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Neptunium(V) and Neptunium(VI) Solubilities in Synthetic Brines of Interest to the Waste Isolation Pilot Plant (WIPP)

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Abstract

The solubility of Np(V) and Np(VI) has been measured in three synthetic Na-K-Mg-Cl brines in the presence of $CO_2(g)$. Experiments were prepared from oversaturation by adding an excess of NpO_2^+ or NpO_2^{2+} to the brines and allowing the neptunium solids to precipitate. Vessels were maintained in contact with fixed $CO_2(g)$ partial pressures at constant pH and 24±1°C. Dissolved Np(V) concentrations decreased several orders of magnitude within the first 100 days of the experiment, while dissolved Np(VI) concentrations decreased initially but then remained relatively constant for more than 400 days. The solid phases formed in all experiments were identified by X-ray powder diffraction as $KNpO_2CO_3 \cdot xH_2O(s)$. Steady state concentrations for Np(V) are similar to those observed for Pu(V) in the same brines under the same conditions, where Pu occurs predominantly as Pu(V). Similarly, steady state concentrations for Np(VI), which was not reduced over a two year period, compare well with measured Pu(VI) concentrations in the same brines before the Pu(VI) was reduced to Pu(V).

Introduction

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy facility being developed for geologic disposal of defense-generated transuranic nuclear waste. The ground waters near the WIPP site range from sea water-like brines (~0.8 molal ionic strength) to highly

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concentrated brines (~8 molal) [1]. WIPP Performance Assessment calculations require information on the solubilities of actinides in these brines [2]. However, environmentally relevant neptunium solubility data in concentrated complex electrolytes are scarce, and most existing data were taken in $NaClO_4$ media [3-11].

This study was initiated to determine the solubility-controlling solid phases and the steady-state dissolved concentrations of Np(V) and Np(VI) in three synthetic WIPP brines called AISinR, H17, and SPC Brines. The experimental results would help determine the applicability of existing Np(V) solubility models, such as the $Np(V)\text{-}Na\text{-}H\text{-}Cl\text{-}ClO_4\text{-}HCO_3\text{-}CO_3\text{-}CO_2(aq)\text{-}OH\text{-}H_2O$ model of Fanghänel et al. [12], to experiments under WIPP-relevant conditions. In contrast to the Np(V) system, little information is available for Np(VI) solubility. This paper documents steady-state Np(V) and Np(VI) concentrations, oxidation state distributions, and solubility-controlling solids in three complex synthetic brines, and compares these results with analogous studies for Pu(V) and Pu(VI) [13, 14].

Experimental

The compositions of the three synthetic WIPP brines are given in Table 1. The total inorganic carbon content in each solution was maintained through contact with individual $CO_2/O_2/Ar$ gas mixtures obtained from Matheson Gas Company. Mean compositions of the gas mixtures are reported in Table 1. Experiments were conducted at 24±1°C.

The hydrogen ion concentration was monitored throughout the experiments using Ross glass combination pH electrodes (Orion Research Incorporated, Boston, MA). Electrodes were calibrated with NIST traceable standard buffers of 7 and 10 before being placed into the brines. The electrode reading, called pHr here, was maintained constant to within ±0.2 units of the values shown in Table 1 through the addition of small amounts (usually between 5 and 50 μL) of HCl or NaOH (0.5-1 M). Correction of the electrode reading to account for the liquid junction potential and choice of hydrogen ion activity coefficient model was unnecessary for the purposes of this study. The pH electrodes, a different one for each of the brines, were removed from the neptunium solutions between measurement.

Stock solutions of $^{237}Np(V)$ and $^{237}Np(VI)$ were prepared independently by electrochemical methods and their purity was verified by UV-NIR absorption spectrophotometry. The equilibration vessels, made from polyetheretherketone cells (materials obtained from Cadillac Plastics, South San Francisco, CA) were machined to specification with ports at the top to accommodate a pH electrode, a 1/16"-diameter Teflon line for the gas mixture, and an opening for withdrawing samples.

Quantitative separation of the aqueous phase from solids or suspended particles was accomplished using Centricon-30 centrifugal filters (Amicon Corporation, Danvers, MA) that contain a YM-type membrane with a calculated pore size of 4.1 nm. Prefiltration with 500 μL of neptunium solution was sufficient to saturate all sorption sites on the filter (see [12] for details). Aqueous concentration measurements were made by γ-spectroscopy using a low-energy germanium counting system of Lawrence Berkeley National Laboratory design. The system was calibrated bi-weekly with neptunium standard solutions.

Initial oxidation state purity was confirmed by absorption spectrophotometry, and final oxidation state distributions were determined once steady-state conditions were reached. These determinations were made with a series of organic solvent extractions for low aqueous Np concentrations, and with conventional absorption spectrophotometry for high aqueous Np concentrations. The extraction method was a modification of an earlier scheme used for plutonium [15], with 1-phenyl-3-methyl-4-benzoy-pyrazol-5-one (PMBP) substituted for thenoyltrifluoroacetone (TTA) because PMBP is more efficient as an extractant and is more resistant to decomposition by oxidants.

Free NpO_2^+ and NpO_2^{2+} have characteristic absorption bands, λ_{max}, at 981 and 1226 nm, respectively, while $NpO_2CO_3^-$ has a λ_{max} at 991 nm in dilute carbonate solution [8]. The extinction coefficients of the uncomplexed peaks are better known than those of the carbonate complexes. For this reason, the spectra were first measured to detect bound and free Np(V) and Np(VI). The solutions were then acidified to convert any bound species to uncomplexed neptunium species. The concentration of carbonate-bound neptunium was calculated by difference after correcting for dilution due to acidification.

Sample of the solids were isolated from the solutions for X-ray powder diffraction analysis. A few micrograms on each neptunium precipitate were placed in a 0.33-mm diameter quartz capillary tube. The tube was mounted in an 11.46-cm diameter Debye-Scherrer camera and then irradiated with X-rays from a Norelco III X-ray generator (Philips Electronics, Inc.). Copper K_α radiation filtered through nickel was used.

Results and Discussion

The dissolved Np concentrations in the initially Np(V) experiments are plotted as a function of time in Figure 1. The aqueous Np concentrations decreased immediately after introduction of NpO_2^+ to each of the brines. Steady-state was achieved after approximately 250 days of reaction time. The NpO_2^{2+} solutions behaved quite differently, as illustrated in Figure 2. After an immediate decrease corresponding to the precipitation of an initial solid, the dissolved Np(VI) concentrations remained approximately constant for the duration of the experiment. The increase in dissolved Np concentrations in the H17 and SPC Brine vessels after 400 days may be due to evaporation of solution. The average steady-state dissolved concentrations of Np(V) and Np(VI) in the three brines are listed in Table 2.

Oxidation state distributions for the Np(V) and Np(VI) experiments, obtained by extraction or spectrophotometry during days 396 to 543 of each experiment, are summarized in Table 3. The data indicate that there were no significant changes in oxidation state in the aqueous phase. The initially Np(V) experiments with AISinR and SPC Brines contained greater than 96% Np(V). Oxidation state data could not be obtained for the initially Np(V) in H17 Brine. However, it is likely that the H17 vessel also contained nearly 100% Np(V) because there was no indication of oxidation state changes in either the AISinR or SPC Brines, and these brines bound the composition of H17 Brine. The initially Np(VI) experiments with each brine contained greater than 92% Np(VI) at the conclusion of the experiments, and each had the yellow-brown color characteristic of Np(VI). The spectroscopic data for AISinR Brine and H17 Brine indicate that the Np(VI) was completely complexed because no absorption band was observed at 1226 nm in the non-acidified spectrum. Furthermore, the data indicate that the small amount of Np(V) present was also bound in carbonato complexes. An unidentified absorption band at 1160 nm in the Np(VI) in AISinR and H17 spectra may correspond to a Np(VI)-carbonate species because this band disappeared and the free Np(VI) peak at 1226 nm appeared when the sample was acidified.

Powder patterns were obtained for solids removed from each vessel near the beginning of the experiments (days 4 to 7). The powder patterns for the solids from the initially Np(V) vessels have essentially the same features as the solids removed at the end of the experiments (see below), regardless of the brine composition from which they came. The powder patterns for the solids from the initially Np(VI) experiments have lines in common with each other, but none correlate completely. The diffraction patterns for solids from the Np(VI) vessels do not match the patterns reported for $UO_2CO_3(s)$ or $PuO_2CO_3(s)$ [16], but do have some features in common with Np(V) solids, suggesting some reduction of Np(VI) to Np(V) occurred early in the experiments.

Solids were also removed from each reaction vessels at the conclusion of the experiments (days 543, 430, and 763 for the Np(V) in AISinR, H17, and SPC Brines, respectively; days 540, 734, and 763 for the Np(VI) experiments in AISinR, H17, and SPC Brines, respectively). The powder patterns from all the solids were the same, regardless of the brine or the initial Np oxidation state. The powder diffraction patterns from the H17 Brine experiments are given in Table 4 along with patterns for $KNpO_2CO_3 \cdot xH_2O(s)$ [17] and $NaNpO_2CO_3 \cdot xH_2O(s)$ [18]. The patterns from the other brines were effectively identical. The powder patterns from the H17 experiments, whether at early or late time and for both the initially Np(V) and initially Np(VI) experiments, agree well with that for $KNpO_2CO_3 \cdot xH_2O(s)$ but not with the sodium pattern. Thus, even though there is up to 87 times more sodium in some of the brines, the solubility-controlling solid for all cases was $KNpO_2CO_3 \cdot xH_2O(s)$. There are no significant differences between the powder patterns from experiments that started with Np(V) and experiments that started with Np(VI).

Existing Np(V) solubility models do not include potassium ion interaction effects or potassium-containing solids such as $KNpO_2CO_3 \cdot xH_2O(s)$ [12]. Sufficient data to determine the standard chemical potential or solubility products are apparently not available. However, the isolation of $KNpO_2CO_3 \cdot xH_2O(s)$ in these brine systems demonstrates the need for thermodynamic information for the K-Np(V)-CO_3 system and suggests that potassium neptunyl carbonate is significantly less soluble than sodium neptunyl carbonate.

The Np(VI) vessels reached steady-state conditions with Np(VI) in solutions and Np(V) in the solid phase. The enhanced stability of Np(VI) carbonate complexes is apparently sufficient to maintain Np(VI) as the dominant aqueous oxidation state.

Comparison with Analogous Pu(V) and Pu(VI) Experiments

The oxidation state analogy for f-elements suggests that the solubility of actinides in the same oxidation state under the same conditions will be similar. Therefore, if identical solubility experiments were conducted with Np(V) and Pu(V), and the actinides remained in the +V oxidation state, the precipitated solids and the measured solubilities should be nearly the same.

The solubility controlling solids in identical experiments with Pu(V) were tentatively identified as $NaPuO_2CO_3 \cdot xH_2O(s)$ [13, 14]. However, re-examination of the X-ray diffraction patterns for these solids suggest that these solids are in fact $KPuO_2CO_3 \cdot xH_2O(s)$. We are synthesizing and characterizing sodium and potassium plutonyl(V) carbonates to provide a more definitive identification of the Pu solids.

The steady-state concentrations of Np(V) and Pu(V) in AISinR [13], H17 [14], and SPC Brines are different by less than an order of magnitude in each of the brines. This information, while not definitive, suggest that a model developed for Np(V) can be used to predict Pu(V) concentrations when +V is the dominant plutonium oxidation state.

A similar comparison of steady-state solubilities of Np(VI) and Pu(VI) is possible only where there is relative confidence that the Pu has remained in the +VI oxidation state. In identical experiments performed with Pu(VI), early time data for Pu that was introduced as Pu(VI) show similar concentrations to those measured for Np(VI). Relatively high dissolved Pu concentrations remained in solution at early times (20, 250, and 400 days for AISinR, H17, and SPC Brines, respectively). Following these initial "incubation" periods, the total dissolved Pu concentrations dropped by several orders of magnitude. The early-time Pu(VI) results are compared with the Np(VI) results in Figure 3. The data show close agreement in the solubility of Np(VI) and Pu(VI) in these solutions at early time, where it is most likely that the Pu had not been reduced. As is the case for the +V data, this information suggest that a model developed for Np(VI) can be used to predict Pu(VI) concentrations when +VI is the dominant plutonium oxidation state. The experiments with Pu(VI) showed steady-state conditions between a Pu(V) solid and dissolved Pu(VI) in H17 Brine [14], as was observed for Np(VI) in the three brines of the current work. The Pu experiments in SPC Brine will be reported fully in a separate manuscript.

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Table 1. Chemical composition of the three WIPP brine simulants.

Species or Quantity	Concentration in AlSinR Brine (Molar)	Concentration in H17 Brine (Molar)	Concentration in SPC Brine (Molar)
Ca^{2+}	0.0171	0.0741	0.0150
Mg^{2+}	0.0215	0.0741	1.44
Na^{+}	0.643	2.40	1.83
K^{+}	0.0082	0.0307	0.767
Cl^{-}	0.568	2.48	5.38
SO_4^{2-}	0.0796	0.0750	0.0437
Br^{-}	——	0.00095	0.00505
B	0.00279	0.00398	0.0204
Total inorganic carbon	0.00178	0.00082	0.0143
Ionic strength (molal)	0.844	2.97	7.78
Operational pH, pHr	7.5±0.1	7.1±0.1	7.3±0.1
log pCO_2	−2.71	−2.56	−3.95
Mean $CO_2(g)$ in gas mixture (ppm)	1885 ± 158	2640 ± 128	114 ± 10
Mean $O_2(g)$ in gas mixture (%)	20.65 ± 0.93	20.57 ± 1.17	20.95 ± 0.97

Table 2. Averaged neptunium solubilities in AlSinR, H17, and SPC Brines.

	Initially Np(V), Molar [days over which average was taken]		Initially Np(VI) [days over which average was taken]	
AlSinR Brine	$(1.94 \pm 0.58) \times 10^{-6}$	[241 to 543]	$(3.23 \pm 0.60) \times 10^{-4}$	[1 to 540]
H17 Brine	$(8.2 \pm 3.9) \times 10^{-7}$	[241 to 430]	$(8.3 \pm 5.1) \times 10^{-4}$	[1 to 734]
SPC Brine	$(2.38 \pm 0.80) \times 10^{-7}$	[241 to 763]	$(6.0 \pm 5.0) \times 10^{-4}$	[1 to 734]

Table 3. Percent of neptunium oxidation states in AISinR, H17, and SPC Brines.

Initial Np Form, Brine, analysis date	NpO_2^+, %	Np(V)-carbonate, %	Total Np(V), %	Np(VI)-carbonate, %	Total Np(VI), %	Analysis Method
Np(V), AISinR, 430	-	-	96 ± 7	-	3.6 ± 0.9	solvent extraction
Np(V), H17	-	-	n/d	-	n/d	
Np(V), SPC, 543	-	-	100 ± 10	-	0 ± 10	solvent extraction
Np(VI), AISinR, 396	4.8 ± 0.8	2.2 ± 0.1	7.1 ± 0.9	93 ± 5	93 ± 5	spectrophotometry
Np(VI), H17, 408	1.2 ± 0.1	1.2 ± 0.1	2.3 ± 0.1	98 ± 6	98 ± 5	spectrophotometry
Np(VI), SPC, 430	n/d	n/d	3.2 ± 0.6	n/d	97 ± 5	spectrophotometry

n/d: not determined

Table 4. Comparison of some X-ray diffraction patterns for Np solids from the H17 Bbrine experiment with literature data for $KNpO_2CO_3(s)$ [17] and $NaNpO_2CO_3(s)$ [18]. Patterns from other brine compositions were similar.

KNpO2CO3(s) [17]	NaNpO2CO3(s) [18]	Initially Np(V) in H17 Brine at day 430	Initially Np(VI) in H17 Brine at day 4	Initially Np(VI) in H17 Brine at day 734
			9.43(4)	
			7.70 (4)	
	5.34 (10)			
5.01 (9)		5.05 (6)	5.05 (2)	5.00 (9)
4.44 (5)	4.43 (10)	4.41 (4)		4.45 (4)
4.06 (10)	4.05 (10)	4.04 (7)	4.04 (4)	4.04 (10)
			3.48 (4)	
3.31 (9)		3.34 (6)	3.31 (2)	3.31 (9)
	3.25 (8)	3.26 (6)	3.24 (2)	
			3.15 (3)	
	2.86 (1)	2.84 (10)	2.82 (10)	
	2.77 (8)			
2.66 (5)	2.67 (2)	2.69 (3)	2.67 (2)	2.65 (5)
2.56 (9)		2.55 (5)	2.55 (2)	2.55 (7)
2.49 (5)	2.43 (3)			
2.28 (5), 2.22 (2)	2.21 (9)	2.28 (4), 2.22 (2)	2.28 (2)	2.26 (4)
2.16 (9)	2.18 (2)	2.16 (5)	2.17 (2)	2.15 (6)
2.02 (5)	2.08(6),2.06(1),2.02(1)	2.00 (10)	2.00 (9)	2.02 (3)
	1.96 (4), 1.91 (1)	1.97 (4)		
1.85 (4), 1.82 (4)	1.83 (1)	1.86 (3), 1.81 (3)	1.85 (2)	1.84 (4)
1.79 (5)	1.76 (1), 1.74 (1)	1.73(6)	1.73 (6)	1.79 (4)
1.65 (7)	1.69(1),1.62(1),1.60(1)	1.66 (3), 1.64 (9)	1.64 (5)	1.68 (1), 1.64 (4)
1.59 (2), 1.50 (2)	1.56(2),1.52(1),1.51(1)	1.59 (2), 1.52 (4)	1.57 (2)	
1.48 (2)	1.46 (1), 1.44 (1)	1.48 (2), 1.42 (5)	1.42 (4)	1.49 (3), 1.42 (1)
	1.39(1),1.38(1),1.35(1)	1.30 (2)		1.4(1),1.37(1),1.33(1)
	1.29(1), 1.24(1)	1.28(2),1.27(9),1.25(6)	1.27 (4)	.29(2),1.27(2),1.24(1),1.22(1)
	1.06 (1)	1.16 (9)	1.16 (6)	1.19 (1), 1.15 (1)

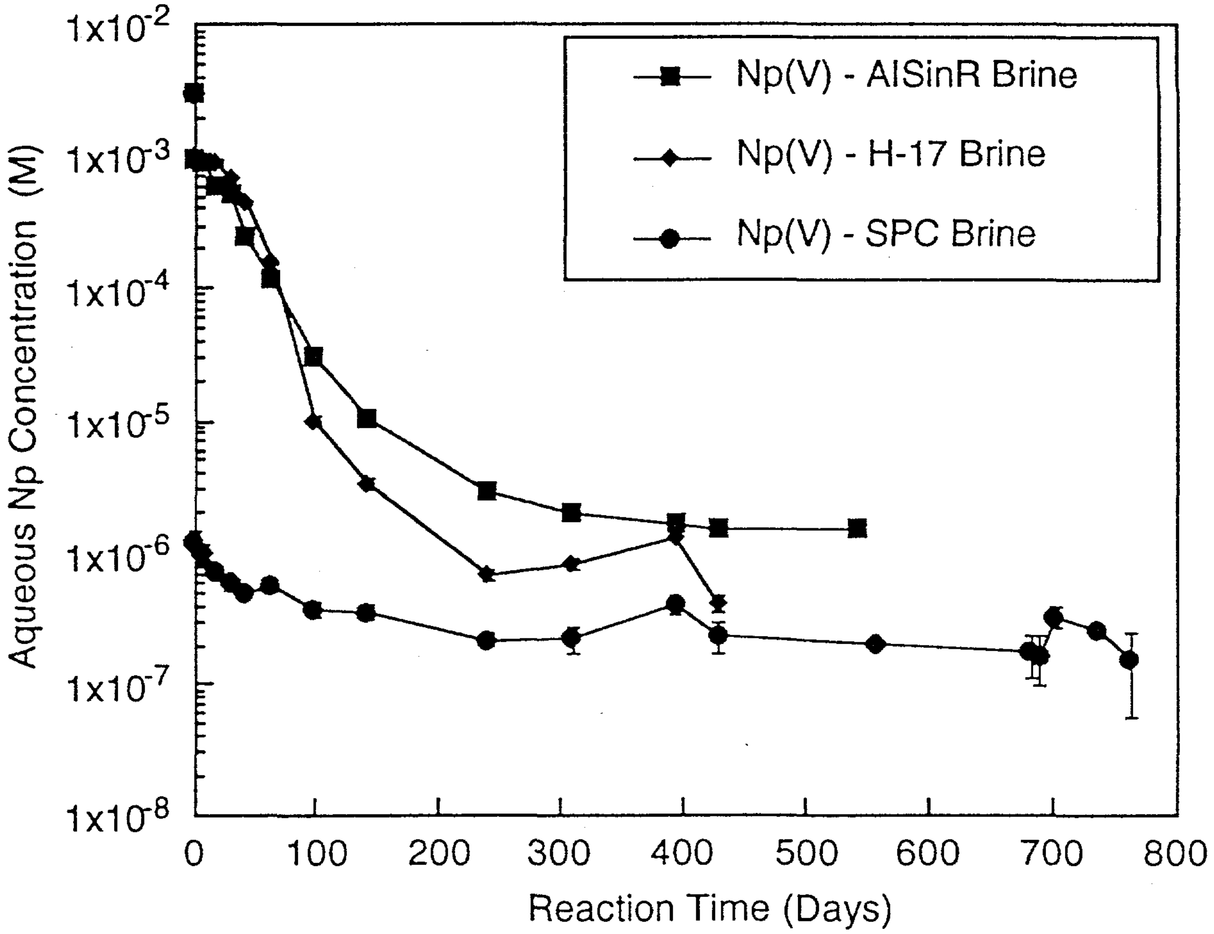

Figure 1. Approach to steady state for initially Np(V) added to AISinR, H17, and SPC Brines. The +V oxidation state was stable over the course of the experiments.

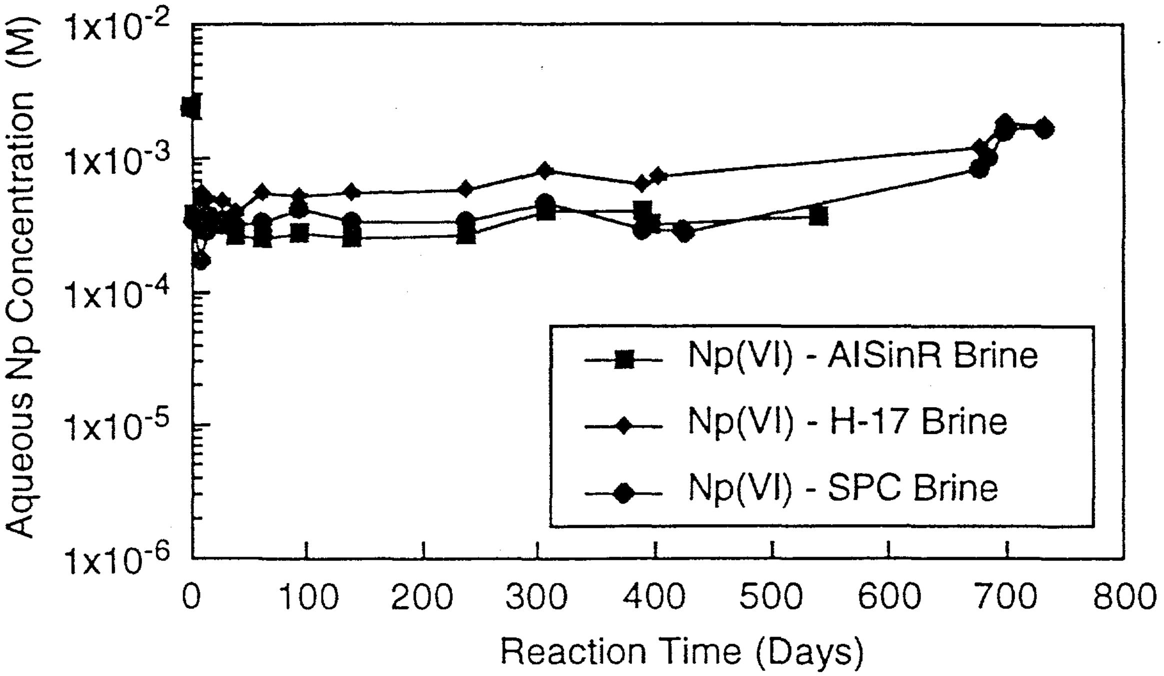

Figure 2. Approach to steady state for initially Np(V) added to AISinR, H17, and SPC Brines. The +VI oxidation state was stable over the course of the experiments (less than 7% conversion to Np(V) was noted).

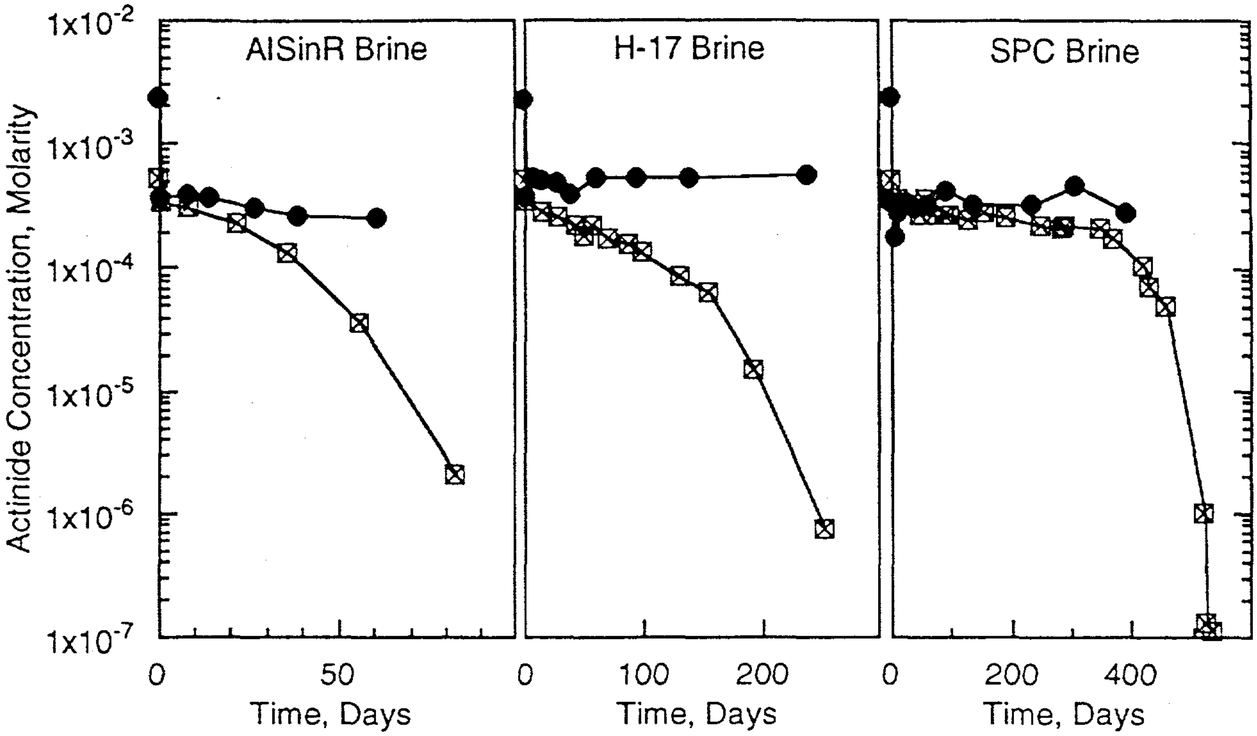

Figure 3. Comparison of steady state concentrations of Np(VI) (circles) with early time concentrations of Pu(VI) (squares, [12,13]) in AlSinR, H17, and SPC Brines under the same chemical conditions. The Np(VI) concentrations remained at the same levels for the course of the experiments, while the dissolved Pu concentrations decreased as the Pu(VI) was reduced to Pu(V).