3)_2$(s) $= 3K^+ + NpO_2^+ + 2CO_3^{2-}$	-15.9 ± 0.7	-2902.0 ± 7.1	(*57*)
$Np(OH)_4$(am) $+ 4H^+ = Np^{4+} + 4H_2O$	1.5 ± 0.3	-1431.3 ± 9.7	(*35*)
NpO_2(s) $+ 4H^+ = Np^{4+} + 2H_2O$	-9.9 ± 1.7	-1021.8 ± 2.5	(*64, 65*)
Auxiliary Aqueous Species			
$H_2O(l)$		-237.2 ± 0.1	(*67, 68*)
OH^-		-157.3 ± 0.1	(*67, 68*)
CO_3^{2-}		-528.0 ± 0.1	(*67, 68*)
HCO_3^-		-586.9 ± 0.1	(*67, 68*)
Na^+		-261.9 ± 0.1	(*67, 68*)
K^+		-282.5 ± 0.1	(*67, 68*)

[a] $\Delta_f G°_{298}$ values of auxiliary species used in the calculations are also provided (*67, 68*). The degree sign (°) indicates the thermodynamic standard state. Uncertainties listed for $\Delta_f G°_{298}$ of neptunium compounds result from the propagation of error (*92*) in converting from log $K°$ or log $\beta°$ to $\Delta_f G°_{298}$.

of Np^{4+} is determined from the standard potential for the Np^{4+}/NpO_2^+ couple and the $\Delta_f G°_{298}$ of NpO_2^+. We applied the S.I.T.-based correction factor of the analogue plutonium system (*26*) to the formal potential of Cohen and Hindeman (*27*) to obtain a standard potential of 0.596 ± 0.078 V and used this value to derive $\Delta_f G°_{298}$ for Np^{4+} (Table 1).

Neptunium Hydroxide Complexes. Two Np(V) hydroxo complexes, $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$, have been shown to exist in carbonate-free aqueous systems (*28–33*). We adopt the formation constants for $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ reported by Neck et al. (*33*) (Table 1) due to their consistency with results from other solubility studies (*28, 32*).

The potential presence of oligomeric and/or polymeric species, $[M(OH)_n]_m$, and the low solubility of amorphous solid Np(IV) oxides or hydroxides may explain the reported inconsistencies in available Np(IV) data. The uncharged species $Np(OH)_4(aq)$ is the most important Np(IV) hydroxo complex in carbonate-free solutions at pH greater than 4 (*3*). We use both the solubility product for $NpO_2 \cdot xH_2O$, log $K_s° = 1.5 \pm 0.3$, and the experimentally determined neptunium solubility of $10^{-8.3}$ mol kg^{-1} at pH above 7 (*34, 35*) to determine log $\beta°_{14}$ (Table 1). We average the available $NpOH^{3+}$ formation constants at standard conditions (*36, 37*) to obtain log $\beta°_{11}$ (Table 1). $Np(OH)_5^-$ (*34*) as well as $Np(OH)_2^{2+}$ and $Np(OH)_3^+$ are rejected as valid or significant species due to the absence of reliable experimental evidence.

Neptunium Carbonate Complexes. Structural (*38*) and thermodynamic data (*39–46*) for the predominant Np(V) carbonato complexes, $NpO_2(CO_3)_n^{1-2n}$ ($n = 1-3$), have been determined. Since published thermodynamic data for all three complexes are in good agreement, we adopt the formation constants reported by Neck et al. (*46*) (Table 1).

Little reliable thermodynamic data are available for Np(IV) carbonato complexes. We assume that Np(IV) carbonate speciation is dominated by the complexes $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ by analogy to the U(IV) carbonate system (*23*). We do not adopt formation constants for the complexes $Np(CO_3)_n^{4-2n}$ ($n = 1-3$) due to lack of evidence for their existence and stability. In the absence of reliable thermodynamic data for $Np(CO_3)_5^{6-}$, we estimate its $\Delta_f G°_{298}$ by correcting the formation constant of $U(CO_3)_5^{6-}$ (*23*) by the difference in $\Delta_f G°_{298}$ between Np^{4+} and U^{4+}. We then apply the stepwise formation constant for $U(CO_3)_5^{6-}$ (*23, 47*) to log $\beta°_{105}$ to estimate the formation constant of $Np(CO_3)_4^{4-}$ (Table 1).

Carbonate complexation and hydrolysis may occur in parallel to form mixed hydroxo-carbonato complexes. While pure Np(IV) hydroxo and carbonato complexes have been sufficient to interpret most Np(IV) solubility experiments, there is evidence for the existence of mixed Np(IV) hydroxo-carbonato complexes (*48*). Although we strongly believe in the formation of mixed hydroxo-carbonato species, we do not adopt data on Np(IV) due to the lack of species characterization. In contrast, spectroscopic evidence shows that mixed Np(V) hydroxo-carbonato complexes exist in basic carbonate-containing solutions (*49–52*), and apparent formation constants have been reported for two species (*53*). We estimate the thermodynamic formation constants of $NpO_2(OH)_2(CO_3)^{3-}$ and $NpO_2(OH)(CO_3)_2^{4-}$ from Neck et al.

(*53*) using S.I.T. ion-interaction parameters for $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ (*46*) (Table 1).

Neptunium Solid Phases. In the absence of carbonate, NpO_2OH and Np_2O_5 are the stable Np(V) solid phases (*28, 33, 54, 55*), while $MNpO_2CO_3 \cdot xH_2O$ and $M_3NpO_2(CO_3)_2$ ($M = Na^+, K^+$) are the stable solid phases in carbonate-bearing systems, depending on the alkali carbonate concentration (*40, 43, 46, 56−58*). We use two solubility products for NpO_2OH which occurs as an amorphous, "fresh" precipitate that changes to a more stable, "aged" state with increasing ionic strength and time (*33, 59, 60*) (Table 1). We accept the solubility product of Np_2O_5 determined from over- and undersaturation solubility studies (*55*). This solubility product agrees well with the value calculated from calorimetry data (*54*) and reduces the value reported by Lemire (*14*) by approximately 4 orders of magnitude. We average the solubility products for $NaNpO_2CO_3 \cdot 3.5H_2O$ and $Na_3NpO_2(CO_3)_2$ determined from solubility experiments (*59, 60*) and adopt the recently reported solubility products for $KNpO_2CO_3$ and $K_3NpO_2(CO_3)_2$ (*57*) as first estimates.

$Np(OH)_4(am)$ and NpO_2 are the stable Np(IV) solid phases in systems low in carbonate (*3, 34, 35, 55*), while Np(IV) carbonates or hydroxo-carbonates are expected to form in carbonate-containing systems. Unfortunately, no reliable thermodynamic or crystallographic data are available for solid Np(IV) (or for the analogue Pu(IV)) carbonates or hydroxo-carbonates of general formula $Np(OH)_m(CO_3)_n^{4-m-2n}$ (*61−63*). We adopt the solubility product of $Np(OH)_4(am)$ determined by Rai et al. (*35*) (Table 1). The $\Delta_f G°_{298}$ for NpO_2 (*4, 14, 35*) is calculated from $\Delta_f H°_{298}$ (*64*) and $\Delta_f S°_{298}$ (*65*) of NpO_2.

Geochemical Modeling

Geochemical modeling and thermodynamic calculations were performed with EQ3NR (*19*) and the Geochemist's Workbench Version 3.0 (*20*) using the b-dot extended Debye−Huckel model (*66*) for activity coefficient calculations. The Geochemist's Workbench was used to construct Eh-pH diagrams, whereas both codes were used to calculate solubility curves and speciation diagrams. The same results were obtained for both codes within experimental uncertainties. The neptunium data resident in the most recent standard thermodynamic database that we use for these codes, com.V8.R6 (dated December 1996 and available by anonymous FTP from Lawrence Livermore National Laboratory), are adapted from Lemire (*14*). Updated thermodynamic data of the most important Np(IV,V) compounds as listed in Table 1 replace existing data in com.V8.R6, while the data for minor neptunium species (i.e. chlorides, nitrates, sulfates) remain as present in com.V8.R6. Neptunium species with no experimental evidence for formation or that lack characterization, as discussed in the Supporting Information, are deleted from com.V8.R6. The values of $\Delta_f G°_{298}$ for water constituents and ligands (*67, 68*) that we use to calculate the $\Delta_f G°_{298}$ of neptunium complexes and solids reported in Table 1 were extracted from the com.V8.R6 database. We use these data, rather than thermodynamic data available from other sources (*69−71*), to maintain internal consistency within the database used by the geochemical codes.

To evaluate the environmental implications of the updated neptunium thermodynamic data, we model and predict the solubility of neptunium solids and the aqueous speciation of neptunium in two groundwaters that represent a range of compositions commonly found in nature (Table 2). Both groundwaters, J-13 and UE-25p#1, occur at Yucca Mountain, NV, site of a potential repository for high-level nuclear waste in the United States. Water from well J-13 is a reference water for the unsaturated zone near the proposed emplacement area. It is typical of many groundwaters in the Western United States with a fairly low ionic strength and carbonate and hydroxide as predominant potential ligands (Table 2). Well UE-25p#1 samples a carbonate aquifer underlying the proposed emplacement horizon. The ionic strength and total carbonate content of UE-25p#1 water is approximately 1 order of magnitude higher than J-13 water. We modeled both groundwaters as closed carbonate systems. The composition of low ionic strength waters proximate to many international sites being studied as nuclear waste repositories are bracketed by the composition of J-13 and UE-25p#1. Examples include a typical groundwater from Gorleben, Germany, with low concentrations of dissolved organic carbon and a nonsaline Swedish reference groundwater from crystalline rocks (Table 2). Most of the international programs will exploit low groundwater flow rates and solubility control of radionuclides in a reducing environment to maintain long-term isolation from the accessible environment. In contrast, the U.S. program proposes to locate a repository within the oxidizing unsaturated zone at Yucca Mountain. In release scenarios for this type of a repository, oxidizing water within the vadose zone penetrates the repository and subsequently infiltrates underlying groundwater that flows to the accessible environment. Our geochemical models span the range of Eh conditions expected for both types of repositories. Consequently, geochemical models for neptunium in J-13 and UE-25p#1 groundwaters are applicable to proposed high-level nuclear waste repositories worldwide as well as at the Yucca Mountain site.

TABLE 2. Analyses of J-13 and UE-25p 1 Waters from the Yucca Mountain Area (*93*), a Groundwater from Gorleben, Germany, with Low DOC Concentration (7.8 mg C L^{-1}) (*94*), and a Swedish Reference Groundwater from Crystalline Rocks (*3*)

species	J-13 (mM)	UE-25p 1 (mM)	Gohy-1011 (mM)	SKI-90 (mM)
Ca	0.29	2.19	1.65	0.50
Mg	0.072	1.31	0.022	0.0823
Na	1.96	7.43	0.8	1.39
K	0.136	0.34		0.0256
Li	0.009	0.046		
Fe	0.0008	<0.002	0.0002	0.0018
Mn	0.00002	0.002		
Al	0.0010	0.003		
SiO_2	1.07	0.62	0.27	0.068
F^-	0.11	0.18		0.14
Cl^-	0.18	1.04	1.7	0.42
SO_4^{2-}	0.19	1.34	0.6	0.042
NO_3^-	0.16	<0.002	0.022	
pH	7.0	6.7	7.9	8.2
Eh (volts)	0.430	0.360		−0.3
total carbonate	2.81	15.31	1.4	2.0
alkalinity (mequiv/L)	2.3	11.44		

Results and Discussion

Aqueous tetravalent and pentavalent neptunium predominate the Eh-pH diagram of both J-13 and UE-25p#1 waters (Figure 1). In neutral solution with redox potentials below approximately 0 V, Np(IV) is the predominant solution species with the tetrahydroxo complex, $Np(OH)_4(aq)$, most stable above pH 5 in both groundwaters (Figure 1). It replaces $Np(OH)_5^-$, the previously predicted predominant Np(IV) species at moderate to high pH (*6, 8, 14*).

Among the minor ligands in natural waters, such as F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- (Table 2), only fluoride significantly affects neptunium speciation (species distribution of 1% or more) (Figure 2). The Np(IV) fluoride complex NpF_2^{2+} is the predominant species at low pH. Under reducing conditions at higher pH, NpF_2^{2+} is overcome by the strong hydrolysis reactions of Np(IV). For phosphate complexation to compete effectively with carbonate and hydroxide com-

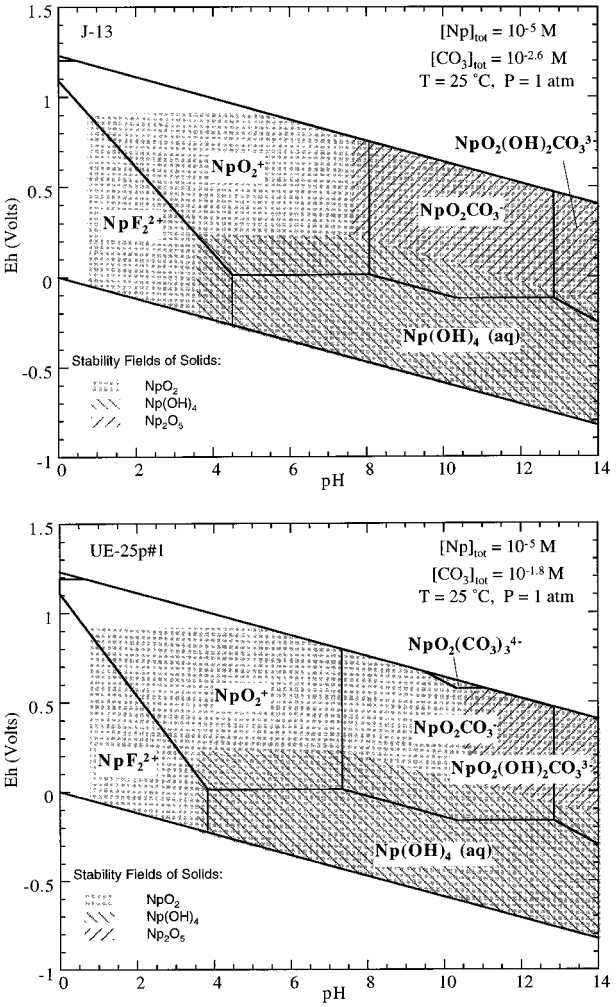


FIGURE 1. Eh-pH diagrams for neptunium (10^{-5} mol kg^{-1}) in J-13 and UE-25p#1 waters. Boundaries for stability fields of aqueous species are shown by solid lines. Stability fields of solid phases are shown by shading.

plexation reactions, the phosphate concentration has to be above 10^{-4} mol kg^{-1} (*73*). However, phosphate concentrations reported for groundwater, surface water, and seawater average about 0.01−0.5 ppm and rarely exceed 1 ppm (*3, 21, 72*).

Neptunyl(V) and its aqueous complexes are the important species at oxidizing conditions in both groundwaters (Figure 1). The neptunyl ion, NpO_2^+, at pH less than 8 and the Np(V) monocarbonato complex, $NpO_2CO_3^-$, in the pH range between 8 and 13 predominate speciation. The biscarbonato complex, $NpO_2(CO_3)_2^{3-}$, is significant only in carbonate-enriched water in the pH range 10−12 (Figure 2). The mixed hydroxo-carbonato complex, $NpO_2(OH)_2(CO_3)^{3-}$, is important above pH 13, whereas $NpO_2(OH)(CO_3)_2^{4-}$ may be ignored. Since the thermodynamic formation constants of $NpO_2(OH)_2(CO_3)^{3-}$ and $NpO_2(OH)(CO_3)_2^{4-}$ are estimated, the stability of these complexes may vary by approximately one logarithmic concentration unit. With lower stability of the Np(V) hydroxo-carbonato complexes, the importance of $NpO_2(CO_3)_2^{3-}$ increases in the pH range 10−12, and the bishydroxo complex, $NpO_2(OH)_2^-$, becomes the important aqueous species at pH greater than 13. The triscarbonato complex, $NpO_2(CO_3)_3^{5-}$, is not important even in the carbonate-enriched water of UE-25p#1 (Figure 2).

The presence of either species, $NpO_2(OH)_2(CO_3)^{3-}$ and $NpO_2(OH)_2^-$, increases the soluble neptunium concentrations in alkaline solutions of pH greater than 12. The distribution

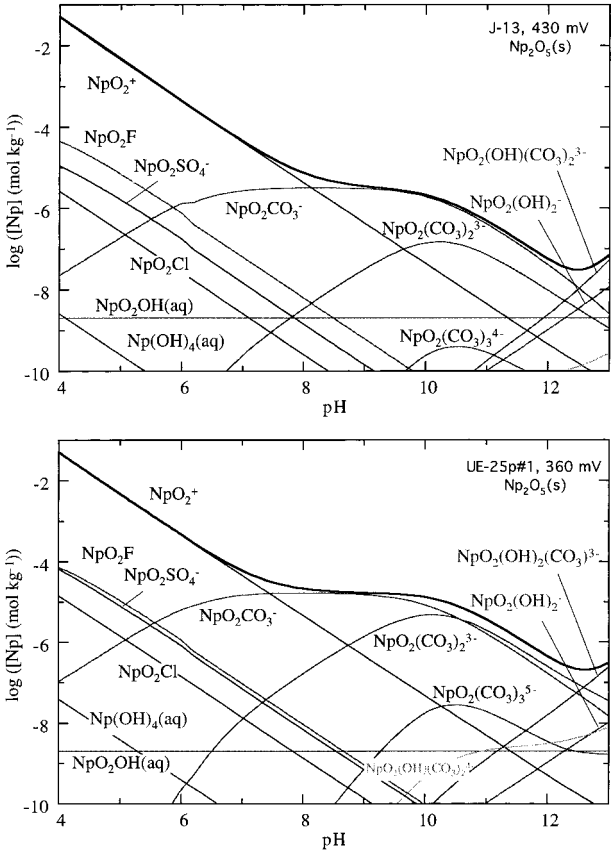


FIGURE 2. Calculated concentrations of neptunium species in J-13 and UE-25p#1 waters at Np_2O_5 saturation and 25 °C.

of aqueous species at high pH is not important for most natural waters (pH 6−9), even those that infiltrate the cementatious waste packaging expected at nuclear waste repositories (*74*−*76*). However, the evolution of the cement/groundwater system will be affected by the hydrogeologic conditions of the system. Studies of cement−water equilibria suggest that the pH of the infiltrating water peaks at approximately 12 and subsequently decreases over time to a pH of approximately 9 or 10 (*77*). In low permeability media, alkaline conditions may persist through the buffer capacity of $Ca(OH)_2$(s) (pH 12−13) over geologic time scales. In addition, speciation at high pH is important for certain alkaline waste systems at DOE sites such as Hanford (*78, 79*).

The Np(VI) carbonate species $NpO_2(CO_3)_3^{4-}$ appears within the water stability range in the carbonate-rich UE-25p#1 water under alkaline conditions (Figure 1). The stability field for this complex is small, and, therefore, it is judged to be unimportant in geochemical systems of low salinity. In the near field of a nuclear waste repository in geologic salt formations, however, Np(VI) species such as $NpO_2(CO_3)_3^{4-}$ may be more relevant due to radiolysis effects (*80*).

Equilibrium thermodynamics predicts NpO_2 as the predominant stable solid for most Eh and pH conditions that span the stability range of both J-13 and UE-25p#1 groundwaters (Figure 1). To date, however, NpO_2 has not been identified as the precipitate in solubility experiments conducted with natural waters. Np(V) (*55*) and amorphous Np(IV) solid phases (*35*) precipitated instead. It is to note that kinetic data for the Np(V)−Np(IV) redox reaction in solution or solid state are scarce and thus not included in any geochemical model. Thus, NpO_2 may be the thermodynamically stable neptunium solid phase for geologic, but not the shorter laboratory, time scales. It is important,

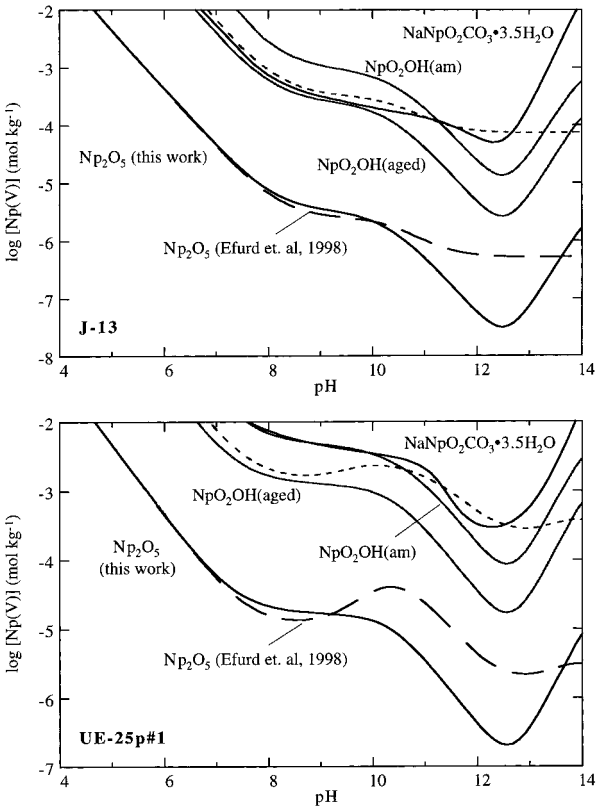


FIGURE 3. Calculated solubility curves for Np_2O_5, $NpO_2(OH)$ (aged), and $NaNpO_2CO_3 \cdot 3.5H_2O$ in J-13 (0.43 V) and UE-25p#1 (0.36 V) waters at 25 °C. The short-dashed lines represent the solubility of Np_2O_5 using the value from Lemire (*14*).

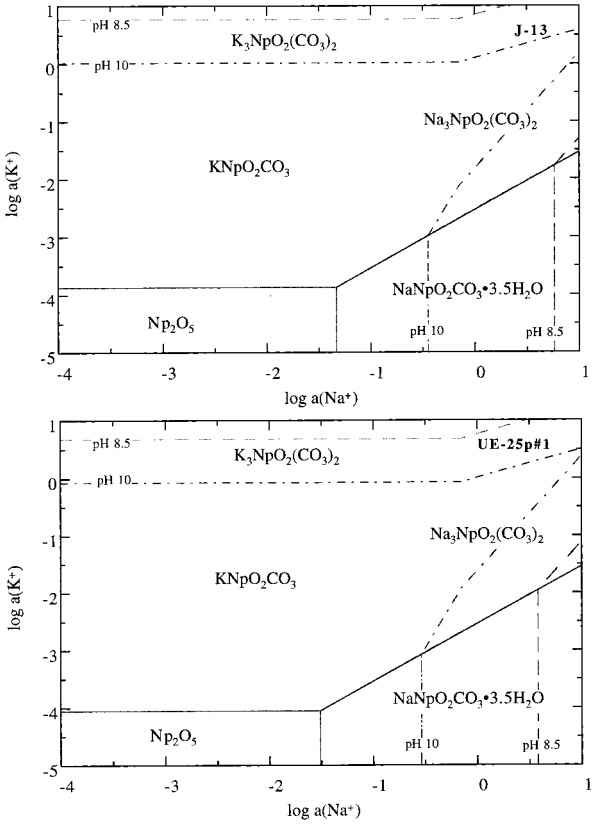


FIGURE 4. Stability regions of Np(V) solid phases in J-13 and UE-25p#1 waters at Eh = 0.4 V at 25 °C and pH 7 (solid field boundaries). Changes in stability of these phases at pH 8.5 (- - -) and 10 (-·-·-) are also illustrated.

therefore, to understand the stability of the metastable phases because these solids will initially control soluble neptunium concentrations. In the absence of NpO_2, Np_2O_5 and $Np(OH)_4$(am) are the stable solids in both groundwaters at oxidizing and reducing conditions, respectively (Figure 1).

Solubility curves calculated for the Np(V) solid phases Np_2O_5, $NpO_2(OH)$ (aged), and $NaNpO_2CO_3 \cdot 3.5H_2O$ suggest that Np_2O_5 is the solubility controlling phase in both J-13 and UE-25p#1 water (Figure 3). Amorphous $NpO_2(OH)$ solid is less stable than its crystalline counterpart, a relationship consistent with fundamental thermodynamic principles. Efurd et al. (*55*) first noted that the data of Lemire (*14*) reversed this relationship. Despite the predominance of Np(V) carbonato complexes in aqueous solution of moderate to high pH (Figure 2), the Np(V) carbonate solid-phase $NaNpO_2CO_3 \cdot 3.5H_2O$ is more soluble, and thus less stable, than Np_2O_5. The predicted neptunium solubility of 3×10^{-5} mol kg^{-1}, based on Np_2O_5 as the solubility controlling phase, matches very well the experimentally determined value (4.7×10^{-5} mol kg^{-1} (*55*)). The Np_2O_5 solubility curve predicted here displays a minimum at approximately pH 12, in contrast to the flat solubility curves determined with the data of Lemire (*14*) and Efurd et al. (*55*). This minimum is due to the reduced stability of NpO_2OH(aq) and the presence of mixed hydroxo-carbonato species of Np(V) at high pH. The stability constant we adopt for NpO_2OH(aq) is 2 orders of magnitude less than the value reported by Lemire (*14*), and credible stability constants for mixed hydroxo-carbonato species of Np(V) were not reported until recently (*53*). The decrease in soluble neptunium concentrations above pH 10 and the solubility minimum at pH 12 are important for effective nuclear waste package design, such as including cement as an engineered barrier and the mixing of highly alkaline solutions with aquifers in release scenarios at nuclear waste sites.

An understanding of Np(V) alkali carbonate solid-phase stability is important for evaluating the neptunium geochemistry in alkaline or increased ionic strength waters. For the sodium and potassium content that characterizes J-13, UE-25p#1, and many other natural waters, Np_2O_5 is the stable solid phase under oxidizing conditions and a wide range of pH (Figures 1, 3, and 4). Sodium concentrations must exceed approximately 0.05 molar at neutral pH to stabilize $NaNpO_2CO_3 \cdot 3.5H_2O$ (Figure 4), a prediction consistent with experimental data (*55, 81*). At pH 10 and millimolar carbonate concentrations, $[Na^+]$ greater than 0.5 molar is required to stabilize $Na_3NpO_2(CO_3)_2$. High $[Na^+]$ as characteristic of brines stabilize $Na_3NpO_2(CO_3)_2$ at a more neutral pH (approximately 4 molar $[Na^+]$ at pH 8.5). In contrast to the sodium system, lower concentrations of potassium stabilize $KNpO_2CO_3$ (Figure 4), but similar amounts of potassium stabilize $K_3NpO_2(CO_3)_2$ (approximately 1 molar $[K^+]$ at pH 10 and 5 molar $[K^+]$ at pH 8.5, Figure 4). Soluble neptunium concentrations in waters containing increased quantities of sodium, potassium, and/or carbonate are 2−3 orders of magnitude higher than in waters in which Np_2O_5 is stable (Figure 3). Such waters may include brines and water impacted by alkaline waste at nuclear waste storage sites such as Hanford (*79*).

The source term of high-level nuclear waste (i.e. spent fuel rods) is a reducing environment that is predicted to minimize access of radionuclides to nature. Potential release scenarios, however, include radionuclide migration to the far field within oxidizing aquifers. These aquifers may change the valence state, and thus the geochemical behavior, of redox-sensitive radionuclides such as neptunium. In an aqueous system of neutral pH and low carbonate content, such as water from well J-13, a redox potential of 0.25 V stabilizes Np_2O_5 (Figure 5). The solubility product of this

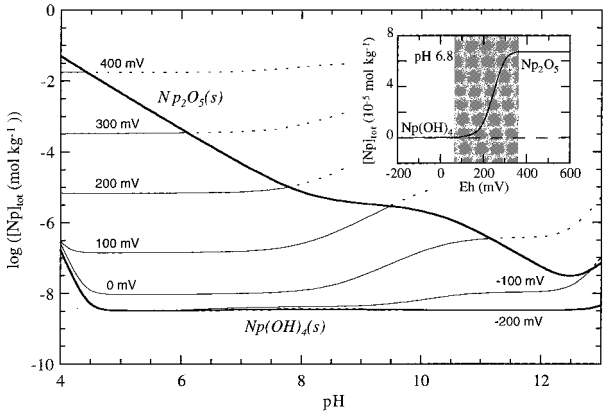


FIGURE 5. Calculated neptunium concentrations in J-13 water at 25 °C as a function of Eh using Np_2O_5 and $Np(OH)_4$(am) as solubility limiting solids. The inset designates regions of solubility control versus redox control (shaded area).

stable solid-phase controls soluble neptunium concentrations even at redox potentials greater than 0.25 V. Under reducing conditions (below 0.10 V), $Np(OH)_4$(am) limits the neptunium concentration to approximately $10^{-8.5}$ molar. In the intermediate range of redox potential between approximately 0.10 and 0.25 V, the soluble neptunium concentration varies between the solubility limits set by $Np(OH)_4$(am) and Np_2O_5 (shaded area in Figure 5 inset). Within this Eh range, the total Np(IV) concentration in solution remains constant at approximately $10^{-8.5}$ molar and is controlled by the solubility of $Np(OH)_4$(am). Increasing the redox potential to approximately 0.25 V favors the successive formation and increasing predominance of Np(V) in solution while maintaining Np(IV) in the solid state. A phase transformation to the Np(V)-bearing solid occurs at about 0.25 V. $Np(OH)_4$(am) is orders of magnitude less soluble than Np_2O_5 only at pH less than 11. At higher pH, the solubility of neptunium is nearly independent of the redox potential and the neptunium oxidation state. Thus, at the pH (5−8) and redox potential (approximately −0.1 to +0.3 V) of most groundwater systems (*21*), soluble neptunium concentrations are mainly controlled by the redox potential of the aquifer. In the specific case of J-13 water at Yucca Mountain, the pH is near-neutral, and the measured redox potential ranges from 0.10 to 0.43 V (Table 2). At 0.10 V, $Np(OH)_4$(am) is predicted to be the stable neptunium solid phase. Consequently, the total Np(IV) content is approximately $10^{-8.5}$ molar as controlled by $Np(OH)_4$(am) solubility (Figure 5). However, the total soluble neptunium concentration, approximately 10^{-7} molar, is slightly greater because the redox potential of J-13 groundwater stabilizes additional Np(V) in solution. In contrast, Np_2O_5 is stable at 0.43 V, and its solubility product fixes the total soluble neptunium concentration at approximately $10^{-4.5}$ molar. Clearly, evaluation of radionuclide mobility in geochemical environments proximate to nuclear waste repositories must account for soluble radionuclide concentrations that are controlled by the redox potential of the system as well as the nature and solubility of the solid phases.

The uranium oxide matrix of spent nuclear fuel contains approximately 0.02−0.1% neptunium as NpO_2 (*82*). In contrast, our geochemical models use thermodynamic data for pure neptunium solids to conservatively assess the environmental implications of neptunium. A more realistic conceptual model may consider the coprecipitation of neptunium and (less soluble) secondary phases within the waste package or the repository host rock. These phases may include ferric oxide hydrates, phosphates, carbonate minerals, and secondary uranyl minerals (including uranyl oxide hydrates and uranyl silicates). Experimental and field evidence suggests that uranium coprecipitates with ferric oxide hydrates (*83*, *84*), whereas X-ray absorption spectroscopy suggests that Np(V) does not coprecipitate with goethite (*85*). Instead, it sorbs on the goethite surface as a mononuclear species with a geometry similar to NpO_2^+ (*85*). Other studies suggest that thorium, uranium, plutonium, and americium coprecipitate with calcite and aragonite (*86*−*88*) and that radionuclides may be incorporated into secondary uranyl minerals (*89*−*91*). Should neptunium coprecipitate with secondary phases, it will be the solubility of these secondary phases, not the solubility of pure neptunium solids, that determines the mobility of neptunium. Consequently, identification and characterization of secondary phases containing neptunium is essential to our understanding of neptunium environmental geochemistry and nuclear waste disposal issues and represents an important area for future study.

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Supporting Information Available

Additional text describing selection of thermodynamic data and a table of available S.I.T. and Pitzer ion-interaction parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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