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BY ORGANIC CHELATING AGENTS

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# REDUCTION OF Np(VI) AND Pu(VI) BY ORGANIC CHELATING AGENTS

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*Plutonium / Neptunium / Waste Isolation Pilot Plant (WIPP) / Organic Chelates / Reduction*

## Abstract

The reduction of  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  by oxalate, citrate, and ethylenediaminetetraacetic acid (EDTA) was investigated in low ionic strength media and brines. This was done to help establish the stability of the An(VI) oxidation state in the presence of organic complexants. The stability of the An(VI) oxidation state depended on the pH and relative strength of the various oxidation state-specific complexes. At low ionic strength and pH 6,  $\text{NpO}_2^{2+}$  was rapidly reduced to form  $\text{NpO}_2^+$  organic complexes. At longer times, Np(IV) organic complexes were observed in the presence of citrate.  $\text{PuO}_2^{2+}$  was predominantly reduced to  $\text{Pu}^{4+}$ , resulting in the formation of organic complexes or polymeric/hydrolytic precipitates. The relative rates of reduction to the An(V) complex were  $\text{EDTA} > \text{citrate} > \text{oxalate}$ . Subsequent reduction to An(IV) complexes, however, occurred in the following order:  $\text{citrate} > \text{EDTA} > \text{oxalate}$  because of the stability of the An(V)-EDTA complex. The presence of organic complexants led to the rapid reduction of  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  in G-Seep brine at pHs 5 and 7. At pHs 8 and 10 in ERDA-6 brine, carbonate and hydrolytic complexes predominated and slowed down or prevented the reduction of An(VI) by the organics present.

## Introduction

The role of organic compounds in defining actinide speciation and mobility in subsurface groundwaters is growing in importance [1-8]. Organic species are present in the subsurface from both natural (e.g. hydro-geological and microbiological activity) and anthropogenic sources [1,2]. In far-field studies, the long-term mobility of actinide species has been linked to their association/interaction with organic species [3]. Enhanced radionuclide migration has been associated with organic complexants [4,5], and natural organics present in the subsurface [6-8].

Organic complexants directly affect the speciation of dissolved actinides in two ways. They can form oxidation state-specific complexes that increase the solubility of the oxidation state and stabilize it to subsequent reduction or oxidation. The second, perhaps less recognized effect, is that many organic chelating agents reduce and/or oxidize the multivalent actinides. The

net effect of organic complexants on actinide speciation is therefore a combination of their indirect effect on biological activity, their complexation, and their ability to reduce or oxidize the multivalent actinides.

Herein we report the results of two studies to establish the effect of oxalic acid, citric acid, and EDTA on the stability of  $\text{PuO}_2^{2+}$  and  $\text{NpO}_2^{2+}$ . We do not address the effects of other reducing agents expected to be present in the WIPP (e.g. iron and iron oxy-hydroxides). First, we established the oxidation state stability of An(VI) in low ionic strength media, at pH ~ 6, in the presence of oxalic acid, citric acid, or EDTA. Second, we investigated the oxidation state stability in simulated WIPP brines as a function of pH, brine composition, and carbonate concentration in the presence of a mixture of citrate, oxalate, and EDTA. The results obtained help establish the effects of organic waste constituents on actinide speciation and solubility in the proposed Waste Isolation Pilot Plant (WIPP) repository.

## Experimental

The isotopic purity of the  $^{242}\text{Pu}$  used was >99% by mass and 50% by curie content. The isotopic impurity in this sample was  $^{238}\text{Pu}$ . The  $^{237}\text{Np}$  used was > 99% pure by mass and ~ 97% pure by curie content. Both plutonium and neptunium were oxidized to the An(VI) oxidation state by fuming in perchloric acid and evaporating to near-dryness. They were dissolved in high-purity water (>18 M-ohm Barnstead Nanopure), checked spectroscopically for oxidation-state purity, and used to prepare the actinide solutions for both the low ionic strength and brine solutions. Citric acid (Aldrich 99.5+ % purity ACS reagent grade), oxalic acid (Aldrich 99+ % reagent grade) and EDTA (Aldrich 99+ % reagent grade) were used for the low-ionic-strength experiments. The monosodium salt of citric acid (Aldrich 99+ % reagent grade), oxalic acid, and the disodium salt dihydrate EDTA (Aldrich 99+ % reagent grade) were used in the brine experiments. All organic reagents were used without further purification.

The low-ionic-strength experiments were conducted at room temperature ( $21 \pm 2$  °C) in high purity water, in the dark, and with an excess of the organic chelating agent of interest. Four experiments were conducted for  $10^{-4}$  M solutions of each actinide in the following systems: (1) high-purity water (i.e., no organic species), (2)  $4.93 \times 10^{-3}$  M Citrate, (3)  $5.07 \times 10^{-3}$  M oxalate, and 4)  $4.98 \times 10^{-4}$  M EDTA. The pH was adjusted to 6 using either sodium hydroxide or hydrochloric acid and was buffered by the organic species present. The actinide oxidation state was monitored as a function of time by absorption spectrometry (CARY-5 spectrometer, see Table 2 for absorption maxima). Actinide concentrations were determined using alpha scintillation counting. The duration of the experiments was 197 days for the neptunium experiments and 110 days for the plutonium experiments performed.

Analogous experiments were done in simulated WIPP brine (see Table 1). Two brines, ERDA-6 at pH 8 and 10 and G-Seep at pH 5 and 7, were investigated. These experiments were performed in a controlled-temperature nitrogen glovebox at  $25 \pm 2$  °C, under anoxic conditions, and in the dark. In these experiments a mixture of oxalic acid, citric acid and EDTA was added. The organic acid concentrations were  $2.0 \times 10^{-4}$  M,  $2.0 \times 10^{-4}$  M and  $2.4 \times 10^{-4}$  M for EDTA, oxalate and citrate respectively. Carbonate, when required, was added to the brine experiments as an actinide-carbonate complex. No change in pH was noted as a result of the addition of the actinide to the brine solution. The duration of these experiments was two months.

## Results and Discussion

### *Reduction of $\text{PuO}_2^{2+}$ by Organic Complexants in Low Ionic Strength Media*

The extent of  $\text{PuO}_2^{2+}$  reduction, as a function of time and organic complexant, is shown in Figure 1. Plutonium (VI) was reduced in all of the systems studied. In high purity water, a slow reduction to Pu( V) was noted and attributed to radiolytic effects. Approximately 60% of

the  $\text{PuO}_2^{2+}$  initially present was reduced to  $\text{PuO}_2^+$  after 110 days. No evidence of further reduction to Pu(IV) species was noted.

At pH 6, all three organic complexants reduced  $\text{PuO}_2^{2+}$ . Oxalate formed a Pu(VI)-oxalate complex ( $\lambda_{\text{max}}$  at 845.5 nm) that was slowly reduced by the oxalate present. For the concentrations investigated, approximately 50% of the Pu(VI)-oxalate complex was reduced after 500 h. This increased to ~ 83% after 110 days. The reduction of the Pu(VI)-oxalate complex did not lead to the buildup of a Pu(V)-oxalate complex. Instead, plutonium polymers were formed that resulted in a net decrease in plutonium concentration in the system.

Citrate formed a Pu(VI)-citrate complex ( $\lambda_{\text{max}}$  at 856.2 nm) that was more rapidly reduced by citrate. Approximately 50% of the  $\text{PuO}_2^{2+}$  initially present in solution was reduced after 100 hours. After 110 days, approximately 5% of the Pu(VI) was still left in solution. The reduction of the Pu(VI)-citrate complex led to the formation of Pu(V)-citrate ( $\lambda_{\text{max}}$  at 549nm) and Pu(IV)-citrate (absorption bands at 689, 657, 506, and 497.5 nm) complexes. After 110 days, the Pu(IV)-citrate complex was predominant.

The reduction of  $\text{PuO}_2^{2+}$  in the presence of EDTA was instantaneous. For this reason, no spectral data on the Pu(VI) EDTA complex could be obtained. Initially, the predominant product was the Pu(V)-EDTA complex ( $\lambda_{\text{max}}$  at 545 nm). This complex was reduced further to form a Pu(IV)-EDTA complex (absorption bands at 655, 686 and 504 nm). Although the rate of reduction to Pu(V) was much more rapid than observed for citrate, net reduction to Pu(IV) species was significantly slower.

The relative rates for reducing Pu(VI) to Pu(V) species were as follows: EDTA >> citrate > oxalate. This is consistent with established trends for the reduction of plutonium by amines, carboxylic acids, and tertiary alcohols. The relative rates for reducing Pu(VI) to Pu(IV) were: citrate > EDTA > oxalate. These results simply reflect the importance of complexation on stabilizing the Pu(V) oxidation state against further reduction to Pu(IV) species. Oxalic acid,

which forms a weak Pu(V) and Pu(IV) complex, did not stabilize Pu(V) or prevent polymer formation at pH 6.

### *Reduction of PuO<sub>2</sub><sup>2+</sup> by Organic Complexants in Simulated Brines*

The stability of PuO<sub>2</sub><sup>2+</sup> in selected WIPP brines (see Table 3) was evaluated by placing a mixture of EDTA, citrate and oxalate in the following simulated WIPP brines: ERDA-6 at pH 8 and 10 with carbonate, ERDA-6 at pH 10 without carbonate, and G-Seep at pH 5 and 7. Spectra and trends obtained were compared to the results obtained in the low ionic strength experiments to identify the oxidation state and/or complex present and establish effects specific to the brine system investigated. The final absorption spectra obtained in each brine are shown in Figure 2.

In G-Seep brine, at both pH 5 and 7, the same result was obtained. The Pu(VI) aquo/chloride species, which we have shown to be stable for more than 18 months [9], was rapidly reduced to form Pu(V) and Pu(IV) organic complexes. These complexes were relatively stable over the duration of our experiments.

In ERDA-6 brine, the presence of carbonate slowed/prevented the reduction of Pu(VI) by the organics present. At pH 8 (experiment Pu-ORG-E8), the initial spectrum was a Pu(VI) aquo/organic species that, over time, was reduced to form Pu(IV) and Pu(V) species that were not well correlated with spectra obtained in G-Seep brine at lower pH. Further work is needed to establish the specific plutonium species observed in these spectra. At pH 10 when carbonate was present, the Pu(VI)-carbonate complex predominated. Little or no reduction occurred. When carbonate was not present at pH 10, the Pu(VI) hydrolytic species ( $\lambda_{\max}$  at 860 nm) was slowly reduced. No significant buildup of Pu(V) or Pu(IV) species was noted so presumably the Pu(IV) generated was being precipitated as a Pu(IV) phase (e.g. Pu polymer or hydroxide phase).

Although there are significant differences between the brine experiments and the low-ionic-strength experiments, some comparisons can be made. At near neutral pH (i.e. the low-ionic-strength experiments and G-Seep brine experiments), all Pu(VI) species were reduced. In

brine, the observed rates of reduction were most similar to those observed in the EDTA low-ionic-strength experiment. This is not surprising since the EDTA in the organic mixture used is the most redox active of the three organic complexants. The Pu(IV) organic complexes are expected to predominate in this pH range.

At higher pHs, carbonate and hydrolytic species compete with the organic complexes and have a substantial effect on the stability of Pu(VI). In the presence of carbonate, Pu(VI) forms stable Pu(VI) carbonate complexes at pH 10 but at pH 8, the Pu(VI) carbonate complex is destabilized by the organics present and Pu(VI) species are reduced to form Pu(IV) and Pu(V) organic complexes. In the absence of carbonate at pH 10, a much slower but definite reduction of Pu(VI) is noted. These data contrast with prior experiments [9], where the carbonate complex at pH 8 and the hydrolytic species at pH 10 were shown to be stable for over 18 months when no organic complexants were present.

#### *Reduction of $\text{NpO}_2^{2+}$ by Organic Complexants in Low Ionic Strength Media*

The neptunium(VI) oxidation state, as expected, was significantly less stable than the corresponding Pu(VI) species in the presence of the organic complexants investigated. The overall tendency was to form a relatively redox-stable Np(V) organic complex, although further reduction to form Np(IV) complexes was noted after 197 days for citrate. The buildup of Np(V) species in solution as a function of time is shown in Figure 3.

In the absence of organic complexants, complete reduction of  $\text{NpO}_2^{2+}$  to  $\text{NpO}_2^+$  occurred under the conditions of our experiments. This was established by monitoring the buildup of Np(V) at 980.4 nm. The % conversion to  $\text{NpO}_2^+$  was 5.1, 15.6, and 24.4% after 1, 16, and 29 days, respectively. Complete reduction to  $\text{NpO}_2^+$  was noted after 90 days. No further change in the absorption spectrum was noted after 197 days. This reduction was attributed to radiolytic effects and corresponds to a  $G[\text{Np(V)}] \sim 2.9$  molec/100 eV.

In the presence of oxalate,  $\text{NpO}_2^{2+}$  was rapidly reduced to form a  $\text{NpO}_2^+$ -oxalate complex (absorption maxima at 1030 and 988 nm). After 1.9 hours, 72% of the  $\text{NpO}_2^{2+}$  had been reduced. After 23 hours, essentially all the neptunium in solution was a  $\text{NpO}_2^+$ -oxalate complex. Once the  $\text{Np(V)}$  complex was formed, no further changes in the spectrum occurred. No spectral evidence for the formation of  $\text{Np(IV)}$  species was observed.

The reduction of  $\text{NpO}_2^{2+}$  was more rapid in the presence of citrate. After 1.6 h. ~ 95% of the neptunium was reduced to form a  $\text{NpO}_2^+$ -citrate complex (absorption bands at 1004 and 982 nm) with trace amounts of a  $\text{Np(IV)}$ -citrate complex (absorption bands at 769 and 737 nm) evident. After 16 days, all of the  $\text{Np(VI)}$  was gone, and there was a significant buildup of the  $\text{Np(IV)}$ -citrate complex in solution. After 197 days, approximately 1/3 of the Np was reduced to a  $\text{Np(IV)}$ -citrate complex.

The reduction of  $\text{NpO}_2^{2+}$  was instantaneous in the presence of EDTA. The predominant complex formed was the  $\text{NpO}_2^+$ -EDTA complex (absorption bands at 1024 and 988 nm) with no spectral evidence for reduction to  $\text{Np(IV)}$ -EDTA complexes, even after 197 days.

The reduction of  $\text{Np(VI)}$ , as expected, was more rapid than the corresponding reduction of  $\text{Pu(VI)}$  species. However, the same order of reactivity was noted: EDTA > citrate >> oxalate. Net reduction to  $\text{Np(IV)}$ -organic complexes was only noted in the case of citrate whereas all three organic complexants formed  $\text{Pu(IV)}$  species. This is consistent with the inherently greater stability of  $\text{Np(V)}$  compared to  $\text{Pu(V)}$ . Under most conditions,  $\text{Np(V)}$  complexes will predominate in the presence of organic species.

It is not clear at this time why citrate alone led to the formation of  $\text{Np(IV)}$  species. Citrate is more susceptible to biodegradation and is more photo-active than EDTA. Although steps were taken to prevent these phenomena (filter-sterilized media were used and experiments were conducted in the dark) additional work is needed to verify/explain the results obtained and establish the reaction mechanism.

### *Reduction of $\text{NpO}_2^{2+}$ by Organic Complexants in Simulated Brines*

The experiments performed in simulated WIPP brine (see Table 3) were analogous to those performed with plutonium and were done with the same simulated brines, pH, and carbonate concentrations. As observed with plutonium, the presence of organics led to the reduction of Np(VI) at a lower pH. At a higher pH, the Np(VI)-carbonate complex was predominant. The final absorption spectrum obtained in each brine is shown in Figure 4.

In G-Seep brine, similar results were obtained at pHs 5 and 7. After 1 day, over 96% of the Np(VI) had been reduced to an Np(V)-organic complex. After 7 days, all of the neptunium in solution had been reduced to Np(V) species. There were no further changes in the spectra for remainder of the two-month experiments. In these experiments, there was no spectral evidence for the formation of Np(IV) species.

The presence of carbonate complexes greatly reduced the rate of Np(VI) reduction in the presence of organics. The Np(VI)-carbonate complex predominated at pHs 8 and pH 10 in ERDA-6 brine. Based on changes in the absorption spectrum with time, we estimate that approximately 95% of the carbonate complex remained in solution after 1 month and over 80% was in solution after two months. The reduction of the Np(VI)-carbonate complex led to the buildup of Np(V)-organic complexes in solution. Some evidence for the formation of Np(IV) species was noted at both pH 8 and pH 10. In the absence of carbonate at pH 10, Np(VI) was rapidly removed from solution by reduction to form Np(V) and Np(IV)-organic complexes and precipitates.

The results obtained in the simulated brines investigated can be compared to both the low-ionic-strength experimental results and the long-term studies we have conducted with no organic complexants present in solution [9]. At near-neutral pH, reduction is rapid, and a stable Np(V) organic complex is formed. The observed rates of reduction in G-Seep brine are again most consistent with the results obtained in the EDTA low-ionic-strength experiments.

Although carbonate complexes predominated, the formation of Np(V) and Np(IV) species was noted at higher pHs. The observed reduction of Np(VI) is attributed to the presence of the organic complexants in solution since the Np(VI)-carbonate complexes were shown to be stable when the organics were absent [9] and no Np(IV/V) species were noted in these longer-term experiments. Reduction to Np(V) and Np(IV) species, along with precipitation, proceeds more rapidly when carbonate is not present to stabilize Np(VI).

### Conclusions and Observations

The presence of organic chelating agents led to the destabilization of the Pu(VI) and Np(VI) oxidation states in most cases investigated. Significant differences in rates of reduction were noted for oxalate, citrate and EDTA. The actinide-organic systems investigated were not at steady-state so it was not possible to experimentally establish the long-term/final oxidation state distribution of the actinide complexes investigated. Evidence to date, however, is consistent with Np(V) and Pu(IV) being the predominant oxidation states in the presence of organics.

There were some similarities in the behavior of the three organic ligands investigated towards neptunium and plutonium. Oxalate, in both cases, led to significantly slower rates of reduction of An(VI). For neptunium, reduction to Np(V) in the presence of both citrate and EDTA was rapid. The resultant Np(V) speciation was, however, more complex. For plutonium, Pu(VI) was reduced more rapidly by EDTA than citrate. The stability of the Pu(V) species generated, however, was much greater with EDTA than citrate, leading to a slower reduction of the Pu(V) EDTA complex. Overall, citrate was a more effective reducing agent from the perspective of the formation of Pu(IV) and Np(IV) species.

In the brine systems investigated, Pu(VI) and Np(VI) were rapidly reduced in G-Seep brine at pHs 5 and 7. In ERDA-6 brine, carbonate complexation stabilized Pu(VI) towards reduction at pH 10 but not at pH 8. Slow reduction of Pu(VI) was noted at pH 10 when

carbonate was not present. For Np(VI), although the carbonate complex predominated at pHs 8 and 10, reduction by the organic complexants present to form Np(IV) and Np(V) species was observed. Reduction was more rapid when no carbonate was present in solution. These data combine to show, with the one exception of the Pu(VI) carbonate system at pH 10, that the presence of organic complexants promote the reduction of Pu(VI) and Np(VI) in brine systems.

### Acknowledgement

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**Table 1. Composition of the G-Seep and ERDA-6 Simulated WIPP Brines**

Element or Species	ERDA-6 <sup>a</sup> (M)	G-Seep <sup>b</sup> (M)
Cl	4.18	4.56
SO <sub>4</sub> <sup>2-</sup>	0.150	0.267
B	0.057	0.13
<sup>c</sup> CO <sub>3</sub> <sup>2-</sup> /HCO <sub>3</sub> <sup>-</sup>	0	0
Br	0.010	0.015
Na	4.37	3.76
K	0.087	0.304
Mg	0.017	0.551
Ca	0.011	0.0069

<sup>a</sup>This is a Castile synthetic brine at pHs 8 and 10.  
<sup>b</sup>This is a Salado synthetic brine at pHs 5 and 7.  
<sup>c</sup>Carbonate was added with the actinide to a concentration of 2 mM

**Table 2. Oxidation-State Specific Absorption Maxima at pH 6 for Plutonium and Neptunium in the Presence of Organic Chelating Agents**

Actinide	Complexant/Species	Oxidation State	Absorption Maxima (nm)
Plutonium	Aquo/Chloride	VI	830.8, 839.5, and 851 depending on pH
		V	569
	Oxalate	VI	845.5
	Citrate	VI	856.2
		V	549 and 569
		IV	689, 657, 506, and 497.5
	EDTA	V	545
		IV	655, 686, and 504
Aquo/Chloride	VI	1223	
	V	980.4	
Neptunium	Oxalate	V	1030, 988, 480, and 445
	Citrate	V	1004 and 982
		IV	769, 737, and 618
	EDTA	V	1024, 988, and 617

**Table 3. Experimental Matrix to Determine the Redox Stability of Pu(VI) and Np(VI) in the Presence of Chelating Agents**

Actinide	Experiment Designation	*Brine and pH
Pu-242	PU-ORG-E8	Organics in ERDA-6 with $10^{-4}$ M Carbonate at pH 8
	PU-ORG-E10	Organics in ERDA-6 with $10^{-4}$ M Carbonate at pH 10
	PU-ORG-E10-NC	Organics in ERDA-6 at pH 10, no carbonate
	PU-ORG-G5	Organics in G-Seep at pH 5
	PU-ORG-G7	Organics in G-Seep at pH 7
Np-237	NP-ORG-E8	Organics in ERDA-6 with $10^{-4}$ M Carbonate at pH 8
	NP-ORG-E10	Organics in ERDA-6 with $10^{-4}$ M Carbonate at pH 10
	NP-ORG-E10-NC	Organics in ERDA-6 at pH 10, no carbonate
	NP-ORG-G5	Organics in G-Seep at pH 5
	NP-ORG-G7	Organics in G-Seep at pH 7
Actinide Blanks	B-ORG-G5	Organics in G-Seep at pH 5
	B-ORG-G7	Organics in G-Seep at pH 7
	B-ORG-E8	Organics in ERDA-6 at pH 8
	B-ORG-E10	Organics in ERDA-6 at pH 10
*Each experiment contained ~ 0.2 mM of EDTA, citrate and oxalate with 0.1 mM of the actinide		

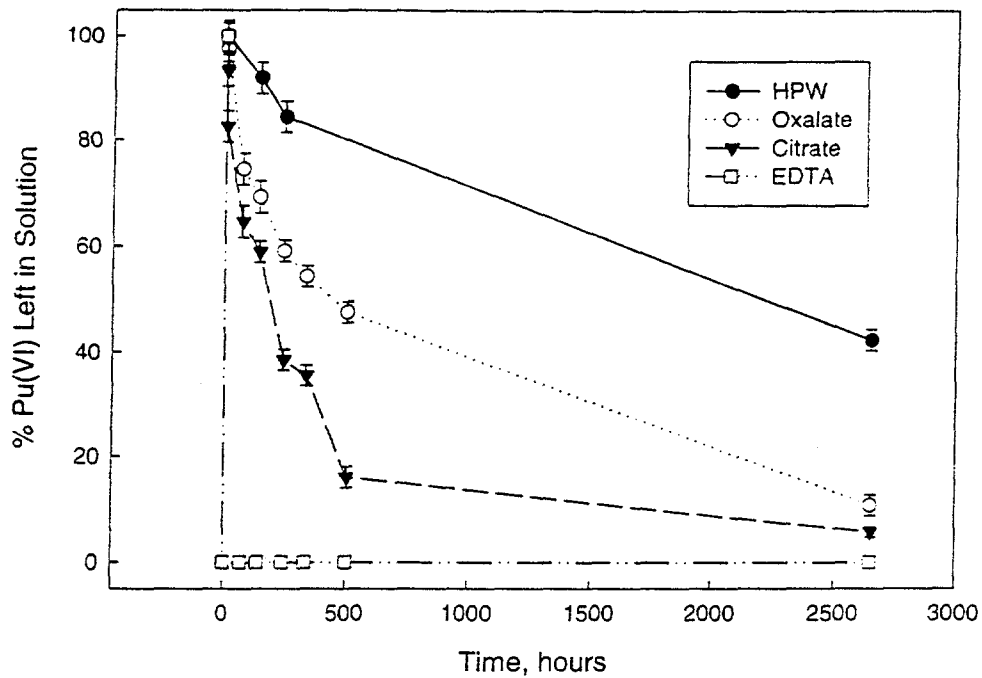


Figure 1. Reduction of Pu(VI) in the Low Ionic Strength Organic Interaction Studies as a Function of the Organic Complexant Present.

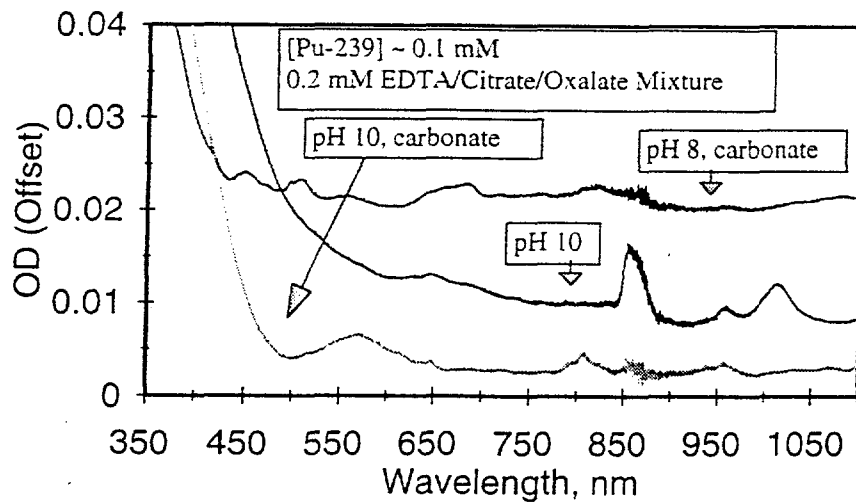
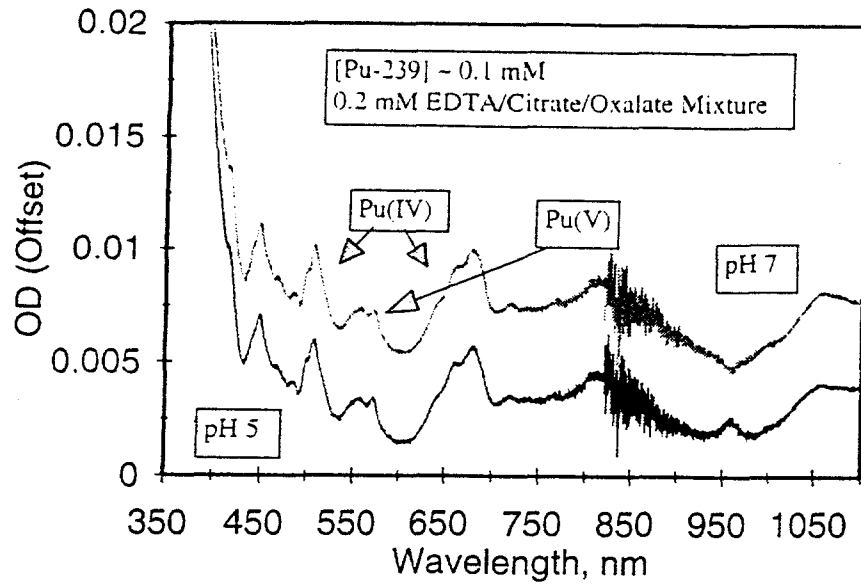
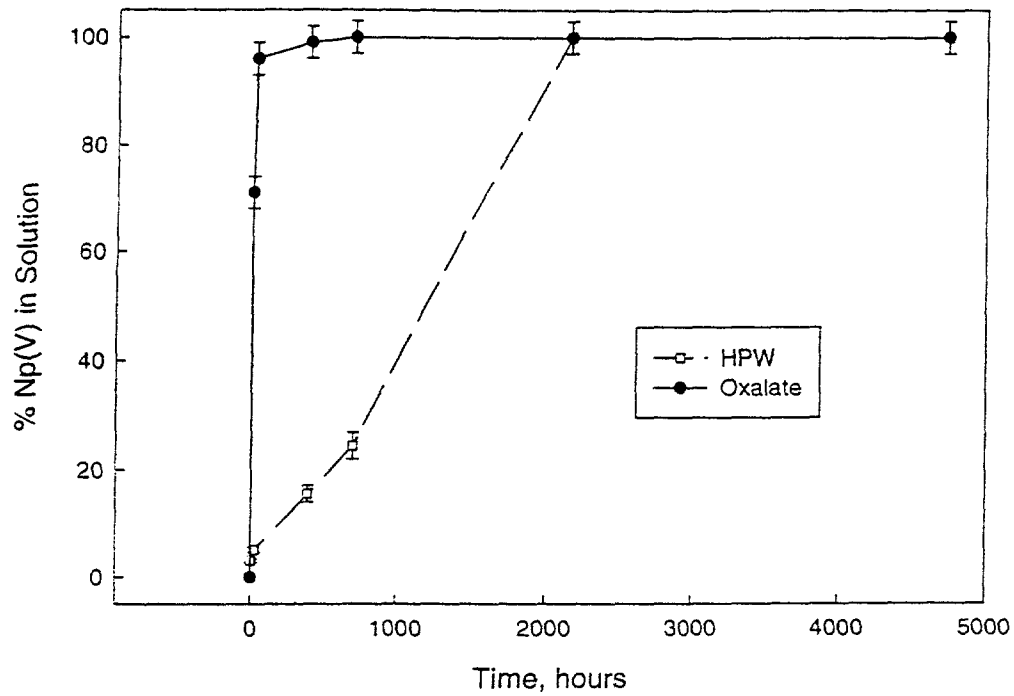
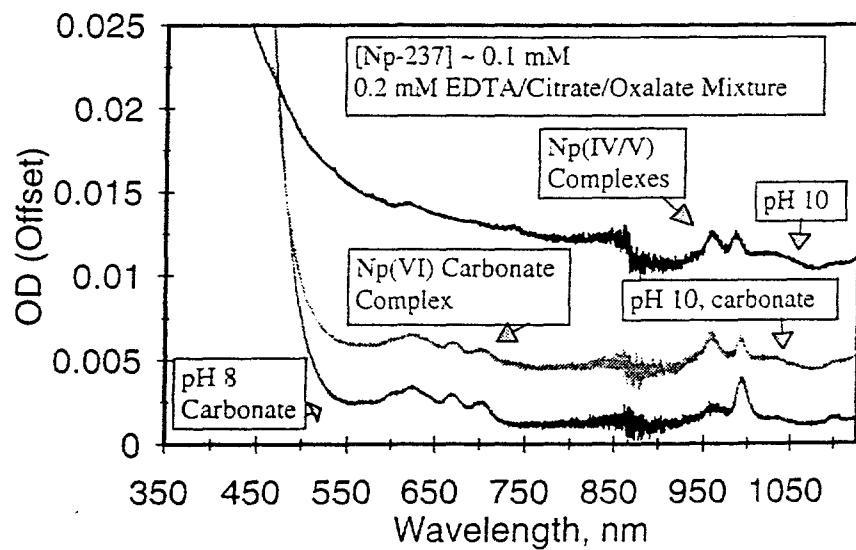
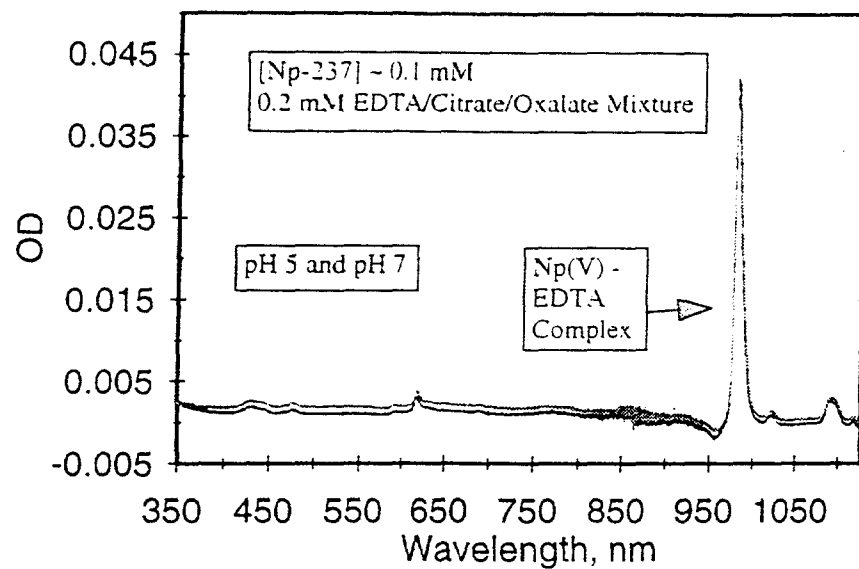


Figure 2. Final Absorption Spectra for Plutonium in the Simulated Brine Experiments for G-Seep Brine (Top) and ERDA-6 Brine (Bottom).



**Figure 3. Buildup of Np(V) as a Function of Time due to Reduction in the Low Ionic Strength Organic Experiments. Reduction for Citrate and EDTA (not shown) was Instantaneous.**



**Figure 4.** Final Absorption Spectra for Neptunium in the Simulated Brine Experiments for G-Seep Brine (Top) and ERDA-6 Brine (Bottom).