

Determining the distribution of Pu, Np, and U oxidation states in dilute NaCl and synthetic brine solutions

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The effect of iron powder (Fe^0) on the reduction of Pu(VI), Np(V), and U(VI) was investigated in dilute NaCl and synthetic brines. The total concentrations and oxidation states of the actinides in these solutions were monitored as functions of pC_{H^+} , E_{H} , and time using techniques including Vis/Near IR absorption spectrophotometry, solvent extraction, α -activity counting, and inductively coupled plasma spectroscopy-mass spectrometry (ICP-MS). When concentrations were too low and the oxidation states could not be directly determined by spectrophotometry or solvent extraction, comparing the measured concentrations with the solubility of reference systems helped to define the final oxidation states. In general, the reduction was more rapid, and could proceed further, in the dilute NaCl solution than in the brine solutions. The experimental observations can be summarized as follows: (1) in the dilute NaCl solutions (pC_{H^+} 7 to 12), all three actinides, Pu(VI), Np(V) and U(VI), were reduced to lower oxidation states (most likely the tetravalent state) within a few days to a few months in the presence of Fe^0 ; (2) in synthetic brines containing Fe^0 (pC_{H^+} 8 to 13), the reduction of Pu(VI) was much slower than in the dilute NaCl solution. The dominant oxidation state of Pu in the brine solution was Pu(V), the concentration of which was controlled by the electrochemical potential and could probably be represented by a heterogeneous redox reaction $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{PuO}_2^{+} + e^-$; (3) in synthetic brines containing Fe^0 (pC_{H^+} 8 to 13), Np(V) was probably reduced to Np(IV) and precipitated from the solution; (4) in synthetic brines containing Fe^0 (pC_{H^+} 8 to 13), no significant reduction of U(VI) was observed within 55 days.

Introduction

To predict the leachability of actinide elements from the nuclear wastes to be disposed of at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, it is essential to understand the chemistry of actinides under the conditions likely to be encountered in the WIPP repository. In particular, because concentrated NaCl brine solutions may exist in this repository,¹ studies of the chemical behavior of actinides in these solutions are of great importance. Experimental studies have been conducted on the solubility of actinide compounds in concentrated electrolyte and brine solutions under the WIPP Actinide Source Term program and other programs.^{2–5} In these studies, oxidation state analogs were used to develop solubility models for actinides of each oxidation state (III, IV, V and VI). Accordingly, these models are specific to a particular oxidation state; they can predict the solubilities of actinides only if the distribution of oxidation states is known or can be estimated.

It is well-known that several actinides (An), especially Pu and Np, are among the elements which exhibit the most versatile redox chemistry.⁶ Depending on the solution conditions, they can exist in oxidation states ranging from III to VII, and several (e.g., Pu (III) to Pu(VI)) can exist simultaneously in significant amounts in solution. These oxidation states have drastically different chemical behavior in terms of

solubility and complexation. For example, tri- and tetravalent actinides readily form solid phases that are very insoluble when compared with the penta- and hexavalent states. Moreover, tetravalent actinides form much stronger complexes with ligands than pentavalent actinides. Consequently, the leachability of actinides from the waste repository will depend on their oxidation state(s) in the repository environment.

Reducing conditions are expected to exist in the WIPP site due to large quantities of iron and microbial activity that can generate reducing agents such as H_2 , reduced sulfur species (e.g., S^{2-}), and organic compounds. It is also known that, in acidic and dilute solutions, several of these inorganic reductants (e.g., Fe^0 and H_2) can reduce actinides to the tetra- and even trivalent states. Sufficient data for various redox reactions of actinides in acidic and dilute media have been published in the literature.^{7–14} However, these conditions (acidic, dilute) are very different from those in the WIPP repository environment (neutral to basic brines). Information is scarce for the redox reactions of actinides in neutral to basic or highly concentrated electrolyte solutions. No data are available that pertain specifically to brine solutions.

In this study, the distribution of oxidation states of Pu, Np, and U in dilute NaCl and synthetic brine solutions at varying pH values was studied in the presence of Fe^0 (probably one of the most abundant reducing agents likely to be encountered in the WIPP repository environment).

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Our objectives were (1) to determine if Pu(VI), Np(V), and U(VI) are reduced in the presence of iron, (2) to determine the final oxidation states of these actinides, if there is reduction, and (3) to compare results for the brine solutions with those for dilute NaCl solutions so the effect of the brine solution can be evaluated. The information obtained from this study will help identify the distribution of actinides in the brine solution and aid in the development of solubility models for individual actinide oxidation states.

Experimental

Reagents and solutions

All reagents used in this study were analytical grade. Thenoyltrifluoroacetone (TTA) and dibenzoylmethane (DBM) were purified by vacuum sublimation at 42 and 125 °C, respectively. Stock solutions of 0.5M TTA, and 0.2M and 0.5M DBM in toluene were prepared and stored in the dark. The TTA-toluene solution used to determine the oxidation states of Pu was treated with an aqueous phase containing 0.01M KBrO₃ prior to use, to remove any impurities resulting from the decomposition of TTA. Di-n-butyl-n-butylphosphonate (DBBP) was used without further purification.

A 0.15M Pu(IV) stock solution was prepared using an anion exchange technique.¹⁵ A Pu(VI) stock solution in 0.35M HNO₃ was prepared electrochemically, based on a procedure described elsewhere.^{16,17} Absorption spectra of this solution confirmed that Pu was present as Pu(VI). Analysis by γ -spectroscopy indicated that the Pu used in this study had the following isotopic composition (by activity): 93.6% ²³⁹Pu and 6.3% ²⁴⁰Pu.

A ²³⁷Np(V) stock solution (0.134M in 1.0N HCl) was prepared based on the procedure described in the literature.¹⁸ After a small amount of solid NaBrO₃ was added to a solution of Np in 1M HClO₄, the solution was warmed to oxidize Np to the hexavalent state. A small amount of NaNO₂ was then added to this solution. The color changed from pink to green, indicating the reduction of Np(VI) to Np(V). The Np(V) was precipitated as NpO₂OH(s) by addition of 1M NaOH to the solution. The precipitate was washed several times with water and dissolved in 1M HCl. The oxidation state of Np in this stock solution was checked spectrophotometrically and confirmed to be Np(V).

A ²³⁸U(VI) stock solution (0.45M in 0.45M HCl) was prepared from a purified U(IV) solution by passing O₃(g) through the solution. The U(VI) oxidation state was confirmed by absorption spectrophotometry.

Table 1. Composition of the synthetic brine solution (ERDA6B)

| Component | Concentration, mole/l |
|---|-----------------------|
| KCl (Fisher) | 0.097 |
| Na ₂ SO ₄ (Baker) | 0.17 |
| NaBr (Merk) | 0.011 |
| NaCl (Aldrich) | 4.71 |
| H ₃ BO ₃ (Mallinckrodt) | 0.063 |

Iron powder (325 mesh, 99.9%) was purchased from Aldrich and was washed with deionized water prior to use in the chamber. Chemicals used in preparing the synthetic brine solution (ERDA6B) were purchased from companies listed in Table 1. The compositions shown in Table 1 are based on the analytical results of a natural brine (ERDA6).¹⁹

Procedure

Silanization of extraction vials: To minimize the adsorption of trace materials on the vials during extraction, the vial walls were coated with trimethylsilane, following the procedure reported in the literature.²⁰ The borosilicate glass vials were washed in 1M NaOH for one hour, soaked in 3M HCl for one day, washed with deionized water, and dried at 100 °C. The dry vials were then soaked in a toluene solution containing 5% trimethylchlorosilane (TMCS) and 5% hexamethyldisilazane (HMDS) for 3 hours and dried before use.

Preparation of sample and control solutions: The redox experiments were conducted in glass centrifuge tubes in an inert atmosphere (Ar gas) chamber at ambient temperature (22±1 °C). Two sets of redox experiments were conducted for each actinide studied: one set for the dilute solution (0.01M NaCl), the other set for the synthetic brine solution. The dilute NaCl solution and the brine were deoxygenated by passing prepurified Ar gas through them for half an hour prior to use. Calculated amounts of actinide stock solutions were added to each tube, so the initial concentrations of those actinides were [Pu(VI)]₀ = 2.5·10⁻⁴M, [Np(V)]₀ = 8.9·10⁻⁵M, and [U(VI)]₀ = 1.5·10⁻²M, respectively. The pH of the initial solutions was adjusted with HCl and NaOH to cover a pC_{H+} range of 2 to 12. The redox reactions started when 100 mg of Fe powder was added to each tube. These solutions were denoted as sample solutions. In parallel to each of the two sets of sample solutions, several control solutions were prepared with the identical initial conditions (the same ionic media, the same pC_{H+} range, and the same initial concentration of actinides), except no Fe powder was added.

Table 2. Sampling schedule

| Actinide | Time elapsed, days | |
|----------|--------------------|-------------------|
| | 0.01M NaCl | Brine |
| Pu | 3, 21, 57, 76 | 3, 10, 41, 56, 72 |
| Np | 10, 16, 30, 66 | 4, 11, 29, 66 |
| U | 15, 27, 55 | 5, 27, 55 |

The results between the sample solutions and the control solutions were compared to illustrate the effect of Fe powder. The centrifuge tubes containing the sample and the control solutions were constantly shaken on an orbital shaker in the chamber until the scheduled sampling time.

Sampling and pH/E_h measurements: The dilute NaCl and brine solutions were sampled at time intervals shown in Table 2. At these sampling intervals, the pH and E_h of the solutions were measured with a Corning 355 pH meter equipped with a combination glass electrode for pH and a combination redox electrode for E_h, respectively. For the pH measurements, the electrode was calibrated with standard buffer solutions of pH 4.00 ± 0.01, 7.00 ± 0.01, and 10.00 ± 0.0. The pH meter readings (pH_{obs}) for brine solutions were converted to the hydrogen ion concentration (pC_{H⁺} = -log[H⁺]) using the equation:

$$pC_{H^+} = pH_{obs} + A \quad (1)$$

where A is the conversion factor that depends primarily on the solution composition. The value of A for the synthetic brine (ERDA6B) was determined to be 0.99 using a titration method developed in previous studies.²¹ For the E_h measurements, the potential, E_{obs}, was measured against a reference electrode made of Ag/AgCl and connected by a KCl bridge. Values of E_{obs} were then converted to the potential, E_h, against the standard hydrogen electrode following calibration of the electrode with pH buffers saturated by quinhydrone, based on the instructions provided by the manufacturer. In this study, only the E_h values against the standard hydrogen electrode were reported.

After measuring pH and E_h, the suspensions were centrifuged. Centriprep-30 filters (40 Å pore size) were washed with the dilute NaCl or the brine solutions prior to use. Then a small aliquot of the supernatant was passed through the filters to saturate any possible adsorption sites on the filters, and the filtration containers and the filtrate were then discarded. Finally, 2 ml of the supernatant of each sample were filtered, and the filtrate was collected for analysis. Detailed procedures for the filtration were given elsewhere.²²

Determining oxidation states: absorption spectrophotometry and solvent extraction: Whenever concentration permitted, absorption spectrophotometry was the preferred method for determining actinides in different oxidation states, because of the characteristic

absorption bands. In this study, the absorption band around 830 to 845 nm was used to monitor Pu(VI), and the band around 980 nm for Np(V). However, the applicability of this method is limited in the study of neutral to basic solutions. The concentrations of actinides are usually too low due to hydrolysis and precipitation. Instead, the solvent extraction technique was used to separate and determine the oxidation states in solutions of lower concentration.

Two solvent extraction schemes were used in the present study. Scheme 1 (Fig. 1a) was used to separate the oxidation states of Pu. Dependency on the pH of different oxidation states was the key factor for efficient separation. In the first step, Pu(III) and Pu(VI) were extracted by 0.5M DBM in toluene from the aqueous solution with pH~8. Pu(IV) and Pu(V) were not extracted. Then the organic solution containing Pu(III) and Pu(VI) was removed from this vial and mixed with an aqueous solution of pH 5 so that Pu(III) was stripped into the aqueous phase, while Pu(VI) remained in the organic phase. In parallel, hydrochloric acid was added to the vial containing the aqueous solution (pH about 8) from the first step, to lower the pH to 4 to 5. This acidified aqueous solution was then shaken with 0.2M DBM in toluene. Under these conditions, Pu(IV) was extracted into the organic phase, while Pu(V) remained in the aqueous phase.²³

Scheme 2 (Fig. 1b) was used to separate lower (III and IV) and higher (V and VI) oxidation states. When this scheme was used to analyze Pu, the solutions were first acidified and treated with KBrO₃ so that any Pu(III) or Pu(V) would be oxidized to Pu(IV) or Pu(VI), respectively. Immediately after the addition of KBrO₃, these solutions should contain only Pu(IV) and Pu(VI), because further oxidation (IV to VI) was much slower. Then the Pu(IV) was extracted with TTA, while Pu(VI) remained in the aqueous phase.²⁴ The second extraction step with DBBP was to separate the Pu(VI) from the non-extractable fraction of Pu. When this scheme was used to analyze Np and U, only the first step with TTA was performed to separate Np(V) from Np(IV) and U(VI) from U(IV).

These two solvent extraction schemes had respective advantages and limitations. For example, Scheme 1 was capable of separating Pu into all four possible oxidation states (III, IV, V, and VI), while Scheme 2 only separated the lower states (III and IV) from the higher states (V and VI). Also, Scheme 1 involved extractions from aqueous solutions of high pH (about 8); the mass balance was not fully maintained even with silanization. Scheme 2 eliminated the problem of adsorption by acidifying the samples; the mass balance was improved. As a result, both schemes were used in this study, and, in the analysis of Pu, they were able to provide complementary results on the distribution of the oxidation states.

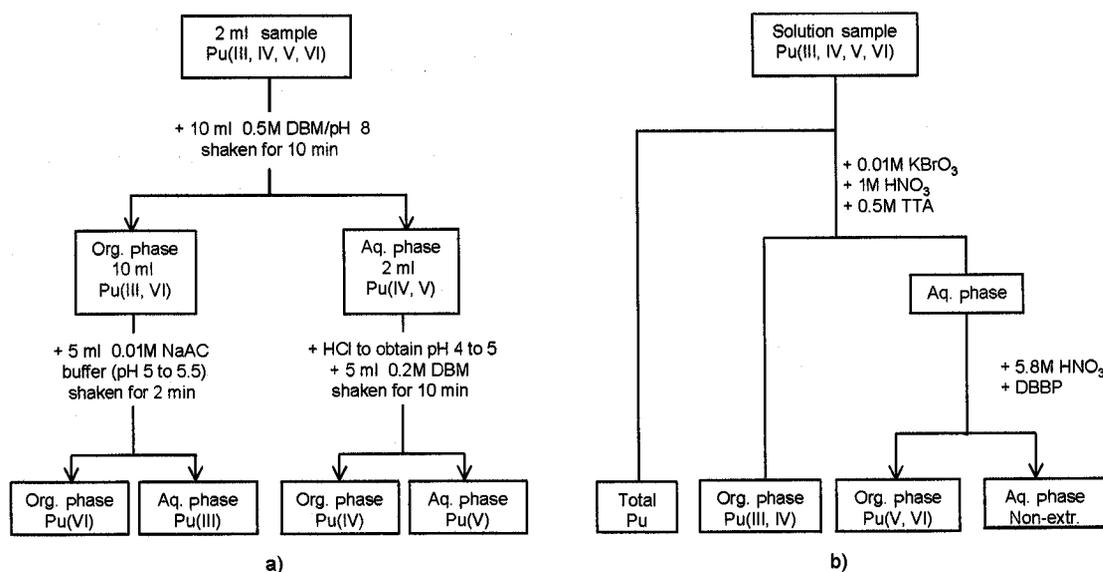


Fig. 1. Separation schemes: DBM solvent extraction (a); TTA/DBBP solvent extraction (b)

Concentrations of Pu and Np were determined by α -counting using a Wallac 1415 liquid scintillation counter. The concentrations of U were determined by ICP-MS, using a VG Elemental Plasma Quad instrument.

Results and discussion

Plutonium in dilute NaCl and the ERDA6B brine solutions

Dilute NaCl solution: Figure 2 shows the values of E_h and pH of the sample and control solutions measured at 76 days. Figure 2 indicates that the E_h and pH of the sample solutions were significantly different from those of the control solutions in two aspects:

(1) Though the initial pH of the sample solutions covered the pC_{H^+} region between 2 and 12 (see the previous section on procedures), the pC_{H^+} shifted to the region of 8 to 12 after the Fe powder was added to sample solutions. This probably resulted from Fe powder reacting in acidic solutions, generating species such as Fe^{2+} . Hydrogen ions were consumed in these reactions (gaseous release was observed in acidic sample solutions), and the generated species Fe^{2+} may have hydrolyzed to form $FeOH^+$ and $Fe(OH)_2$. Thus, Fe^{2+} behaved as a buffer and maintained the solution pH around 8.

(2) The E_h for the control solutions was positive (+500 to +900 mV in the pC_{H^+} region of 2.8 to 10), while the E_h for the sample solutions was negative (-200 to -500 mV).

Figure 3 shows the measured concentrations of Pu as a function of time and pC_{H^+} in 0.01M NaCl. Figure 3 indicates that concentrations of Pu in the sample solutions decreased with time, and nearly reached the lower detection limit (about $10^{-9}M$) at the 76-day interval. The concentration of Pu in the control solutions did not change in the acidic region ($2.5 \cdot 10^{-4}M$), and decreased only slightly in the region of $pC_{H^+} > 9.3$.

The positive E_h values of the control solutions (Fig. 2) and the nearly constant concentration of Pu (Fig. 3) indicated that the oxidation state of Pu in these solutions did not change after 76 days of equilibration, implying that Pu(VI) was stable in the absence of Fe^0 . However, the E_h values of the sample solutions containing Fe^0 were negative (-500 to -200 mV, Fig. 2). The concentration of Pu in the sample solutions decreased by five orders of magnitude after a couple of months (Fig. 3), which strongly suggests that Pu(VI) was reduced and precipitated from the solution in the presence of iron. However, determination of the final oxidation states of Pu in these solutions was not attempted because the concentration of Pu was near the detection limit. Such low concentrations did not allow direct determination of oxidation states, even using the solvent extraction technique.

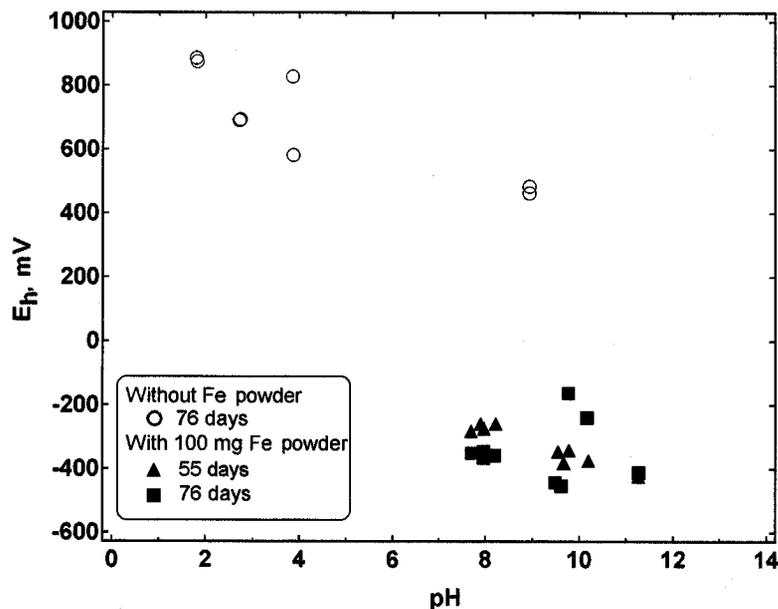


Fig. 2. Measured E_h and pH values of NaCl solutions containing Pu(VI) with and without iron powder after 76 days of equilibration

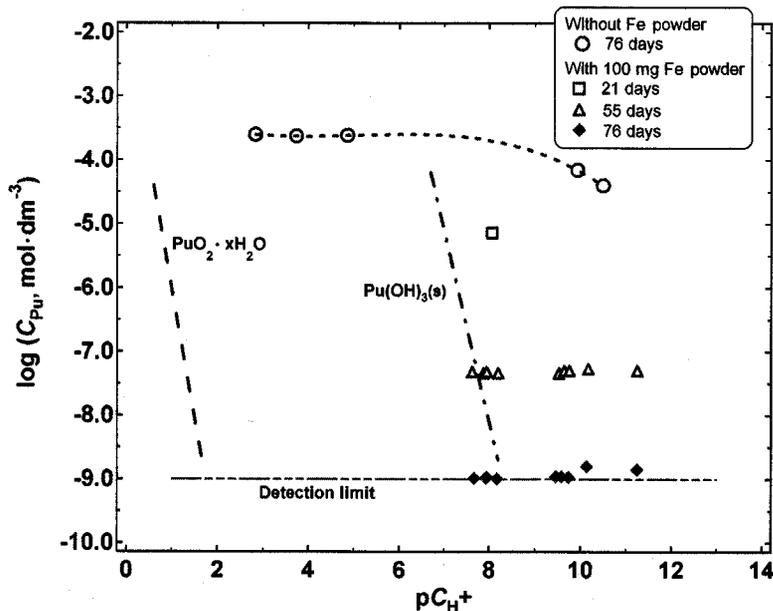


Fig. 3. Effect of iron powder on observed Pu concentrations in 0.01M NaCl solutions

Figure 3 also shows the solubility lines of $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{Pu}(\text{OH})_3(\text{s})$ in dilute NaCl solutions based on data in the literature.^{25,26} Comparing these lines with the concentrations of Pu in the sample solutions (i.e., dilute NaCl with Fe powder) suggested that Pu precipitated from the sample solution as either $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ or $\text{Pu}(\text{OH})_3(\text{s})$. Because the measured

aqueous concentration of Pu was at the detection limit and concentrations in equilibrium with $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{Pu}(\text{OH})_3(\text{s})$ should also be at the detection limit in the pH region from 8 to 12, it was not possible to determine the dominant oxidation state of Pu in the precipitate (i.e., whether it is $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ or $\text{Pu}(\text{OH})_3(\text{s})$).

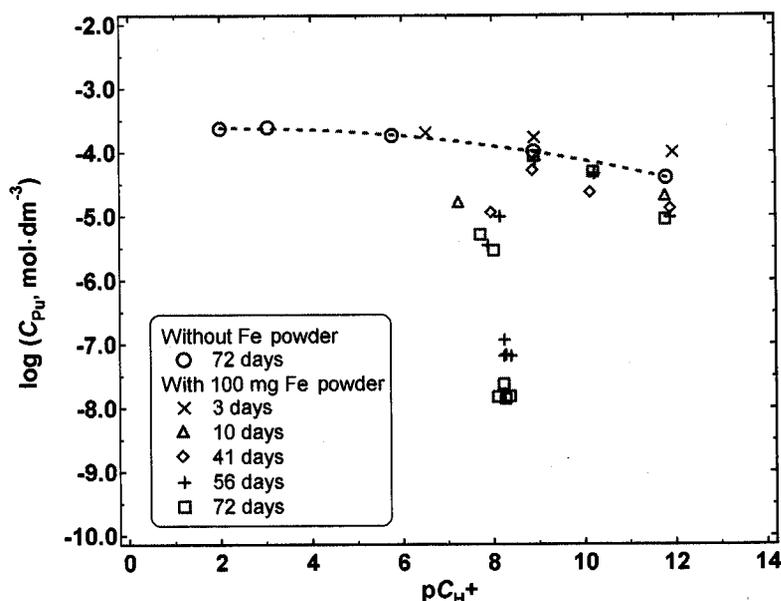


Fig. 4. Effect of iron powder on observed Pu concentration in the ERDA6B brine solution

Table 3. Pu concentrations, after 7 days of equilibration, in ERDA6B brine after addition of different amounts of Fe powder to samples that originally contained 100 mg of Fe powder and were equilibrated for 72 days

| Sample No. | Fresh Fe ⁰ added, mg | Before Fe ⁰ addition 72-day equilibration | | | After Fe ⁰ addition 7-day equilibration | | |
|------------|---------------------------------|---|---------------------|----------|---|----------|---------------------|
| | | pC _{H⁺} | E _h , mV | log [Pu] | pC _{H⁺} | log [Pu] | E _h , mV |
| Sb-07PU | 90 | 8.91 | 671 | -4.06 | 8.95 | -7.26 | -294 |
| Sb-08PU | 50 | 10.21 | 630 | -4.31 | 10.20 | -4.20 | 426 |
| Sb-09PU | 90 | 11.79 | 470 | -5.05 | 11.81 | -5.80 | -268 |

No detailed experiments on the reduction mechanism were pursued in this study. It remained unclear whether Pu(VI) was reduced by Fe⁰, Fe(II), or the H₂ released by the reaction of iron. It was likely that all these reducing species could be involved in the reduction.

Brine solution: Figure 4 shows the measured concentrations of Pu as a function of pC_{H⁺} in the synthetic brine solution. The results for the control solutions (without Fe⁰) of the brine were very similar to those for the control solutions of dilute NaCl. The concentration of Pu in these solutions did not change from the initial concentration in the acidic region (2.5·10⁻⁴M) and decreased slightly in the region of higher pC_{H⁺}. However, the results for the sample solutions (containing Fe⁰) of the brine were very different from those of dilute NaCl: dramatic decreases in total Pu concentrations were observed at all pC_{H⁺} values in the case of NaCl, while significant decreases in total Pu concentration was observed only between pC_{H⁺} values of 7 and 9 in the case of brine samples.

If the decrease in Pu concentration resulted from the reduction of Pu(VI) in the presence of iron, the results

indicated that the reduction of Pu(VI) from the brine solutions proceeded more slowly than in the dilute NaCl solutions. The concentrations of Pu in the pH region below 9 decreased to the range of 10⁻⁵ to 10⁻⁸M, while the concentrations of Pu in the pH region between 9 and 12 decreased only slightly – by less than one order of magnitude. The E_h values of the brine solutions of pC_{H⁺} values between 9 and 12 were positive (+470 to +670 mV), while the E_h values of solutions between pC_{H⁺} values between 7 and 9 were negative (-290 to -400 mV). Evidently this difference in the electrochemical potential was responsible for the observed Pu concentration behavior.

Positive electrochemical potentials implied that insufficient reducing agents existed in those few solutions (pC_{H⁺} 9 to 12). Although the amounts of Fe powder initially added to each centrifuge tube were excessive relative to the amount of Pu to be reduced, it was probable that the Fe powder lost its reducing activity due to the formation of a surface coating of hydroxides in basic solutions. Based on this assumption, the higher the pC_{H⁺}, the less active the Fe powder became.

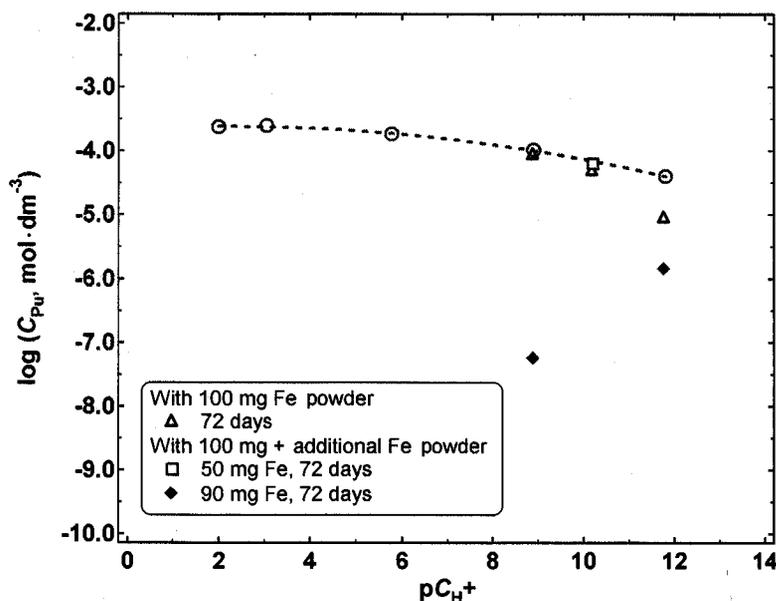


Fig. 5. Effect of iron powder on Pu concentrations in the high pC_{H^+} ERDA6B brines. Different amounts of Fe powder (50 or 90 mg) were added to solutions originally containing 100 mg Fe powder and equilibrated for 72 days. After Fe addition, these samples were then equilibrated for an additional 7 days

Thus, Pu would be reduced less. To test this assumption, more fresh Fe powder was added to these three brine sample solutions after 72 days. Sampling and analysis were then performed. These three solutions were labeled Sb-07PU, Sb-08PU and Sb-09PU, respectively; the results are summarized in Table 3 and Fig. 5.

As shown in Fig. 5, Fe powder (90 mg) was added to solutions Sb-07PU and Sb-09PU. Plutonium concentration in both solutions was further decreased, but to a very different extent: $3 \cdot 10^{-8}M$ for Sb-07PU and $8 \cdot 10^{-5}M$ for Sb-09PU. The E_h values of these samples were observed to decrease by >700 Mv (7 as/e 3). This result suggests that more iron was needed to maintain the same reducing conditions in brine solutions of higher pC_{H^+} . In Sb-08PU, although an additional 50 mg of iron were added, the E_h values were still positive (Table 3) and no further decrease in Pu concentration was observed suggesting that the amount of active iron was still insufficient.

Because of the higher concentrations of Pu in the brine experiments than in the experiments with dilute NaCl, it was possible to analyze the oxidation states of Pu in the brine solutions. It was found that 85 to 90% Pu in all brine solutions existed as Pu(V). The decrease in the concentration of Pu(V) upon the addition of iron could have resulted from a finite amount of irreversible reduction of Pu(V) to Pu(IV) and precipitation as hydrous oxide. As a result, the concentration of Pu(V) in the solution could probably be controlled by the following heterogeneous redox reaction:



As pointed out by RAI et al.,²⁵ the concentration of Pu(V) in a solution equilibrated with $PuO_2 \cdot xH_2O(s)$ was controlled by pH and the electrochemical potential. For instance, if the E_h of the solution was made negative (e.g., by adding more Fe powder), reaction (2) would be shifted to the left, and the concentration of Pu(V) would decrease as more Pu precipitated from the solution as $PuO_2 \cdot xH_2O(s)$. This was consistent with the observation for samples Sb-07PU, Sb-08PU, and Sb-09PU.

The observation that the redox potential (E_h) in several brine solutions (Sb-07PU, Sb-08PU, and Sb-09PU) was high and positive (+470 to +670 mV) is consistent with previous studies. RUNDE and KIM²⁷ and RAI et al.²⁸ reported that an increase in the redox potential was observed during α -radiolysis in concentrated NaCl solutions. The radiolytically formed hydroxyl radicals react with chloride ions to form an oxidizing medium²⁷ consisting of Cl_2 , $HClO$, and ClO^- . It is likely that, in the present study of ^{239}Pu , α -radiolysis had a significant effect on the redox potential and stabilized Pu(V) in NaCl brine solutions.

Absorption spectrophotometry was used to monitor the change of Pu(VI) in the presence of Fe powder. Ten mg of Fe powder were added to 3.0 ml of brine solution (pC_{H^+} 8.9) initially containing $1.5 \cdot 10^{-3}M$ Pu(VI). The absorption spectra of this solution were then followed for as long as 55 days. Results indicated that the absorption band at 845 nm, assigned to hydrolytic

species of Pu(VI), decreased with time and disappeared after 55 days (Fig. 6). Therefore, Pu(VI) was reduced and precipitated from the solution in the presence of Fe powder. Although no significant absorption peaks for Pu(V) (around 569 nm) were observed for this solution, Pu in this solution could still be Pu(V) in equilibrium with $\text{PuO}_2 \cdot x\text{H}_2\text{O}(s)$, since the concentration of Pu(V) in this solution was below the detection limit for spectrophotometric determination.

REED et al. monitored the absorption band of Pu(VI) in actual WIPP ERDA6 brines for one year.²⁹ Without added reducing agents such as iron, the absorbance at 845 nm for Pu(VI) decreased by about 25 to 30% after 290 days. REED et al. attributed this to the auto reduction of Pu(VI) toward Pu(V). Regardless of the mechanism responsible, the reduction rate observed by REED et al. was much slower than the reduction of Pu(VI) in the presence of iron observed in the present study.

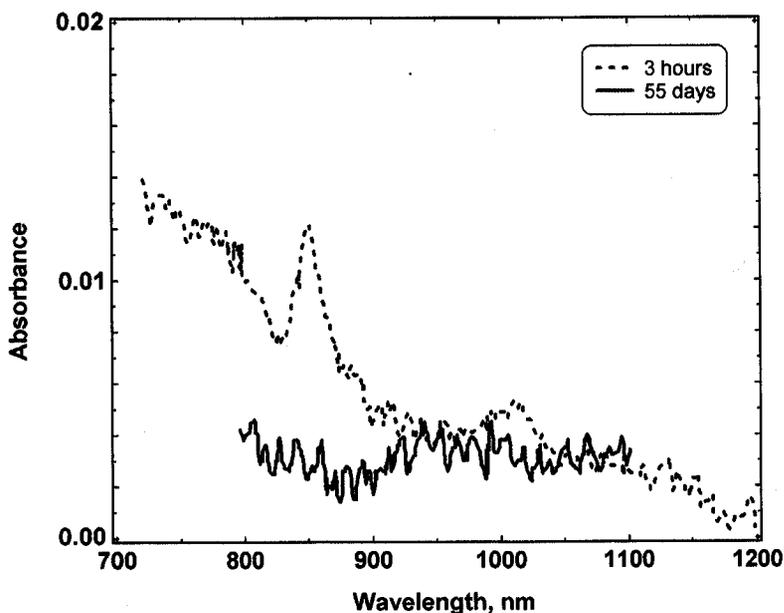


Fig. 6. Absorption spectra of Pu in the ERDA6B brine solution (3 ml of 0.0015M Pu(VI) at pC_{H^+} 8.9 containing 10 mg Fe powder) at different equilibration periods

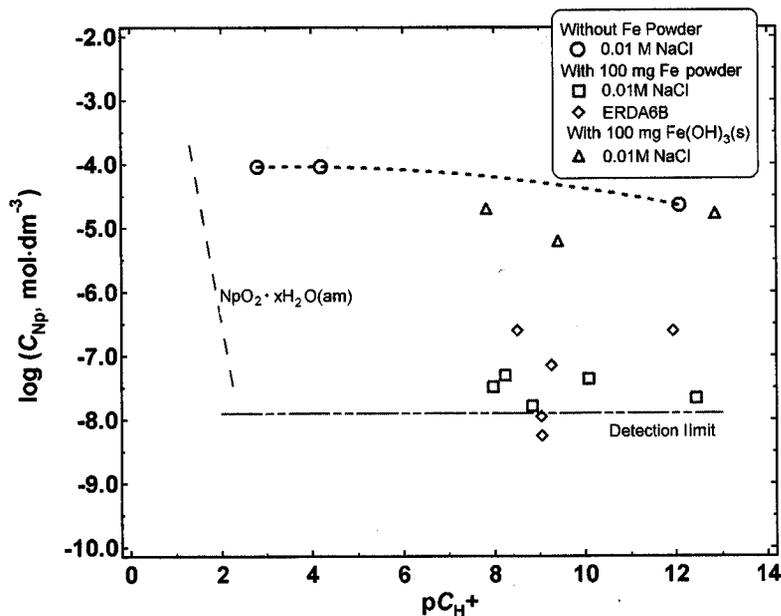


Fig. 7. Effect of iron powder on observed Np concentration in 0.01M NaCl containing Fe powder or $\text{Fe}(\text{OH})_3(s)$ and Np(V), and ERDA6B brines containing Np(V) with and without Fe powder. All samples were equilibrated for 66 days

Neptunium in dilute NaCl and the ERDA6B brine solutions

Similar to the studies of Pu, two sets of redox experiments with Np were performed in 0.01M NaCl and the brine solution, respectively. In each set, several sample solutions (with Fe⁰) and control solutions (without Fe⁰) were studied, with an initial pC_H⁺ region of 2 to 12. For the same reasons discussed in the previous section, the pC_H⁺ of the sample solutions shifted to a region of 7 to 12.

The total concentration of Np in the solution was determined by liquid scintillation counting at time intervals indicated in Table 2. The oxidation states of Np were determined with solvent extraction and spectrophotometry whenever feasible. As shown in Fig. 7, the concentration of Np in the control solutions did not change significantly; the concentration of Np in the sample solutions decreased to 10⁻⁸ to 10⁻⁷M in 2 months. Spectrophotometric measurements of the sample solutions were consistent with these results, the absorption peak of Np(V) at 980 nm decreased rapidly in the presence of Fe powder, and the total aqueous Np concentration dropped below the detection limit of absorption spectroscopy.

The concentrations of Np in the control solutions were high enough (10⁻⁵ to 10⁻⁴M) to use solvent extraction experiments to determine the oxidation state. Neptunium remained as Np(V) in the control solutions after 66 days. Unfortunately, the final concentrations of Np in the sample solutions were too low (10⁻⁸ to 10⁻⁷M) to determine oxidation states, even with solvent extraction.

The very low concentrations of Np in the presence of Fe powder strongly suggest the reduction of Np(V) to Np(IV) and precipitation of Np as NpO₂·xH₂O (am). However, it is possible that some adsorption of Np(V) on Fe powder or Fe hydroxide, produced from oxidation of Fe⁰, could have occurred and accounted for the low concentration of Np. To test this latter possibility, an

adsorption experiment was performed with γ-Fe(OH)₃ in the pC_H⁺ region of 8 to 12. Fe(OH)₃ was used because it was expected to adsorb Np(V) more strongly than Fe powder or Fe(OH)₂, which also could have been present. The amount of Fe(OH)₃ added to each tube was equivalent to the Fe powder used in the redox experiments, so the maximum adsorption effect could be evaluated even if all the Fe powder was converted to Fe(OH)₃. The adsorption experiment in the pC_H⁺ region of 8 to 12 demonstrated that if Np(V) was not reduced to Np(IV), adsorption of Np(V) on Fe(OH)₃ decreased the concentration of Np(V) by only 50%, to a final value of approximately 10⁻⁵M. This value is 2 to 3 orders of magnitude higher than those in the presence of Fe powder (10⁻⁸ to 10⁻⁷M, Fig. 7). Furthermore, in our redox experiments, it was very unlikely that significant amounts of Fe(OH)₃ would be present in the reaction tubes. Instead, a mixture of unreacted Fe powder and Fe(OH)₂ should be the major components of the solid phase. Adsorption of Np(V) on Fe powder or Fe(OH)₂ was expected to be less significant than on Fe(OH)₃. Obviously, adsorption was not a significant process that determined the final concentration of Np in the redox experiments.

As a result, even though the oxidation state of Np in the sample solutions could not be experimentally determined, the results strongly indicate that Np(V) was reduced to Np(IV) in the presence of Fe powder and precipitated from the solution as NpO₂·xH₂O (am). Comparing the concentrations of Np in the sample solutions with the solubility of NpO₂·xH₂O (am) in dilute solutions^{30,31} provides further support for this assumption (Fig. 7). The concentrations of Np in the sample solutions were near the detection limit, and those in equilibrium with NpO₂·xH₂O (am) were also expected to be near the detection limit in the pC_H⁺ region of 8 to 12.^{30,31} This suggests that Np(V) was reduced in the presence of Fe powder and precipitated from solution as NpO₂·xH₂O (am).

Table 4. Concentrations of U in the synthetic brine solution (initial [U(VI)] = 0.015M)

| Solution No. | After 27 days | | After 55 days | |
|------------------|------------------------------|---------|------------------------------|---------|
| | pC _H ⁺ | log [U] | pC _H ⁺ | log [U] |
| Sb-05U (sample) | 8.96 | -5.80 | 8.93 | -5.77 |
| Rb-05U (control) | 8.95 | -5.83 | 8.90 | -5.76 |
| Sb-06U (sample) | 13.41 | -6.41 | 13.20 | -6.13 |
| Rb-06U (control) | - | - | 13.15 | -6.06 |

Uranium in dilute NaCl and the ERDA6B brine solutions

In the experiments with U, the initial solutions contained 0.015M U(VI). Results with U can be summarized as follows: (1) in the dilute NaCl media, concentrations of U in the sample solutions decreased after 27 days to 10^{-8} M. This concentration was much lower than in the control solutions; (2) in the brine media, concentrations of U in the sample solutions were similar to those in the control solutions, even after 55 days, as shown in Table 4.

Solvent extraction analyses and spectrophotometric measurements indicated that U existed as U(VI) in the control solutions and that U(VI) was stable in the absence of Fe powder. No data on the oxidation states were obtained by solvent extraction or spectrophotometric methods for the sample solutions because of the low concentrations. However, using the approach of comparing solubility of known solids with the observed concentrations, as discussed previously, the decrease in U concentrations in 0.01M NaCl solutions containing Fe^0 was attributed to the reduction of U(VI) to U(IV) and subsequent precipitation of U(IV) hydrous oxide, which has very low solubility under these conditions.³ The lack of reduction of U(VI) in brine solutions could be attributed to the lower reducing capacity of Fe powder in brines than in dilute solutions. This was supported by observations that the reduction of Pu(VI) was slower, and Pu(V) tended to stabilize in brine solutions.

Conclusions

A combination of solubility measurements, solvent extraction, and spectrophotometry were used in this study to determine the oxidation state distributions of Pu, Np, and U in dilute NaCl and brine solutions. In dilute NaCl solutions (pC_{H^+} 7 to 12), all three actinides in their initial oxidation states (i.e., Pu(VI), Np(V), and U(VI)), were reduced to lower oxidation states and precipitated from the solution in the presence of Fe^0 within a few days to a few months. The solid phase precipitated from the solutions was most likely the tetravalent hydrous oxides of the actinides ($\text{AnO}_2 \cdot x\text{H}_2\text{O}$). However, in the synthetic brine solutions with Fe^0 (pC_{H^+} 8 to 13), the three actinides exhibited different behavior. For Pu(VI), the reduction in the brine was much slower than in the dilute NaCl solution, and the dominant oxidation state of Pu in the solution was Pu(V). The concentration of Pu(V) in the brine solution (with Fe powder) was probably controlled by the electrochemical potential and could best be represented by the heterogeneous redox reaction: $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s}) = \text{PuO}_2^+ + e^-$. For Np(V), reduction occurred in the presence of Fe^0 , and Np

precipitated from the brine solution probably as Np(IV) hydrous oxide. For U(VI), no significant reduction was observed in the brine solution with Fe^0 within 55 days.

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