Combined Studies Pertaining to the Solubility of Neptunium in Oxidizing Aqueous Systems

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**Introductory Commentary**
(T.J. Wolery)

The report combines two separate studies dealing with different aspects of the behavior of neptunium in oxidizing aqueous systems. The goal of both studies is to obtain a better understanding of what would control the concentration of neptunium in oxidizing groundwaters upon release from a geologic high-level waste repository. [237]Np has a very long half-life, and consequently tends to appear as a component of concern in long-term dose calculations. Part A examines the formation of NpO_2 [Np(IV) oxide] from aqueous Np(V) under oxidizing conditions, using elevated temperature as a means of accelerating putative slow kinetics. According to thermodynamic data, NpO_2 should be the stable Np solid, even though Np is generally thought to be mainly some form of Np(V) under oxidizing conditions. The first observed precipitation of this solid from aqueous solution under any conditions is reported. This result suggests, but does not prove, that long-term very slow formation of NpO_2 might be an important long-term control on neptunium migration. Even at 200°C, the kinetics can be sluggish on typical experimental time scales. Though not reported in Part A, a similar situation may exist for Pu, and NpO_2 and PuO_2 may potentially form solid solutions. Under reducing conditions, UO_2 might join in. Part B examines the interaction of Np(V) with the uranium mineral schoepite. Is neptunium incorporated into the crystal structure as a solid-solution component, or does it just sorb onto the mineral surface? The results presented here suggest that it basically just sorbs onto the surface, which would be a less effective process in limiting neptunium migration. This is not a surprising result, as schoepite is a relatively simple solid of U(VI). There is no obvious means to compensate for the charge difference between U(VI) and Np(V) without introducing unfavorable energetics. However, the results reported here do not rule out a possible substitution of Np(VI) in schoepite or other U(VI) minerals. This may be significant especially at higher pH, where the formation of Np(VI) species is more favored relative to Np(V). Both studies reported here suggest that there is much to learn about the actual long-term behavior of Np in the geologic environment.

Part A. Experimental Investigation of the Formation of NpO₂ at Elevated Temperature
(K.E. Roberts, T.J. Wolery, and C.E.A. Palmer)

A.1. Summary

Recent experimental investigations measuring the solubility of neptunium in aqueous solutions relevant to Yucca Mountain led to calculated potential doses exceeding proposed long-term regulatory limits. In contrast, calculations using previously accepted thermodynamic data at 25° C obtained from the literature (Lemire 1984) showed that the observed aqueous Np concentrations were substantially supersaturated with respect to the rather insoluble solid NpO_2. In order to test the validity of the accepted thermodynamic data, neptunium solubility experiments were performed at 200° C to accelerate possible slow reaction kinetics in the hopes of observing the following chemical reaction:

$$NpO_2^+ + {}^1\!/_2 \; H_2O = NpO_{2(s)} + H^+ + {}^1\!/_4 \; O_2$$
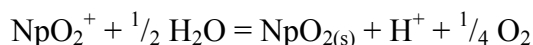
Solubility experiments were performed by introducing ionic NpO_2^+ to very dilute solutions of NaCl with initial pH values ranging from 6 to 10. Decreases in the aqueous Np concentrations and solution pH were observed in all experiments consistent with the above reaction, and steady state was reached within a few months. The precipitates that formed were collected and analyzed by x-ray powder diffraction (XRD), x-ray absorption spectroscopy (XAS), and scanning electron microscopy (SEM). In all cases, the solids were identified as high purity crystals of NpO_2 (Palmer, Wolery et al. 1998; Wolery, Palmer et al. 1998; Roberts 1999).

A.2. Introduction

In order to help determine the suitability of Yucca Mountain as a site for a potential geologic nuclear waste repository, among other activities, the Yucca Mountain Project has engaged in an effort to understand and document the aqueous geochemistry of the site as well as the stability of various radionuclides that may be accessible to the environment should all barriers engineered to contain the high-level nuclear waste fail.

Of the radioactive components in spent nuclear fuel, four actinides (uranium, neptunium, plutonium, and americium) are the most important because of the quantity contained within the spent fuel and the relatively long half lives associated with these radionuclides (Silva and Nitsche 1995). Of these four actinides, the radioisotope [237]Np is of particular concern. With its lengthy half-life of 2.14 million years, [237]Np will be the major contributor to potential radiation doses in the accessible environment because it will be the predominant isotope in the repository inventory 10,000 to 1,000,000 years after permanent closure of the repository (Sassani 1998). The potential radiological hazard for long disposal times associated with the long half-life of this isotope is compounded by the fact that neptunium most often is found in the 5+ oxidation state when in aqueous solution. Actinides in the 5+ oxidation state tend to be the most soluble in aqueous solution and the least sorbing on geologic media. Therefore, in evaluating the "worst-case-scenario" for an underground repository, where the man–made containment has been breached, or has ultimately failed, and the groundwater of the geologic medium controls the chemistry of the waste components, those actinides that exist in the 5+ oxidation state will

potentially be the most concentrated and the least retarded by sorption on the host rock (Wilson 1996).

Values of neptunium release were initially based on the assumption that crystalline NpO_2 would be the solubility-limiting solid phase in the repository environment. Based on thermodynamic data critically reviewed by R.J. Lemire (Lemire 1984), this leads to a calculated aqueous neptunium concentration that is well below 10^{-13} M for conditions associated with Yucca Mountain.

An initial "Total System Performance Assessment" was prepared in 1992 for the Yucca Mountain Site Characterization Project in order to calculate the possible release of Np from the potential waste repository (Barnard, Wilson et al. 1992). The assessed Np release was determined to be on the order of 10^{-9} to 10^{-8} M based on data obtained in several spent nuclear fuel dissolution studies (Bruton and Shaw 1987; Wilson and Bruton 1989; Wilson 1990a; Wilson 1990b).

If studies like these were indicative of the potentially attainable levels of soluble neptunium in aqueous solution, then radiation dose calculations based on these levels in the environment would fall below safety limits proposed by the EPA. However, to supplement thermodynamic data in the database used by EQ3/6, neptunium solubility studies were performed by H. Nitsche et al. at the Lawrence Berkeley National Laboratory in support of performance assessment for the proposed geological repository at Yucca Mountain (Nitsche, Gatti et al. 1993; Nitsche, Roberts et al. 1993; Nitsche, Roberts et al. 1994). Neptunium solubility studies were performed from supersaturation by introducing aqueous neptunium in the 5+ oxidation state to groundwaters found at Yucca Mountain. Experiments were performed at 25 and 60° C in J-13 and UE25-p #1 waters and also at 90° C in J–13 water. Aqueous Np concentrations were monitored, and steady state was demonstrated by achieving constant aqueous Np concentrations over time. Total aqueous Np concentration ranged from micromolar to millimolar in the pH and temperature ranges that were investigated (pH values 6, 7, and 8.5 and temperatures of 25, 60, and 90° C). The precipitated Np solid phases were characterized by x–ray powder diffraction and were found to be, in almost all cases, sodium neptunium(V) carbonates, $Na_xNpO_2(CO_3)_y$ where x and y varied. In one elevated temperature experiment, neptunium(V) oxide, Np_2O_5, was also observed to precipitate.

The aqueous Np concentrations reported by Nitsche et al. posed a potentially serious problem with regard to the suitability of the proposed geological repository at Yucca Mountain. When using the relatively high solubilities reported by Nitsche et al. in a new set of performance assessment calculations for the potential release rates of radionuclides over extended periods of time, levels of Np release now yielded possible concentrations up to a level of 10^{-2} M (Andrews, Dale et al. 1994; Wilson, Gauthier et al. 1994).

To address this potential issue, further modeling calculations using EQ3/6 were performed using existing thermodynamic data at 25° C. The results showed that the experimentally observed $\sim 10^{-3}$ M Np concentrations in J-13 groundwater at near-neutral pH reported by Nitsche et al. were grossly supersaturated with respect to the formation of NpO_2, yet these modeling efforts were unable to explain why NpO_2 did not form (Wolery, Palmer et al. 1995). It was suggested that the formation of NpO_2 was kinetically limited and not observed because of the relatively short experimental duration of several months.

Since the work of Nitsche et al., additional solubility experiments of a very similar nature conducted for over a year at the Los Alamos National Laboratory by W. Efurd et al. resulted in slightly, but not significantly, lower Np solubilities for the same solution conditions.(Efurd, Runde et al. 1998) In this case, the investigators identified the solid phases as dineptunium pentoxide, Np_2O_5.

The solid phases observed in both the Nitsche et al. and Efurd et al. experiments were all Np(V) solid phases. If it could be demonstrated that NpO_2 will precipitate, given time, from an aqueous solution of initially Np(V), then the solubility of Np at extended time periods may in fact be governed by the much more insoluble Np(IV) oxide solid phase. Accordingly, the precipitation of NpO_2 from aqueous NpO_2^+ at 200° C was studied. If this precipitation could be observed experimentally, it would contribute to a better understanding of the ambient-temperature equilibrium distribution of the Np(IV) and Np(V) solution and solid species.

A.3. Experimental

A concentrated NpO_2^+ stock solution was purified by ion exchange chromatography and verified by absorption spectrophotometry. Distilled, deionized water filtered through a Milli-Q water filtration system was used in all experiments. All chemical reagents were high purity and used as received. The initial aqueous Np concentration for the elevated temperature experiments was chosen to be 10^{-4} M so as to avoid precipitation of Np(V) solid phases. Initial pH values ranged from 6 to 10, and the background electrolyte was ~0.001 M NaCl. Solution pH was measured using semi-micro, glass combination pH electrodes from Orion Research after calibration with NIST traceable buffers at pH 4 and 7 obtained from VWR Scientific. Aqueous and solid Np species were separated by filtration through microcentifugal filtration devices containing a nylon membrane with a pore size of 0.2 μm. Aqueous Np concentrations in filtered samples were determined by gamma spectroscopy using a low-energy germanium crystal counting system calibrated with a NIST Standard Reference Material Np-237 source. Both Teflon-lined stainless steel and passivated titanium metal reaction vessels were used in the elevated temperature experiments. Solids were collected by centrifugation, dried, and then transferred to quartz capillaries. The capillaries were sealed and examined by XRD using a Debye-Scherrer camera. The subsequent film was digitized using Filmscan software from Materials Data Inc. on a personal computer with a scanner. The diffraction patterns were compared with the Powder Diffraction File (PDF) database from the International Center for Diffraction Data (ICDD). XAS data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) by measuring the Np L_{III} absorption edge on wiggler beamline 4-1. SEM measurements were made at Argonne National Laboratory (ANL) using a Topcon ABS 60 scanning electron microscope.

All elevated temperature solubility experiments were conducted in an air atmosphere in order to provide an oxidizing environment (~20 % oxygen) for the aqueous neptunium.

A.4. Results and Discussion

Initial solubility experiments were small scale, ~15 mL, and were conducted primarily to see if a decrease in soluble Np would occur at 200° C in 2 to 4 weeks. Four small scale experiments were conducted and a decrease in soluble Np from the initial concentration of 10^{-4} M at pH 6 accompanied by the formation of a finely divided solid phase was observed each case. The small-scale experiments were conducted in both Teflon and titanium metal reaction vessels, and

the results obtained in the two different types of vessels were similar. The amount of solids produced was very small, but the solids were collected for analysis by XRD.

While these solids were being analyzed by XRD, additional, larger-scale experiments, 80 mL, were initiated to monitor aqueous Np concentrations over time. Figure A.1 shows the aqueous neptunium concentrations as a function of time for the 80 mL neptunium solubility experiments. Figure A.2 shows the measured pH values as a function of time for the same experiments. The data are listed in Table 1. In all cases, the steady-state aqueous Np concentrations dropped to $\sim 10^{-5}$ M or lower in the steady-state pH range of 4 to 9. As the aqueous Np concentrations decreased, a decrease in the solution pH was also observed consistent with the chemical reaction listed in the summary. Periodic adjustment (titration) of the solution pH by addition of dilute NaOH can be seen in the three, higher pH experiments as periodic increases that decrease with reaction time. This was done to broaden the pH range investigated. Once some stability in pH over time was observed, pH adjustment ceased. The possibility of measuring the production of oxygen to again support the reaction listed in the summary was discussed, but no efforts were made. This was due to the fact that these solubility experiments were all conducted under an atmosphere of air, and quantification of the production of such a small amount of molecular oxygen in the presence of a 20 % initial concentration seemed impossible.

Upon reaching steady state, the larger scale experiments were terminated and the solids that formed were collected for analysis. Figure A.3 shows a representative XRD pattern for the solids obtained. It was clear from the diffraction patterns that the solids collected were crystalline NpO_2. Here again the results support the reaction listed in the summary.

In order to compliment/confirm the solids analysis by XRD, a solid sample was then examined by XAS at SSRL in comparison with standards of ionic NpO_2^+ and solid NpO_2. Again, the results from both x-ray absorption near-edge structure (XANES are shown in Figure A.4) as well as the extended x-ray absorption fine structure (EXAFS are shown in Figure A.5) indicated that the solid material obtained in the elevated temperature experiment was structurally identical to the reference NpO_2 solid and not the NpO_2^+ aqueous ion.

For even further confirmation, this sample was then shipped to ANL for examination by SEM. Figure A.6 and A.7 show micrographs of this solid material. According to C.B. Finch and G.W. Clark(Finch and Clark 1970) the structure of crystalline neptunium(IV) dioxide takes on one of two forms of the fluorite structure, cubic or octahedral, depending on the level of impurities contained within the crystal lattice. In their publication, they report on the formation of crystalline neptunium dioxide from "high temperature solutions." In their case, high temperature solutions meant PbF_3-B_2O_3-NpO_2 and Li_2O-MoO_3-NpO_2 solutions at 1250-1350° C in contrast to this work in aqueous solution at 200° C. Neptunium dioxide that formed from solutions of PbF_3-B_2O_3-NpO_2 took on a cubic (100) growth habit, whereas, the neptunium dioxide that formed from solutions of Li_2O-MoO_3-NpO_2 took on an octahedral (111) growth habit. The authors attributed this difference in habit formation to the level of impurities contained within the fluorite structure of the NpO_2 that formed. In the case of the PbF_3-B_2O_3-NpO_2 solution growth of NpO_2, levels of contaminant Pb and B were on the order of 1000 and 200 PPM, respectively. In the case of the Li_2O-MoO_3-NpO_2 solution growth of NpO_2, levels of contaminant Mo and Li were on the order of 10 and 2 PPM, respectively. The octahedral growth habit was therefore attributed to the growth of the relative pure form of the NpO_2.

A.5. Conclusions

This result seems rather significant for the Yucca Mountain Project because previous experimental efforts in measuring the solubility of aqueous Np(V) spanning the near-neutral pH range, using temperatures ranging from ambient to 90° C, and reaction times of up to a year have all failed to produce steady-state solubilities below 10^{-5} M. Also, the solids obtained in the previous experiments were *all* Np(V) solid phases, which appear to be more soluble than NpO_2.

It was the simple goal of this research effort to try to eliminate any kinetic barrier to the precipitation of NpO_2 from a solution initially containing Np(V). Even under an oxidizing atmosphere, this precipitation reaction was observed when allowing the system to react at 200°C.

This result does not conclusively answer the high versus low Np solubility question for the Yucca Mountain Project, as it remains unknown whether long-term growth of NpO_2 would actually occur at lower temperature in a real geologic system. Further work is required to answer that question.
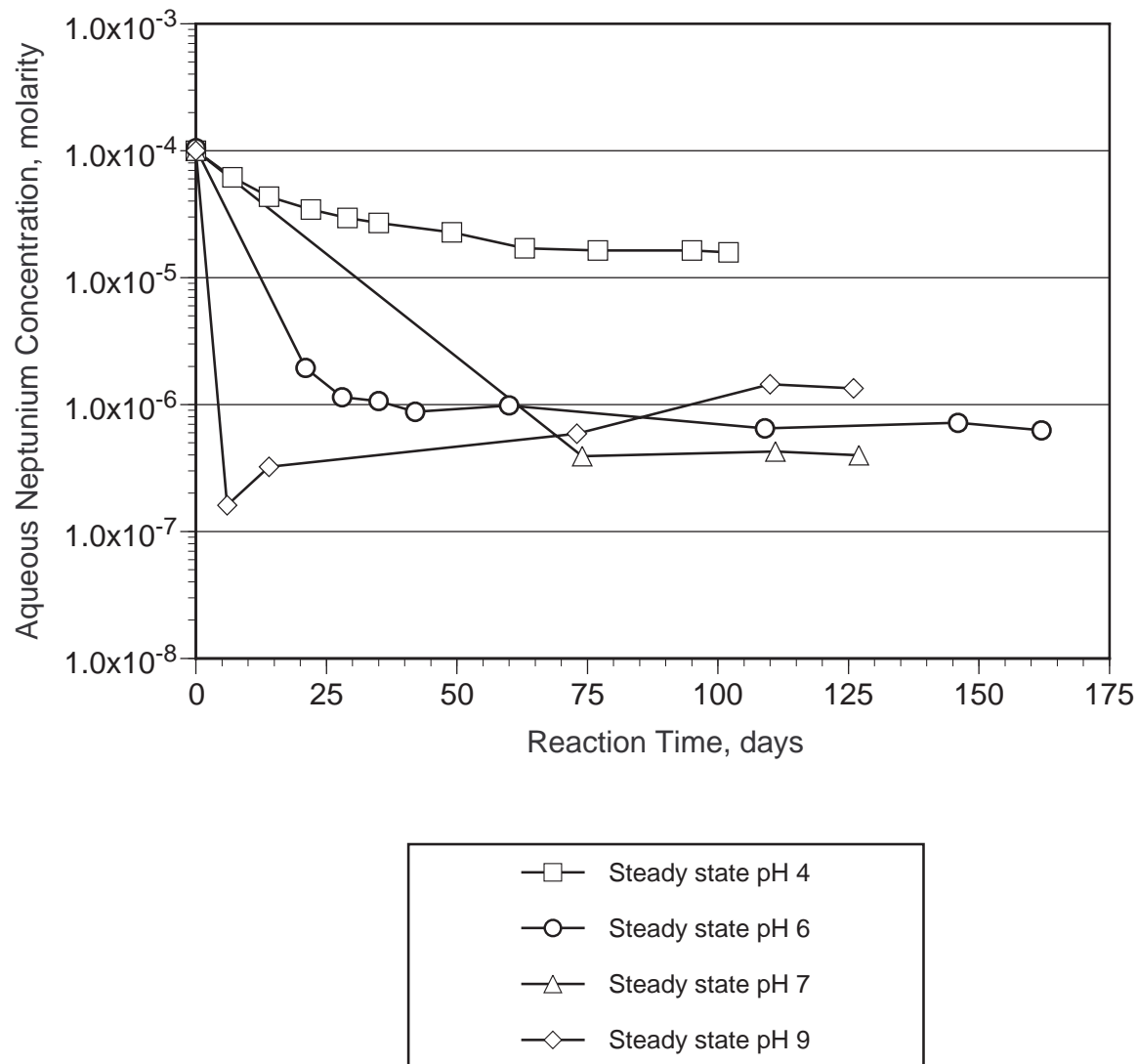
Figure A.1.   Aqueous neptunium concentrations as a function of time the larger scale solubility experiments.
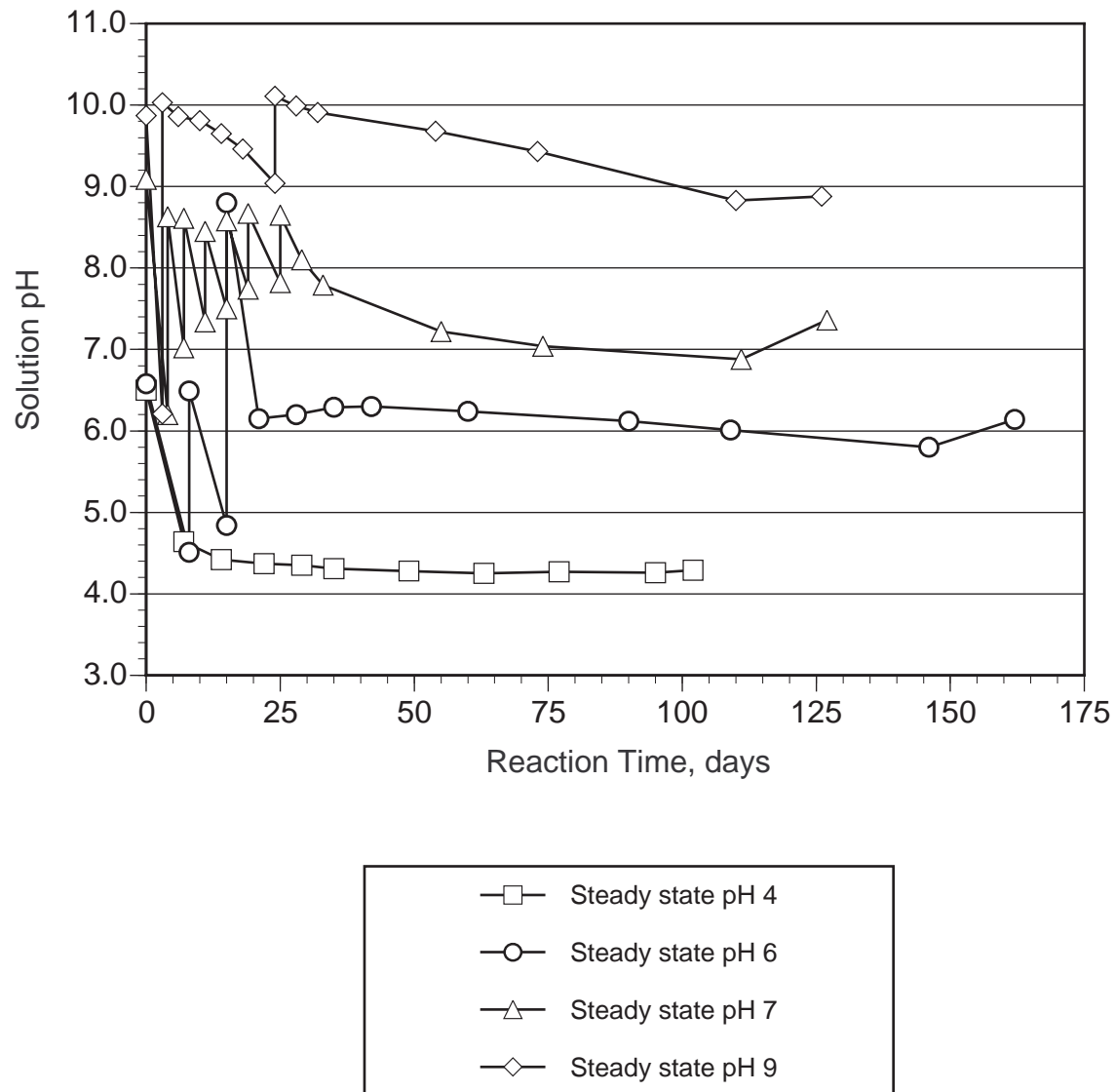
Figure A.2.   Measured pH as a function of time for the larger scale solubility experiments.

Table A.1. Values for the reaction time, solution pH, and neptunium concentrations for the larger scale solubility experiments.

Days	pH	Np Conc. (M)	Days	pH	Np Conc. (M)
0	6.50	1.000E-04	0	6.58	1.045E-04
7	4.64	6.153E-05	8	4.51	
14	4.42	4.342E-05	8	6.49	
22	4.37	3.440E-05	15	4.84	
29	4.35	2.959E-05	15	8.80	
35	4.31	2.701E-05	21	6.15	1.941E-06
49	4.28	2.271E-05	28	6.20	1.141E-06
63	4.25	1.705E-05	35	6.29	1.064E-06
77	4.27	1.634E-05	42	6.30	8.761E-07
95	4.26	1.634E-05	60	6.24	9.833E-07
102	4.29	1.583E-05	90	6.12	
			109	6.01	6.481E-07
			146	5.80	7.166E-07
			162	6.14	6.255E-07

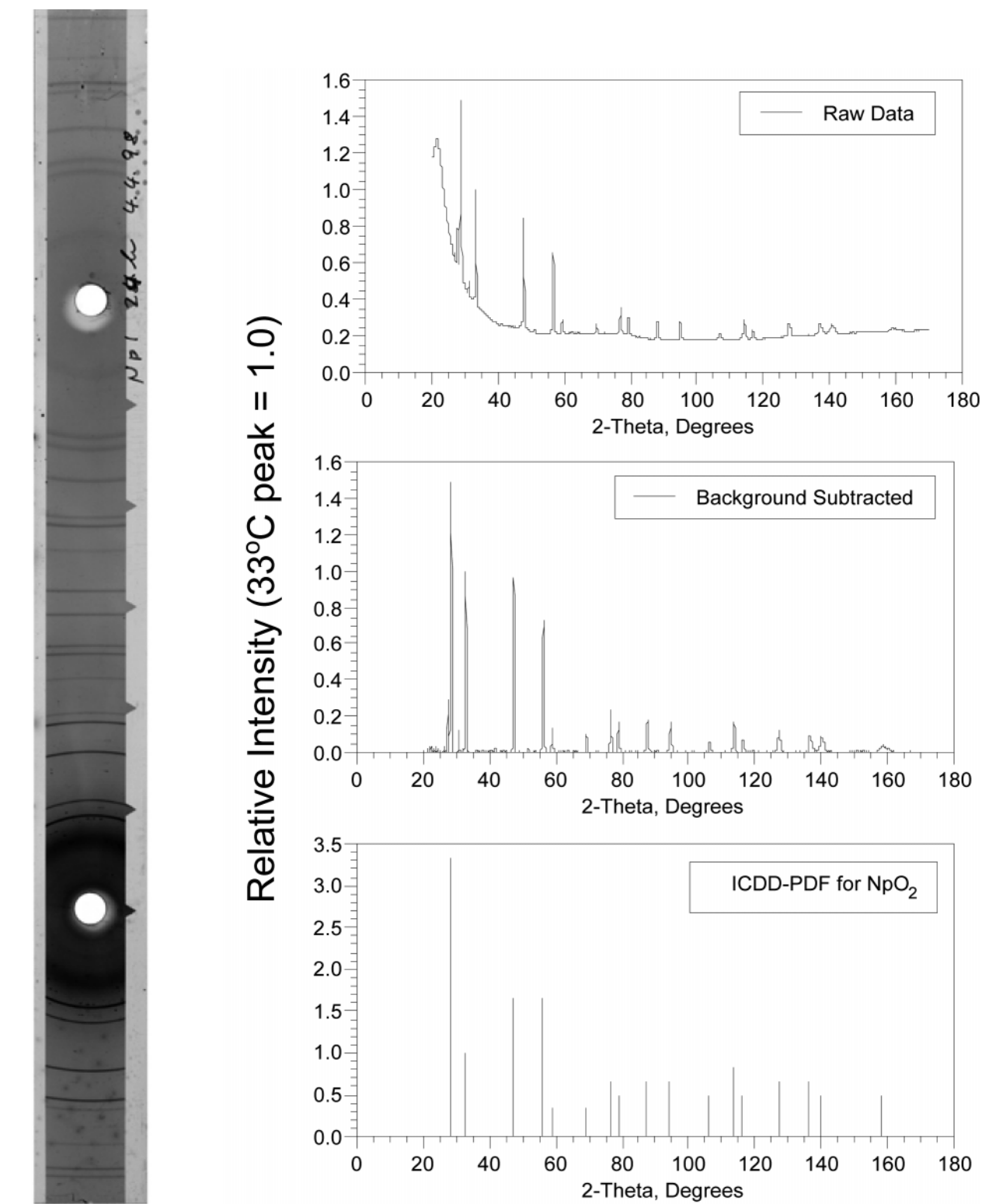| Days	pH	Np Conc. (M)	Days	pH	Np Conc. (M)
0	9.09	1.000E-04	0	9.87	1.000E-04
4	6.20		3	6.21	
4	8.63		3	10.03	
7	7.02		6	9.86	1.605E-07
7	8.61		10	9.81	
11	7.34		14	9.65	3.230E-07
11	8.45		18	9.46	
15	7.50		24	9.04	
15	8.58		24	10.11	
19	7.74		28	9.99	
19	8.67		32	9.91	
25	7.82		54	9.68	
25	8.65		73	9.43	5.900E-07
29	8.10		110	8.83	1.444E-06
33	7.79		126	8.88	1.344E-06
55	7.22				
74	7.04	3.922E-07			
111	6.88	4.262E-07			
127	7.36	3.989E-07			

Figure A.3.   X-ray powder diffraction film of sample "Np1" and plots showing digitized intensity as a function of diffraction angle, 2-theta.
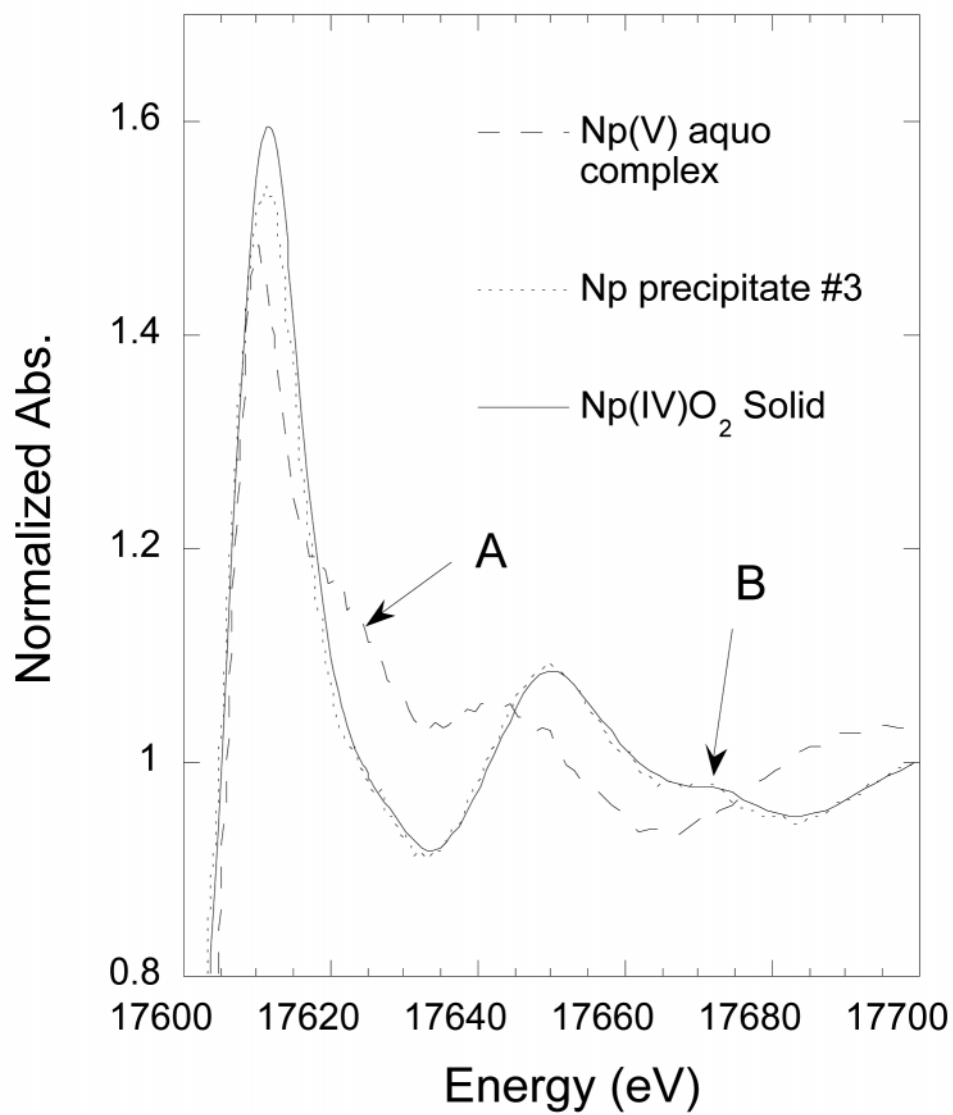
Figure A.4.   The neptunium L_{III} x-ray absorption near edge structure for the aqueous dioxo-neptunium(V) cation, NpO_2^+, (dashed line), crystalline neptunium(IV) dioxide, NpO_2, (solid line), and the solid material obtained in the solubility experiment at pH 4 (dotted line).
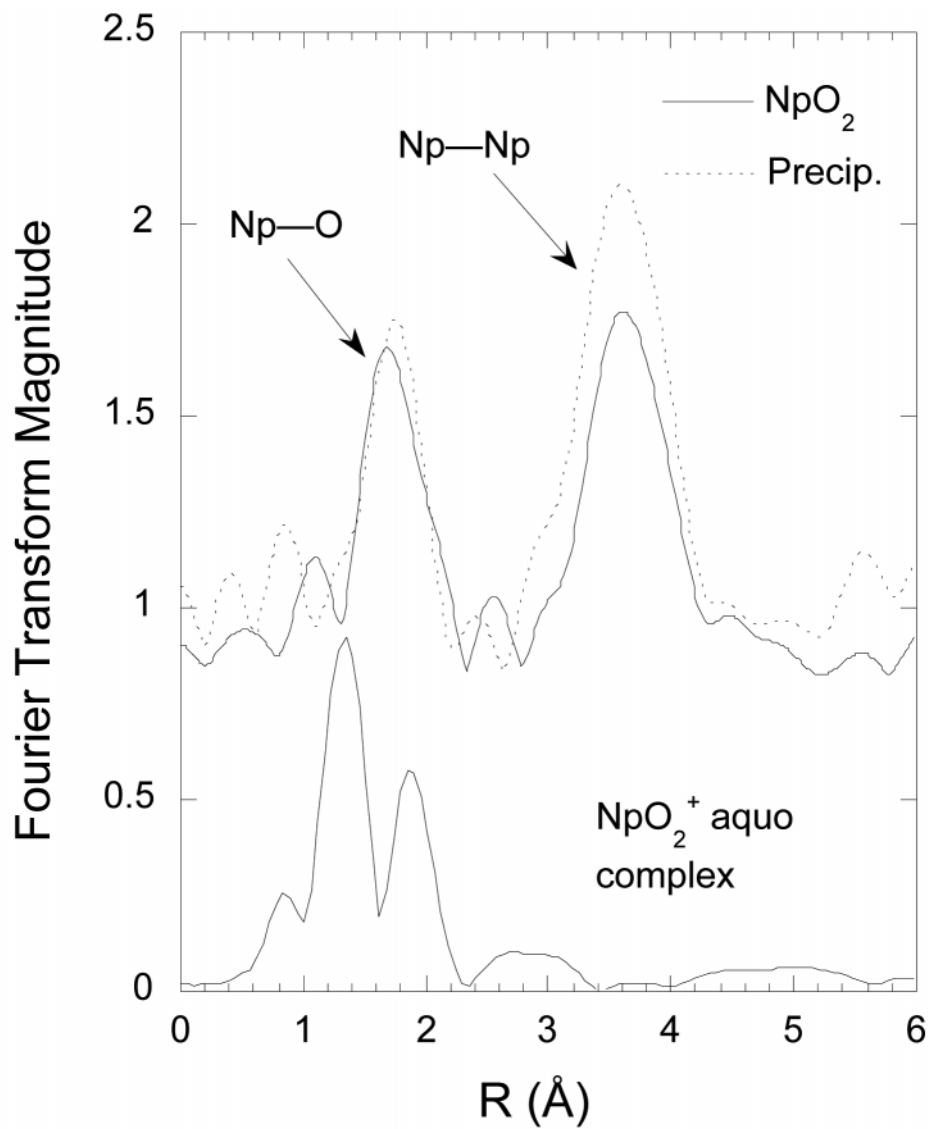
Figure A.5. The neptunium L_{III} extended x-ray absorption fine structure for crystalline neptunium(IV) dioxide, NpO_2, (solid line) and the solid material from our experiment (dotted line) are shown at the top of the plot. Also shown in the plot (bottom, solid line) is the neptunium L_{III} extended x-ray absorption fine structure for the aqueous dioxo-neptunium(V) cation, NpO_2^+.
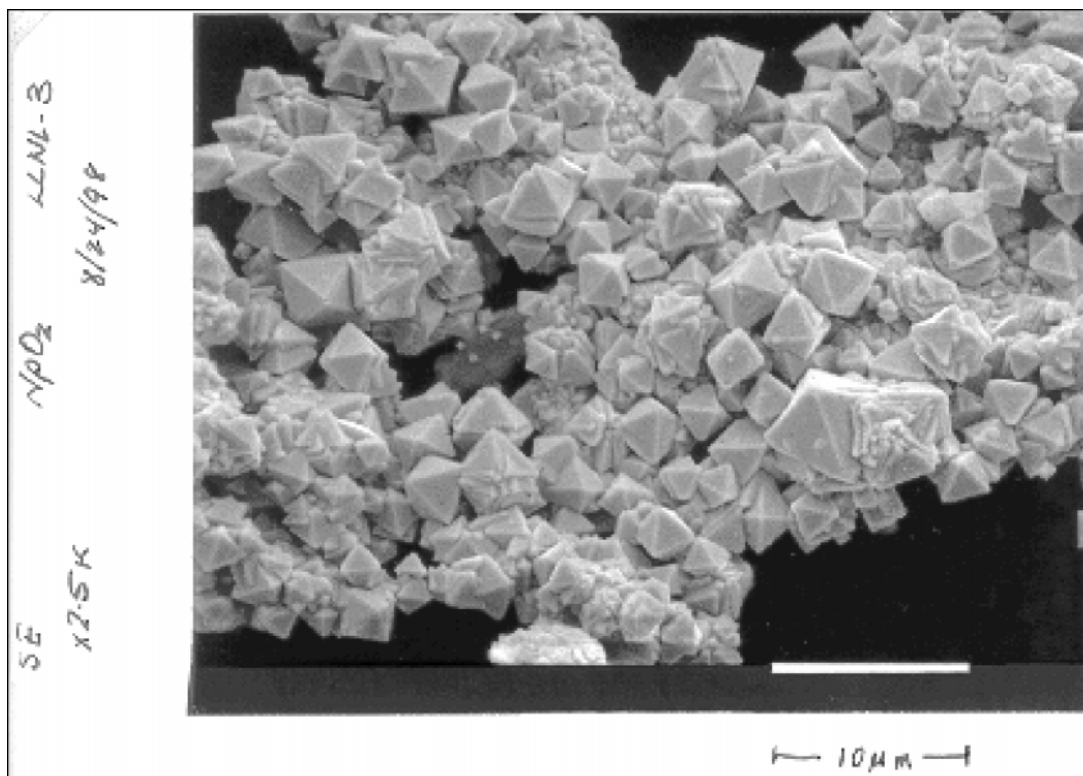
Figure A.6.   Scanning electron micrograph of the solid Np3a from the larger scale experiment with a steady-state pH of 4 (white bar = 10 micrometers).
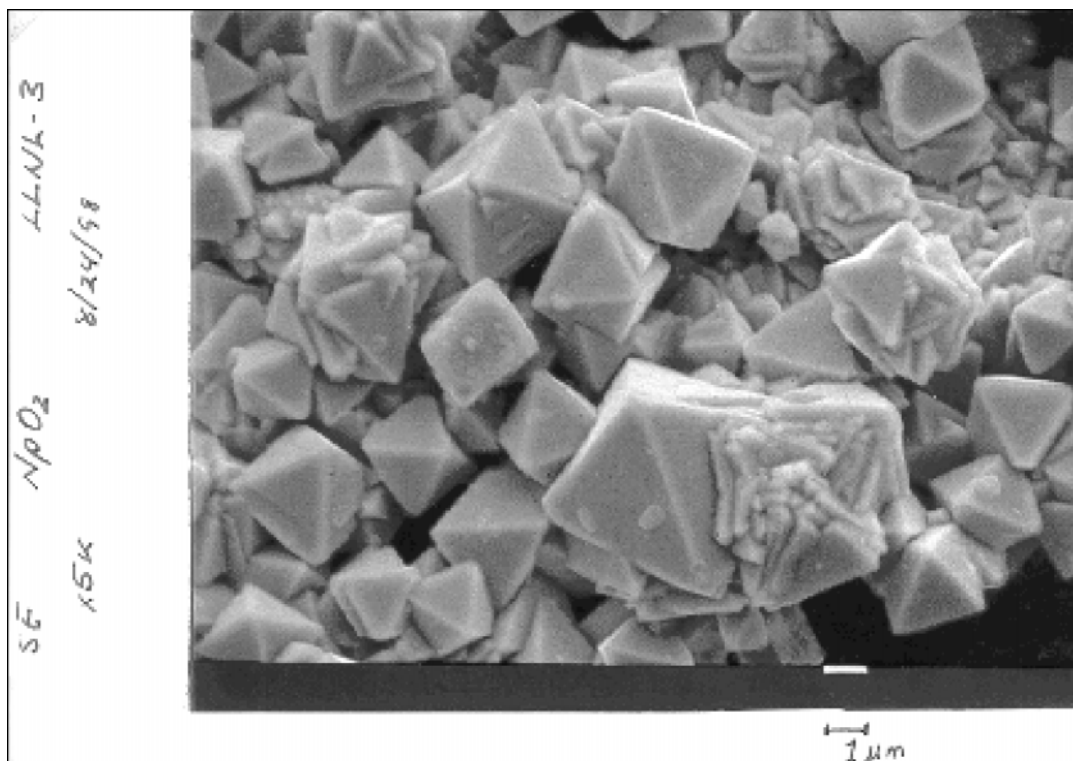
Figure A.7.   Scanning electron micrograph of the solid Np3a (closer up) from the larger scale experiment with a steady-state pH of 4 (white bar = 1 micrometer).

A.6. References

Andrews, R. W., T. F. Dale, et al. (1994). Total System Performance Assessment-1993: An Evaluation of the Potential Yucca Mountain Repository. LAS VEGAS, INTERA, INC.

Barnard, R. W., M. L. Wilson, et al. (1992). TSPA 1991: An Initial Total-System Performance Assessment for Yucca Mountain. Albuquerque, Sandia National Laboratories.

Bruton, C. J. and H. F. Shaw (1987). Geochemical Simulation of the Reaction Between Spent Fuel Waste Form and J-13 Water at 25° C and 90° C. Scientific Basis for Nuclear Waste Management XI, Pittsburg, Materials Research Society.

Efurd, D. W., W. Runde, et al. (1998). "Neptunium and Plutonium Solubilities in a Yucca Mountain Groundwater." Environmental Science & Technology **32**(24): 3893-3900.

Finch, C. B. and G. W. Clark (1970). "High-Temperature Solution Growth of Single-Crystal Neptunium Dioxide." Journal of Crystal Growth **6**(3): 245-8.

Lemire, R. J. (1984). Assessment of the Thermodynamic Behaviour of Neptunium in Water and Model Groundwaters from 25 to 150 degrees C. Chalk River, Ontario, Atomic Energy Canada Ltd.**:** 53.

Nitsche, H., R. C. Gatti, et al. (1993). Measured Solubilities and Speciations of Neptunium, Plutonium, and Americium in a Typical Groundwater (J-13) from the Yucca Mountain Region. Los Alamos, Los Alamos National Laboratory**:** 127.

Nitsche, H., K. Roberts, et al. (1993). Radionuclide Solubility and Speciation Studies for the Yucca Mountain Site Characterization Project.

Nitsche, H., K. Roberts, et al. (1994). Measured Solubilities and Speciations from Oversaturation Experiments of Neptunium, Plutonium, and Americium in UE-25p #1 Well Water from the Yucca Mountain Region. Los Alamos, Los Alamos National Laboratory**:** 95.

Palmer, C. E. A., T. J. Wolery, et al. (1998). Neptunium Solubility: Kinetic or Thermodynamic Control? White Paper. Livermore, Lawrence Livermore National Laboratory.

Roberts, K. E. (1999). Precipitation of Neptunium Dioxide from Aqueous Solution. Chemistry. Stockton, University of the Pacific**:** 169.

Sassani, D. C. (1998). Constraints on Solubility-Limited Neptunium Concentrations for Use in Performance Assessment Analyses. Las Vegas, TRW**:** 26.

Silva, R. J. and H. Nitsche (1995). "Actinide Environmental Chemistry." Radiochimica Acta **70-1**: 377-396.

Wilson, C. N. (1990a). Results from NNWSI Series 2 Bare Fuel Dissolution Tests, Pacific Northwest National Laboratory.

Wilson, C. N. (1990b). Results from NNWSI Series 3 Spent Fuel Dissolution Tests, Pacific Northwest National Laboratory.

Wilson, C. N. and C. J. Bruton (1989). Studies on Spent Fuel Dissolution Behavior Under Yucca Mountain Repository Conditions. Fourth International Symposium on Ceramics in Nuclear Waste Management, American Ceramic Society.

Wilson, M. L., J. H. Gauthier, et al. (1994). Total System Performance Assessment for Yucca Mountain - SNL Second Iteration (TSPA-1993). Albuquerque, Sandia National Laboratories.

Wilson, P. D. (1996). The Nuclear Fuel Cycle : From Ore to Wastes. Oxford ; New York, Oxford University Press.

Wolery, T. J., C. E. A. Palmer, et al. (1995). The Neptunium Solubility Problem in Repository Performance Assessment: A White Paper. Livermore, Lawrence Livermore National Laboratory.

Wolery, T. J., C. E. A. Palmer, et al. (1998). The Hydrothermal Growth Kinetics of Np(IV) Oxide. Presented at the 8th annual Goldschmidt Conference, Toulouse, France, August 30 to September 4.

B. Interaction of Np with U(VI) Hydroxide Solids
(D.A. Wruck, A. Brachmann and C.E.A. Palmer)

B.1. Summary

The distribution of ^{237}Np(V) between aqueous $NaHCO_3$ solutions and U(VI) hydroxide solids was investigated. Equilibrium was approached via two different kinetic pathways: addition of U solids to Np solutions and coprecipitation of U and Np. The two paths resulted in similar equilibrium conditions. The Np distribution ratio was 5-44 mL/g in the pH range 6-8. The results are consistent with adsorption of Np by the solids and provide no evidence of Np incorporation in the bulk solid. According to analyses by infrared absorption spectroscopy and U L_{III} extended X-ray absorption fine structure (EXAFS) spectroscopy, the solid phase in these experiments was synthetic schoepite.

This report is based on experimental data recorded in LLNL YMP controlled scientific notebook #00410.

B.2. Introduction

An understanding of mechanisms controlling the release of radionuclides during corrosion of spent nuclear reactor fuel is essential for the long-term performance analysis of a spent fuel repository. In an oxidizing water, oxidative dissolution of the UO_2 waste form leads to precipitation of U(VI) alteration products such as uranyl oxide hydrates or uranyl silicates (Wronkiewicz et al. 1996). Adsorption or incorporation of impurities by the uranium alteration phases may affect the release rate of certain radioelements (Burns et al. 1997, Quinones et al. 1996, Finn et al. 1996, Buck et al. 1998). Only a few experimental studies of these processes are available. Eu, Am and Cm coprecipitation with Na polyuranates in 5 m NaCl was consistent with spent fuel leaching results in the same medium (Quinones et al. 1996). Sr, Cs and Pu were identified in U(VI) alteration products of spent fuel (Finn et al. 1996).

UO_2^{2+} and NpO_2^+ are linear molecular ions of similar size. If local charge-balancing processes (e.g., parallel uptake of alkali metal cations) occur, then Np(V) may form substitutional impurities in U(VI) phases (Burns et al. 1997). The ratio of Np to U in dehydrated shoepite ($UO_3 \cdot 0.8H_2O$) crystallites formed on spent fuel was observed to be 6 to 12 times larger than the ratio of Np to U in the spent fuel (Buck et al. 1998). However, Np may have been present as an adsorbate, a solid solution component or a microprecipitate in the experiments. The chemical form is important for repository performance assessment, because a strong tendency toward adsorption or solid solution formation can result in aqueous Np concentrations well below the solubility-limited values based on Np(V) solid phases.

The objective of the present work was to investigate Np adsorption or incorporation by U(VI) oxide hydrates in equilibrium with air-saturated aqueous bicarbonate solutions near pH 7. Synthetic schoepite was studied because it is a common alteration phase of spent fuel corrosion and is readily formed as a precipitate and a stable solid under these conditions. Equilibrium was approached via two different kinetic pathways: addition of U solids to Np solutions and coprecipitation of U and Np. Experiments were conducted for Np:U molar ratios up to 5% and equilibration times of several months in order to look for evidence of Np substitution in the bulk solids.

B.3. Experimental Procedure

The ^{237}Np chloride stock solution was prepared by anion exchange followed by precipitation and dissolution of NpO_2OH. Optical absorption spectroscopy over the 400-1400 nm wavelength range indicated $\geq$ 98% of the Np was in the +5 oxidation state (Fahey 1986 pp. 467 and 486.). Alpha spectrometry and low energy (10-310 keV) gamma spectrometry revealed no radioactive impurities except for the ^{233}Pa daughter. Np concentrations were measured using the 29 keV gamma ray. The counting efficiency was determined with a NIST ^{237}Np standard. The U starting material was reagent grade $UO_2(NO_3)_2 \cdot 6H_2O$.

Sample Set I: The solid was prepared by addition of NH_4OH to a uranyl nitrate solution until a stable pH 5.5 was attained. The yellow precipitate was aged for 3 days in the mother liquor, rinsed with deionized water and dried at 30°C. Each sample was prepared by mixing a weighed quantity of about 30 mg solid and 25 mL aqueous $NaHCO_3/NpO_2Cl$ solution. The initial Np concentration was 1.54×10^{-5} or 1.51×10^{-4} M. Samples were equilibrated in closed polycarbonate tubes on an orbital shaker at 23°C for 93 days. Sample pH reached $\pm$ 0.1 unit of the equilibrium value in 10-20 days.

Sample Set II: Aqueous solutions of uranyl nitrate and NpO_2Cl were titrated with NaOH and $NaHCO_3$ to pH 6-8 to form yellow precipitates. After precipitation each sample contained about 34 mg solid and 38 mL liquid. In sample set II, ionic strength was adjusted to 18 mM with $NaClO_4$. The initial Np concentration was 1×10^{-5} or 1×10^{-4} M. The samples were equilibrated in closed polycarbonate tubes on an orbital shaker at 23°C for 116 days.

After equilibration the samples were centrifuged to separate the liquid and solid phases. A portion of each solid was dissolved in aqueous HCl solution, U was determined using the 414 nm optical absorption peak, and Np was determined using the 29 keV gamma ray. The amount of Np per g of solid was calculated from the Np:U molar ratio and a formula weight of 322 g/mole U. The quantity of Np in the liquid was calculated as the initial quantity minus the quantity in the solid. The distribution coefficient K_d was calculated as n_s/n_l, where n_s = moles of Np per g of solid and n_l = moles of Np per mL of liquid.

The solids were prepared for infrared analysis as pressed CsI pellets containing about 1 mg of sample and measured over the wavenumber range 400-4000 cm^{-1} at 4 cm^{-1} resolution using an FTIR spectrometer.

B.4. Results and Discussion: Liquid-Solid Equilibrium

The equilibrium liquid compositions, solid phase Np:U molar ratios and distribution coefficients are listed in Tables 1 and 2. Similar results were obtained for the two different initial conditions, addition of U solids to Np solutions (sample set I) and coprecipitation of U and Np (sample set II). In all cases, the solid phase Np:U molar ratios are too small to clearly demonstrate formation of a solid solution. The results are consistent with Np adsorption by the solids. The average particle size of the solids is approximately 3 μm based on microscopic examination and sedimentation behavior. Reasonable estimates of the density (4 g cm^{-3}) and sorbate surface density (4 nm^{-2}) lead to a solid phase Np:U molar ratio of 10^{-3}, which is consistent with the experimental values.

Table 1. Equilibrium data for sample set I

Sample Number	pH	$[CO_3^{2-}]_{Tot}$ (mM)	Ion.Str. (mM)	[Np] (M)	Solid phase Np:U ratio	K_d (mL/g)
138	6.3	0.89	1.71	1.53×10^{-5}	2.5×10^{-5}	5
140	7.1	0.61	1.01	1.49×10^{-5}	1.5×10^{-4}	32
137	7.2	0.93	1.51	1.48×10^{-5}	1.6×10^{-4}	33
139	7.4	0.69	1.01	1.47×10^{-5}	1.9×10^{-4}	40
136	7.9	0.97	1.01	1.48×10^{-5}	1.7×10^{-4}	37
133	6.5	0.89	1.82	1.47×10^{-4}	1.3×10^{-3}	27
135	7.1	0.62	1.14	1.45×10^{-4}	1.6×10^{-3}	33
132	7.2	0.93	1.63	1.44×10^{-4}	2.0×10^{-3}	44
131	7.4	0.97	1.14	1.46×10^{-4}	1.5×10^{-3}	32
134	7.4	0.70	1.14	1.45×10^{-4}	1.7×10^{-3}	36

Table 2. Equilibrium data for sample set II

Sample Number	pH	$[CO_3^{2-}]_{Tot}$ (mM)	[Np] (M)	Solid phase Np:U ratio	K_d (mL/g)
146	7.0	6.1	1.05×10^{-5}	3.3×10^{-5}	9.7
148	7.7	1.9	9.87×10^{-6}	3.2×10^{-5}	10
150	7.9	2.2	9.63×10^{-6}	2.9×10^{-5}	9.4
143A	7.2	2.1	9.90×10^{-5}	4.6×10^{-4}	14
145	7.6	1.7	1.06×10^{-4}	4.6×10^{-4}	13

The Np distribution coefficients are nearly constant as the aqueous Np concentration is changed by a factor of 10. This supports the use of a simple K_d value to characterize the sorption behavior. The K_d values are in the range 5-44 mL/g over the pH range 6-8. There is no obvious pH dependence in the data. The observed K_d values and the pH behavior are consistent with measurements of Np(V) sorption on various minerals under similar aqueous conditions (Triay et al. 1997). In particular, the interaction of Np(V) with U(VI) hydroxide appears to be most similar to the sorption behavior of Np on non-reducing oxides. The observed variation in the distribution coefficients may be primarily due to variation in the surface area of the solids.

B.5. Results and Discussion: Solid Phases

Similar infrared absorption spectra were obtained for the initial solid of sample set I and the equilibrium solids of both sample sets. A representative spectrum is shown in Figure B.1. The UO_2^{2+} asymmetric stretch is seen as a strong single band at 916-923 cm^{-1}. The observed frequency and absence of splitting are consistent with uranyl solids rather than uranates (Hoekstra and Siegel 1973, Allen et al. 1996, Volkovich et al. 1998). In pure $UO_3 \cdot 2H_2O$ the uranyl stretch occurs at 958 cm^{-1} (Hoekstra and Siegel 1973). The lower frequencies observed here indicate weaker uranyl bonding, which may result from the presence of ammonium or sodium in the solids. Estimated ammonium- or sodium-to-uranium ratios are about 1:3 based on the methods of preparation (Wamser et al. 1952, Cordfunke 1962). In sample set I, the strong band observed at 1400-1410 cm^{-1} corresponds to the ammonium ν_4 mode (Nakamoto 1970). In all samples, a lattice mode is observed at 461-465 cm^{-1}, the H_2O bend is observed at 1630-1635 cm^{-1} and broad OH stretching bands are observed at 2800-3600 cm^{-1}.
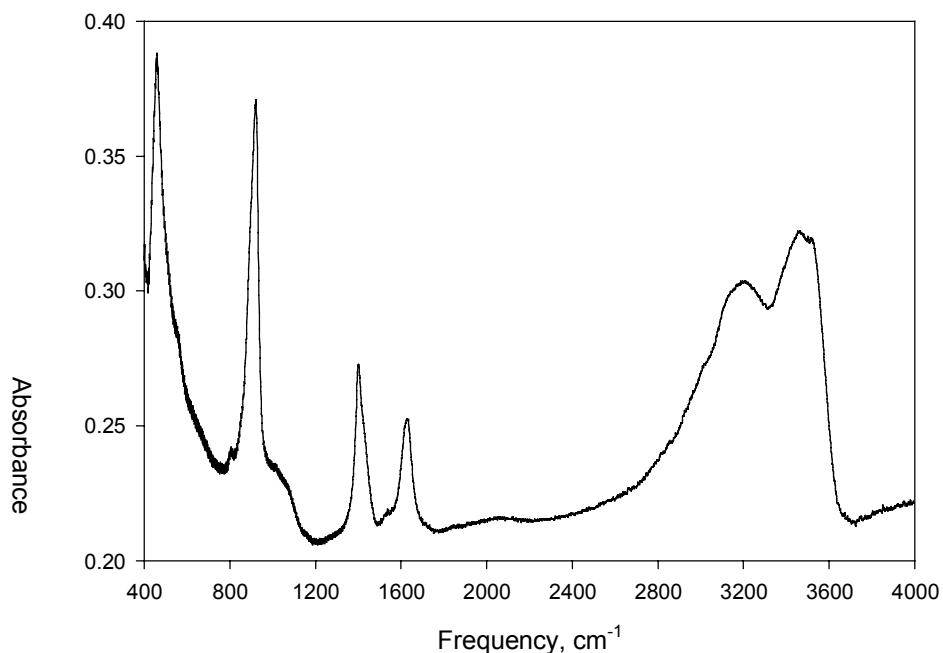
Figure B.1. Infrared spectrum of solid from sample 136.

X-ray absorption measurements on samples 131-135 have been reported elsewhere (Wruck et al, 1999). The EXAFS spectra and curve fits for all samples closely matched synthetic schoepite precipitates. There was no evidence of uranyl-carbonate bonding in the EXAFS data.

B.6. Conclusions

The distribution of Np(V) between aqueous $NaHCO_3$ solutions and synthetic schoepite solids was investigated. Equilibrium was approached via two different kinetic paths, addition of U solids to Np solutions and coprecipitation of U and Np. The Np distribution ratio was 5-44 mL/g in the pH range 6-8. Results were consistent with adsorption of Np and do not provide evidence of Np incorporation in the bulk solid.

B.7. References

Allen, P.G., Shuh, D.K., Bucher, J.J., Edelstein, N.M., Palmer, C.E., Silva, R.J., Nguyen, S.N., Marquez, L.N. and Hudson, E.A. 1996. "Determinations of Uranium Structures by EXAFS: Schoepite and Other U(VI) Oxide Precipitates." *Radiochim. Acta* **75**, 47-53.

Buck, E.C., Finch, R.J., Finn, P.A. and Bates, J.K. 1998. "Retention of Neptunium in Uranyl Alteration Phases Formed during Spent Fuel Corrosion." *Scientific Basis for Nuclear Waste Management XXI. Proceedings held September 28-October 3, 1997, Davos, Switzerland.* edited by I.G. McKinley and C. McCombie. Pittsburgh, Pennsylvania: Materials Research Society.

Burns, P.C., Ewing, R.C. and Miller, M.L. 1997. "Incorporation Mechanisms of Actinide Elements into the Structures of U^{6+} Phases Formed during the Oxidation of Spent Nuclear Fuel." *J. Nucl. Mater.* **245**, 1-9. TIC: 235501.

Cordfunke, E.H.P. 1962. "On the Uranates of Ammonium-I. The Ternary System NH_3-UO_3-H_2O." *J. Inorg. Nucl. Chem.* **24**, 303-307.

Fahey, J.A. 1986. "Neptunium." *The Chemistry of the Actinide Elements.* edited by J.J. Katz, G.T. Seaborg and L.R. Morss. New York, New York: Chapman and Hall.

Finn, P.A., Hoh, J.C., Wolf, S.F., Slater, S.A. and Bates, J.K. 1996. "The Release of Uranium, Plutonium, Cesium, Strontium, Technetium, and Iodine from Spent Fuel under Unsaturated Conditions." *Radiochim. Acta* **74**, 65–71. TIC: 237843.

Hoekstra, H.R. and Siegel, S. 1973. "The Uranium Trioxide-Water System." *J. Inorg. Nucl. Chem.* **35**, 761.

Nakamoto, K. 1970. *Infrared Spectra of Inorganic and Coordination Compounds.* New York, New York: Wiley-Interscience.

Quinones, J., Grambow, B., Loida, A. and Geckeis, H. 1996. "Coprecipitation Phenomena during Spent Fuel Dissolution. 1. Experimental Procedure and Initial Results on Trivalent Ion Behaviour." *J. Nucl. Mater.* **238**, 38-43.

Triay, I.R., Meijer, A., Conca, J.L., Kung, K.S., Rundberg, R.S., Strietelmeier, B.A., Tait, C.D., Clark, D.L., Neu, M.P. and Hobart, D.E. 1997. *Summary and Synthesis Report on Radionuclide Retardation for the Yucca Mountain Site Characterization Project.* LA-13262-MS. Los Alamos, New Mexico: Los Alamos National Laboratory.

Volkovich, V.A., Griffiths, T.R., Fray, D.J. and Fields, M. 1998. "Vibrational Spectra of Alkali Metal (Li, Na and K) Uranates and Consequent Assignment of Uranate Ion Site Symmetry." *Vibrational Spectroscopy* **17**, 83-91.

Wamser, C.A., Belle, J., Bernsohn, E. and Williamson, B. 1952. "The Constitution of the Uranates of Sodium." *J. Am. Chem. Soc.* **74,** 1020-1022.

Wronkiewicz, D.J., Bates, J.K., Wolf, S.F. and Buck, E.C. 1996. "Ten-Year Results from Unsaturated Drip Tests with UO_2 at 90°C: Implications for the Corrosion of Spent Nuclear Fuels." *J. Nucl. Mater.* **238**, 78–95. ACC: MOL.19971218.0965.

Wruck, D.A., Brachmann, A., Sylwester, E.R., Allen, P.G. and Palmer, C.E.A. 1999. *Sorption of Np(V) by U(VI) Hydroxide Solids.* UCRL-JC-135791. Livermore, California: Lawrence Livermore National Laboratory.

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