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Enhanced Chemical Cleaning of SRS Waste Tanks to Improve Actinide Solubility

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EXECUTIVE SUMMARY

Processes for the removal of residual sludge from SRS waste tanks have historically used solutions containing up to 0.9 M oxalic acid to dissolve the remaining material following sludge removal. The selection of this process was based on a comparison of a number of studies performed to evaluate the dissolution of residual sludge.[1] In contrast, the dissolution of the actinide mass, which represents a very small fraction of the waste, has not been extensively studied. The Pu, Np, and Am in the sludge is reported to be present as hydrated and crystalline oxides.[2-4] To identify aqueous solutions which have the potential to increase the solubility of the actinides, the alkaline and mildly acidic test solutions shown below were selected as candidates for use in a series of solubility experiments.

8 wt % (0.9 M) oxalic acid
2 wt % (0.22 M) oxalic acid
1.8 wt % (0.2 M) oxalic acid/0.1 M citric acid
0.18 M HNO_3/0.5 wt % (0.056 M) oxalic acid
0.18 M HNO_3/0.2 M $NaMnO_4$
0.18 M HNO_3
10 M NaOH
10 M NaOH/0.2 M $NaMnO_4$
1 M $NaHCO_3$/Na_2CO_3 at pH 9.5
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ at pH 9.5
0.05 M DTPA at pH 2-4
0.18 M HNO_3 blank
10.0 M NaOH blank
1 M $NaHCO_3$/Na_2CO_3 at pH 9.5 blank

The efficiency of the solutions in solubilizing the actinides was evaluated using a simulated sludge prepared by neutralizing a HNO_3 solution containing Pu, Np, and Am. The hydroxide concentration was adjusted to a 1.2 M excess and the solids were allowed to age for several weeks prior to starting the experiments. The sludge was washed with 0.01 M NaOH to prepare the solids for use. Following the addition of an equal portion of the solids to each test solution, the concentrations of Pu, Np, and Am were measured as a function of time over a 792 h (33 day) period to provide a direct comparison of the efficiency of each solution in solubilizing the actinide elements. Although the composition of the sludge was limited to the hydrated actinide oxides (and did not contain other components of demonstrated importance), the results of the study provides guidance for the selection of solutions which should be evaluated in subsequent tests with a more realistic surrogate sludge and actual tank waste.

The results from the solubility experiments showed that the test solutions containing 0.2 M $NaMnO_4$ were highly effective in solubilizing the Pu. The order of the solutions from the highest to the lowest concentrations achieved was as follows:

0.18 M HNO_3/0.2 M $NaMnO_4$,
> 10 M NaOH/0.2 M $NaMnO_4$,
> 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$.

The concentrations after 792 h (33 days) fell in the range of 0.4-2.0E-02 mol/L (1.0-4.8 g/L); although, the Pu in each solution was at or near its maximum concentration after 168 h (1 week). The concentrations of Pu in these solutions were higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (5.2E-03 mol/L or 1.2 g/L) except for the concentration in $NaHCO_3/Na_2CO_3/NaMnO_4$ solution which was slightly lower.

The three solutions containing $NaMnO_4$ and the 0.18 M HNO_3 solution were highly effective in solubilizing the hydrated NpO_2 in the surrogate sludge. The order of the solutions from the highest to the lowest concentrations achieved after 792 h (33 days) was as follows:

0.18 M HNO_3/0.2 M $NaMnO_4$,
= 10 M NaOH/0.2 M $NaMnO_4$,
> 0.18 M HNO_3,
> 1 M $NaHCO_3/Na_2CO_3$/0.2 M $NaMnO_4$.

The concentrations in the final samples fell in the range of 3.2-4.6E-04 mol/L (0.08-0.10 g/L). The Np in these solutions was also at or near its maximum concentration after only 168 h (1 week). The concentrations were all significantly higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (6.5E-05 mol/L or 0.015 g/L).

The high concentrations of Pu and Np in the test solutions containing permanganate were due to the oxidation of the Pu(IV) and Np(IV) to higher and more soluble valences (i.e., Pu(VI) and Np(V)/Np(VI)). The increased solubility of Np in the 0.18 M HNO_3 is a result of the accessibility of the more soluble higher valence states during dissolution in contrast to Pu which prefers to remain in the less soluble 4+ valence.

The Am concentrations measured in the test solutions show that 0.18 M HNO_3 was the most effective solution investigated for the dissolution of the hydrated Am_2O_3. The Am_2O_3 dissolved quickly and the concentration remained constant during the course of the experiment. The final concentration after 792 h (33 days) was 4.0E-05 mol/L (0.01 g/L). The concentration of Am in the HNO_3 solution was nearly two order of magnitude higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (4.4E-07 mol/L or 0.00011 g/L). At the beginning of the experiment, the next highest Am concentration was measured in the solution containing 0.18 M HNO_3/0.2 M $NaMnO_4$; however, over the course of the experiment the Am concentration decreased almost two orders of magnitude. The decrease in the concentration is attributed to the oxidation of Am(III) to Am(V) and coprecipitation with MnO_2. The next most effective solutions in solubilizing the Am were 0.05 M DTPA and the two remaining solutions containing $NaMnO_4$; although, the Am concentration in the 10 M NaOH/0.2 M $NaMnO_4$ started to decrease after 336 h (2 weeks), perhaps due to reaction with the permanganate to produce Am(V) which coprecipitated with other solids in the test solution.

The remaining solutions evaluated in the experiments were not effective in solubilizing the Pu, Np, and Am from the surrogate sludge. One notable exception was the 0.9 M oxalic acid. The Pu concentration after 792 h (33 days) was comparable to the concentrations measured in the 10 M NaOH/0.2 M $NaMnO_4$ solution; however, the concentrations measured in the earlier samples were lower and exhibited a somewhat cyclic behavior (peaking twice at lower concentrations during the test period). The actinide concentrations in other solutions containing oxalic acid (0.22 M oxalic acid and 0.2 M oxalic acid/0.1 M citric acid) also showed similar behavior. This behavior may result from changes in the actinide speciation which produced soluble and insoluble species which changed with time. The solution containing 0.18 M HNO_3/0.056 M oxalic acid was an effective precipitant for Np and Am oxalates. The use of 1 M $NaHCO_3$/Na_2CO_3, 0.05 M DTPA (except for Am), and 10 M NaOH were inferior choices to solubilize the actinides from the surrogate sludge. It is likely that higher Pu and Np solubilities could be obtained in 10 M NaOH if the solution is actively purged with air or ozone to facilitate the oxidation of Pu(IV) and Np(IV) to higher valences.

Based on the results from the solubility experiments, we recommend performing additional studies to evaluate the use of a dilute HNO_3 solution containing $NaMnO_4$ and the use of a basic solution (either NaOH or $NaHCO_3$/Na_2CO_3) containing $NaMnO_4$ as potential reagents for enhancing the solubility of the actinide elements during waste tank cleaning. These studies should be performed using a surrogate sludge with a chemical composition similar to real waste. The studies should also include solubility experiments with actual SRS waste.

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LIST OF ABBREVIATIONS

APHA	alpha pulse height analysis
ECC	enhanced chemical cleaning
DTPA	diethylenetriaminepentaacetic acid
GPHA	gamma pulse height analysis
ICPES	inductively-coupled plasma emission spectroscopy
MDA	minimum detection of analysis
NA	not applicable
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTA	thenolytrifluoroacetone
UL	upper limit

1.0 Introduction

The process historically used for removing residual sludge in SRS waste tanks utilized solutions containing up to 0.9 M oxalic acid to dissolve the remaining material following sludge removal. The selection of this process was based on a comparison of a number of studies performed to evaluate the dissolution of residual sludge.[1] In contrast, the dissolution of the actinide mass, which represents a very small fraction of the waste, has not been extensively studied. Minimal actinide removal has been observed during the use of the oxalic acid treatment, probably due to the low solubility of the actinide compounds formed when the acid solutions were pH adjusted in the separations facilities. During the pH adjustment, the waste solutions were adjusted to nominally 1.2 M excess hydroxide and subsequently transferred to the waste tanks.

The Pu in the waste tank sludge is reported to be present as hydrated and crystalline oxides.[2] The other predominate transuranic actinides (i.e., Np and Am) are also present as similar solids.[3-4] To improve the dissolution of the actinides during tank cleaning, a solvent in which the actinides have increased solubility can be used; however, the solvent must be compatible with the carbon steel waste tanks and downstream waste processing. To identify aqueous solutions which have the potential to increase the actinide solubility, alkaline and mildly acidic test solutions were selected for use in a series of solubility experiments.

Previous studies have evaluated the solubility of hydrated Pu oxides in alkaline solutions including some studies of Hanford and SRS wastes.[4-7] These studies were used to guide the selection of several alkaline solutions as candidates to increase the solubility of the actinides in residual sludge. The solubility of Pu increases sharply with the concentration of alkaline hydroxides (e.g., Li, Na, and K). Above approximately 2 M NaOH, the solubility of Pu observed in aerated pure NaOH solution increases by a factor of 10 with each 2-3 M increase in the NaOH concentration.[8] Based on these results, we selected 10 M NaOH as a candidate test solution. The solubility of Pu also increases in the presence of carbonate/bicarbonate solutions compared to solutions at the same pH in the absence of carbonate. The solubility is also sensitive to pH. The solubility of Pu(IV) is about 200 times more soluble at pH 9.4-10.1 than at pH 12-13. At 1 M carbonate (pH 9-10), the solubility of Pu approaches 10^{-3} M (240 μg/mL).[10] Based on these data, a 1 M $NaHCO_3/Na_2CO_3$ solution at pH 9.5 was selected as a test solution.

The solubility of Pu in NaOH solutions is also influenced by the valence state. The solubility generally increases with increasing oxidation state (i.e., Pu(VI) > Pu(V) >Pu(IV)).[9] The same trend is also observed in carbonate/bicarbonate solutions. Plutonium (VI) carbonate is highly soluble, exceeding 0.3 M in 0.5 M Na_2CO_3.[10] Therefore, the oxidation of Pu(IV) to Pu(VI) in the residual waste tank sludge should be an effective means to increase the solubility of Pu in alkaline solutions. Many reagents have been used for the oxidation of Pu(IV) to Pu(VI). For the solubility experiments, we chose to add 0.2 M $NaMnO_4$ to solutions containing both 10 M NaOH and 1 M $NaHCO_3/Na_2CO_3$ at pH 9.5. Permanganate is an effective oxidation reagent for Pu. The time required to oxidize one-half of the Pu(IV) in a solution using 0.001 M permanganate in a 1 M HNO_3 was reported as 50 min.[11] We chose to use 0.2 M $NaMnO_4$ to ensure that an excess of the oxidant was present. Based on equation 1, the $NaMnO_4$ was in excess of the stoichiometric requirement by an approximate 11:1 ratio.

$$3Pu^{4+} + 2MnO_4^- + 2H_2O \rightarrow 3PuO_2^{2+} + 2MnO_2 + 4H^+ \tag{1}$$

Since oxalic acid is presently used to remove residual sludge from SRS waste tanks, [12] a 0.9 M (8 wt %) solution was selected as the baseline test solution for the solubility experiments. The use of this concentration will allow a direct comparison with the solubility data obtained from the other test solutions. In addition several other solutions containing oxalic acid were also selected for use in the experiments. An enhanced chemical cleaning (ECC) process is currently under development to remove residual sludge from SRS waste tanks. The new process uses 0.22 M (2 wt %) oxalic acid for sludge dissolution. This concentration of oxalic acid was selected for use in the experiments to provide actinide solubility data at this concentration. The use of a combination of oxalic and citric acids for the dissolution of simulated and actual SRS high level waste sludges was previously evaluated. In a limited number of tests with actual SRS sludges, 100% of the Pu dissolved at a 50:1 acid:sludge ratio using a mixture of the acids.[6] Based on these results, a 0.2 M (1.8 wt%) oxalic acid/0.1 M citric acid solution was selected for use in the solubility experiments.

The use of solutions more acidic than oxalic or citric acids was also evaluated in the solubility experiments. In a recent study, a combination of nitric and oxalic acids was evaluated as an aggressive cleaning agent for SRS waste tanks in a series of electrochemical corrosion studies.[13] The results from these studies showed that elevated, but potentially manageable corrosion rates of carbon steel were achieved at mineral acid concentrations less than 0.2 M and at low temperatures (< 50 °C). The mineral acid solutions contained 0.11 M (1 wt %) oxalic acid. The study recommended future dissolution and corrosion testing be performed using a combination of a dilute mineral acid (i.e., HNO_3) and dilute oxalic acid. These results were used as the basis for recommending optimized conditions for sludge heel dissolution experiments using actual SRS waste. The recommended solution composition was 0.18 M HNO_3 containing 0.056 M (0.5 wt %) oxalic acid.[14] This composition was utilized in the experimental program to provide actinide solubility data for a solution of this composition.

The oxidation of Pu(IV) to the more soluble Pu(VI) valence state has been used to facilitate the recovery of Pu from refractory materials.[15-16] The addition of a strong oxidant (such as $NaMnO_4$) to a dilute HNO_3 solution should increase the solubility of Pu from residual waste tank sludge. Based on this concept, we chose to use a 0.18 M HNO_3 solution containing 0.2 M $NaMnO_4$ as a test solution in the solubility experiments. We also chose to perform a solubility experiment using pure 0.18 M HNO_3 to allow data comparisons with the experiments in which HNO_3 was combined with $NaMnO_4$ and with oxalic acid.

The actinides form highly stable complexes with diethylenetriaminepentaacetic acid (DTPA). Stability constants for Np, Pu, and Am are summarized in Table 1-1.

Table 1-1. Formation Constants for Transuranic Actinides with DTPA

Actinide	Oxidation State	Formation Constant	Reference
Np	4+	$10^{30.3}$	[17]
Pu	4+	$10^{29.5}$	[18]
Am	3+	$10^{22.9}$	[19]

The stability of these complexes has the potential to increase the solubility of the actinides in residual waste tank sludge. For the solubility experiments, we chose to use a 0.05 M DTPA solution in water following adjustment of the pH to a value between 2 and 4. A pH in this range is typically used in the TALSPEAK solvent extraction process for the separation of actinide from lanthanide elements. In this process, 0.05 M DTPA is used to form highly stable complexes with the actinides to prevent their extraction into the organic phase.[20]

1.1 Objectives

A series of alkaline and mildly acidic test solutions were selected as candidates which could potentially increase the solubility of the actinides in residual waste tank sludge. To test the efficiency of the solutions in solubilizing the actinides, a simulated actinide sludge was prepared by neutralizing a HNO_3 solution containing Pu, Np, and Am. The hydroxide concentration was adjusted to a 1.2 M excess and the solids were allowed to age for several weeks prior to starting the experiments. The sludge was subsequently washed with 0.01 M (i.e., pH 12) NaOH to prepare the solids for use. Following the addition of an equal portion of the solids to each test solution, the concentrations of Pu, Np, and Am were measured as a function of time to provide a direct comparison of the efficiency of each solution in solubilizing the actinide elements. The experimental methods used to perform the solubility measurements and a discussion of the results are presented in subsequent sections.

1.2 Functional Classification

Only scoping experiments were performed in this study where the use of the data obtained is limited to the identification of preferred candidates for follow-up studies (outside the current experimental program). Consistent with a Functional Classification of Process Support, data obtained from this study are not planned to support nuclear criticality, nor safety class/safety significant arguments as part of a Document Safety Analysis.

2.0 Experimental Procedure

2.1 Preparation of Actinide Sludge

2.1.1 *Neutralization of Actinide Solution*

Although increasing the solubility of Pu in the residual waste tank sludge was the primary objective of this study, the addition of tracer level concentrations of Np and Am to the Pu solution prior to pH adjustment was planned to obtain solubility data for these elements. The Pu solution used for the study was generated during the dissolution of approximately 23 g of metal in a 4 M HNO_3 solution containing 0.1 M KF. A characterization of the solution is provided in Table 2-1.

Table 2-1. Characterization of Pu Used in Solubility Experiments

Component	Concentration (g/L)	Concentration (M)
Pu	29.4	
Am	0.055	
K		0.084
HNO_3		3.63

The minimum target Am concentration in the Pu stock solution prior to pH adjustment was 1E+07 dpm/mL. An activity of this magnitude was considered sufficient to provide enough soluble Am in the test solutions for an accurate analysis by gamma pulse height analysis (GPHA). The Am present in the stock solution (from the decay of ^{241}Pu) already exceeded this value (i.e., 0.055 g/L = 4.2E+08 dpm/mL); therefore, it was not necessary to add Am to the Pu stock solution. A Np stock solution containing 31.9 g/L (4.98E+07 dpm/mL) was used as the Np source for the solubility experiments. A characterization of the solution is provided in Table 2-2.

Table 2-2. Characterization of Np Used in Solubility Experiments

Component	Concentration	Concentration
	(g/L)	(M)
Np	31.9	
^{238}Pu	0.12	
HNO_3		1.5

The actinide solution used to generate the sludge for the solubility experiments was prepared by combining 75 mL of the Pu stock solution and 1.5 mL of the Np stock solution. The composition of the solution based on the analyses given in Tables 2-1 and 2-1 is given in Table 2-3.

Table 2-3. Composition of Actinide Solution Used for Sludge Preparation

Actinide	Concentration	Concentration
	(g/L)	(M)
Pu	28.8	1.20E-01
Np	0.63	2.64E-03
Am	0.05	2.23E-04
HNO_3		3.6

In preparation for the solubility experiments, the actinide solution was neutralized and the pH adjusted with an excess of 50 wt % (19.4 M) NaOH to achieve a 1.2 M excess hydroxide concentration in the sludge supernate. Twenty-three milliliters of the NaOH solution were required to neutralize the solution and achieve the desired excess hydroxide concentration. Calculations and assumptions used to perform the neutralization and pH adjustment are summarized in Appendix A. A few milliliters of the NaOH was added to the actinide solution at a time over approximately 40 min to allow the dissipation of the heat generated during the neutralization and pH adjustment.

2.1.2 *Sludge Washing*

The actinide sludge was allowed to age for 17 days (to promote crystal growth) prior to the completion of a series of washing steps. The solids were washed with 0.01 M NaOH to reduce the excess free hydroxide concentration. Our main objective was to minimize the concentration of NaOH associated with the solids to prevent significant changes in the test solution compositions upon the addition of the sludge. To remove the supernate from the solids, the tip of a transfer pipette was held just below the surface during the removal of solution to minimize the pick-up of any solids. Seven successive wash cycles were performed over a period of 14 days. Prior to the addition of the first wash solution, 65 mL of supernate were removed from the actinide sludge. A 50-mL aliquot of 0.01 M NaOH was then added to the sludge. All volumes were measured with a graduated cylinder. In successive wash cycles, 50 mL of supernate were removed from the sludge followed by the addition of 50 mL of 0.01 M NaOH. The calculated free hydroxide concentration in the sludge supernate following the final wash cycle was approximately 0.01 M. The wash cycles and the composition of the supernate are summarized in Table 2-4.

Table 2-4. Actinide Sludge Wash Cycles

Wash Cycle	Initial Volume (mL)	Volume Removed (mL)	Wash Volume (mL)	Calc. Free NaOH Concentration (M)
1	104	65	50	0.54
2	89	50	50	0.24
3	89	50	50	0.11
4	89	50	50	0.06
5	89	50	50	0.03
6	89	50	50	0.02
7	89	50	49	0.01

2.2 Test Solution Preparation

A series of alkaline and mildly acidic test solutions were selected as candidates which could potentially increase the solubility of the actinides in residual waste tank sludge. The solutions selected for testing are shown in Table 2-5.

Table 2-5. Test Solutions for Actinide Solubility Experiments

Solution Composition
8 wt % (0.9 M) oxalic acid
2 wt % (0.22 M) oxalic acid
1.8 wt % (0.2 M) oxalic acid/0.1 M citric acid
0.18 M HNO_3/0.5 wt % (0.056 M) oxalic acid
0.18 M HNO_3/0.2 M $NaMnO_4$
0.18 M HNO_3
10 M NaOH
10 M NaOH/0.2 M $NaMnO_4$
1 M $NaHCO_3$/Na_2CO_3 at pH 9.5
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ at pH 9.5
0.05 M DTPA at pH 2-4
0.18 M HNO_3 blank
10.0 M NaOH blank
1 M $NaHCO_3$/Na_2CO_3 at pH 9.5 blank

Preparation of the test solutions is described in Appendix B. The solutions were prepared without difficulty with the exception of the solutions containing $NaMnO_4$. Complete dissolution of 0.2 M $NaMnO_4$ in the 0.18 M HNO_3, 10 M NaOH, and 1 M $NaHCO_3$/Na_2CO_3 was difficult to verify due to the dark color of the solutions. A fine residue was observed in the volumetric flask used to prepare the 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ indicating that complete dissolution was not achieved. It also appeared that MnO_2 solids were produced in the 0.18 M HNO_3 solution due to oxidation by HNO_2 (equation 2).

$$2MnO_2 + 3NO_2^- + 2H^+ \rightarrow 2MnO_2 + 3NO_3^- + H_2O \qquad (2)$$

Since some uncertainty existed in the concentration of the $NaMnO_4$ in the test solutions due to the presence of solids, the Mn concentration was analyzed by inductively-coupled plasma emission spectroscopy (ICP-ES). The samples of the 0.18 M HNO_3/0.2 M $NaMnO_4$ and 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ solutions were filtered using a 0.1 µm disk filter (Whatman, Puradisc 25 syringe filter) to remove any solids prior to the analyses. The results of the analyses are given in Table 2-6.

Table 2-6. Concentration of $NaMnO_4$ in Test Solutions

Solution	Measured	Relative	Prepared
	Concentration	Standard Dev.	Concentration
	(M)	(%)	(M)
0.18 M HNO_3	0.20	10.0	0.20
10 M NaOH	0.14	10.2	0.20
1 M $NaHCO_3$/Na_2CO_3	0.19	10.0	0.20

The measured concentrations of $NaMnO_4$ in the 0.18 HNO_3 and 1 M $NaHCO_3$/Na_2CO_3 are consistent with the prepared concentrations. However, the measured concentration of $NaMnO_4$ in the 10 M NaOH is significantly lower than the prepared value. This observation is surprising since complete dissolution of the permanganate in the 10 M NaOH was observed during preparation. It is possible that the low measured value could be attributed to the sample preparation. A two hundred-fold dilution of the 10 M NaOH/0.2 M $NaMnO_4$ solution was performed during the analysis.

2.3 Initiation of Solubility Experiments

Fifty milliliter conical centrifuge tubes were used for the solubility experiments. A 30-mL aliquot of each solution (Table 2-4) was transferred to a centrifuge tube using an electronic pipette. In preparation for the solubility experiments, a 57-mL aliquot of supernate was removed from the sludge. Excess supernate was removed to limit the amount of liquid transferred with the sludge to the test solutions. The actinide-containing sludge was added to the centrifuge tubes in a drop-wise manner using a transfer pipette. The sludge was evenly divided among the 11 solutions. A few milliliters of 0.01 M NaOH was added to the sludge bottle to rinse material from the wall and bottom of the container. The solids were subsequently added to the test solutions. The centrifuge tubes (including the three blanks) were placed on two Fisher Scientific Labquake™ tube shakers to provide mixing. The temperature of the solutions was not controlled, but was generally monitored on a daily basis. The average temperature was 20.5 ± 1.0 °C. The tube shakers were started on April 28, 2011. The experiments were terminated on May 31, 2011.

2.4 Sampling and Preparation of Samples for Analysis

Samples of the test solutions were periodically removed for Pu, Np, and Am analyses. The samples were taken at nominally 24, 96, 168, 336, 504, and 792 h (1, 4, 7, 14, 21, and 33 days). Initially the centrifuge tubes were removed from the tube shakers to allow the solids to settle. At least 2 h were allowed before starting the sampling procedure. To prepare the samples for analysis, it was necessary to filter the solutions once removed from the centrifuge tubes and then acidify the solutions with HNO_3. The samples were removed from the centrifuge tubes using a disposable 10-mL plastic syringe. A 4-in piece of Teflon® tubing was fitted to the syringe to allow the withdrawal of 2 to 3 mL of solution. The Teflon® tubing was removed and the syringe was fitted with a disposable 0.02-µm filter disk (Whatman, Anotop 25 syringe filter). The solution was expelled from the syringe into a 1 dram vial. During the preparation of samples from the 0.9 M oxalic acid and 0.18 M HNO_3 solutions, we were unable to filter samples with a 0.02-µm filter disk due to the presence of very fine solids in the solution. When the filtration problems occurred, a 0.01-µm filter disk (Whatman, Puradisc 25 syringe filter) was successfully used to filter the sample.

To prepare the samples for analysis, we targeted a 1 to 2 M concentration of HNO_3 in the filtered solutions. Five molar HNO_3 was used for the sample acidifications. Neutralization of the samples containing 10 M NaOH and 1 M $NaHCO_3/Na_2CO_3$ were based on equations 3 and 4. Nitric acid was also added to the acidic test solutions to obtain a final free acid concentration in the 1 to 2 M range.

$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O \tag{3}$$

$$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O \tag{4}$$

The volumes of 5 M HNO_3 (Table 2-7) were added to 1 or 2 dram sample vials using a calibrated electronic pipette prior to placing the vials in the glovebox where the solution equilibrations were performed. The precisions and accuracies of the calibrated pipettes were less than 1%.

Table 2-7. Volume of HNO_3 Required to Acidify Test Solution Samples

Solution Composition	5 M HNO_3
	(mL)
8 wt % (0.9 M) oxalic acid	0.5
2 wt % (0.22 M) oxalic acid	0.5
1.8 wt % (0.2 M) oxalic acid/0.1 M citric acid	0.5
0.18 M HNO_3/0.5 wt % (0.056 M) oxalic acid	0.5
0.18 M HNO_3/0.2 M $NaMnO_4$	0.5
0.18 M HNO_3	0.5
10 M NaOH	3.0
10 M NaOH/0.2 M $NaMnO_4$	3.0
1 M $NaHCO_3/Na_2CO_3$ at pH 9.5	1.0
1 M $NaHCO_3/Na_2CO_3$/0.2 M $NaMnO_4$ at pH 9.5	1.0
0.05 M DTPA at pH 2-4	0.5
0.18 M HNO_3 blank	0.5
10.0 M NaOH blank	3.0
1 M $NaHCO_3/Na_2CO_3$ at pH 9.5 blank	1.0

To complete the sample preparation, a 1-mL aliquot of the filtered solutions was transferred to the prepared sample vials using a calibrated Rainin FSL-1000 fixed volume pipette. The precision and accuracy of the pipette was less than 1%. After the sampling was complete, the centrifuge tubes were returned to the tube shakers for continuous mixing. The test solution samples were analyzed for Pu by thenolytrifluoroacetone (TTA) extraction and alpha pulse height analysis (APHA) and for Np and Am by GPHA.

3.0 Results and Discussion

The activities of Pu, Np, and Am measured in the samples from each test solutions are provided in Appendix C. The appendix also summarizes the calculations used to convert the actinide activities to molar concentrations. The concentrations of Pu, Np, and Am in the test solutions are plotted as a function of time on Figures 3-1 – 3-3, respectively. The Pu, Np, and Am concentrations are also plotted as a function of time for each test solution in Appendix D.

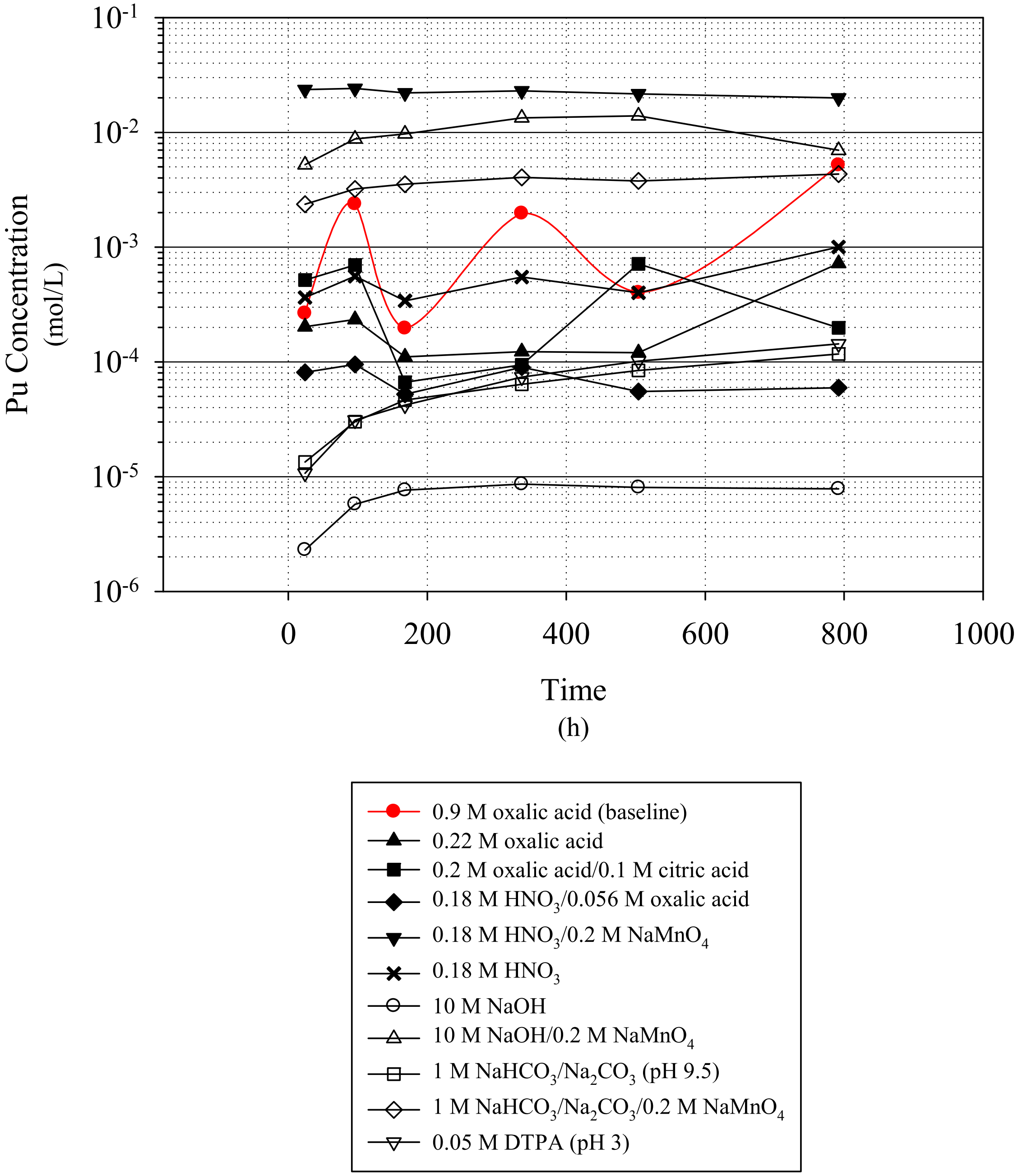

Figure 3-1. Pu Concentration Over Time in ECC Test Solutions

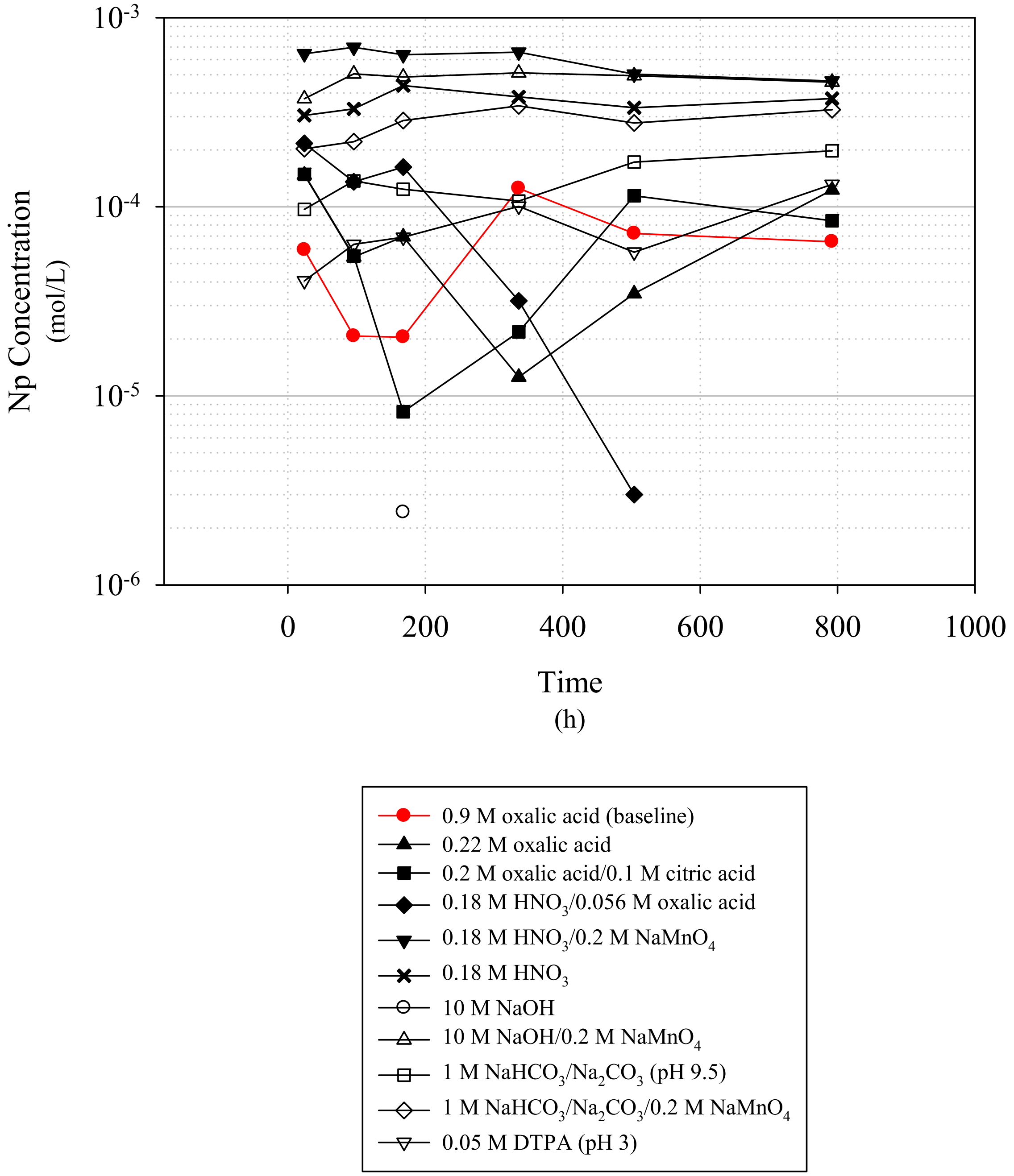

Figure 3-2. Np Concentration Over Time in ECC Test Solutions

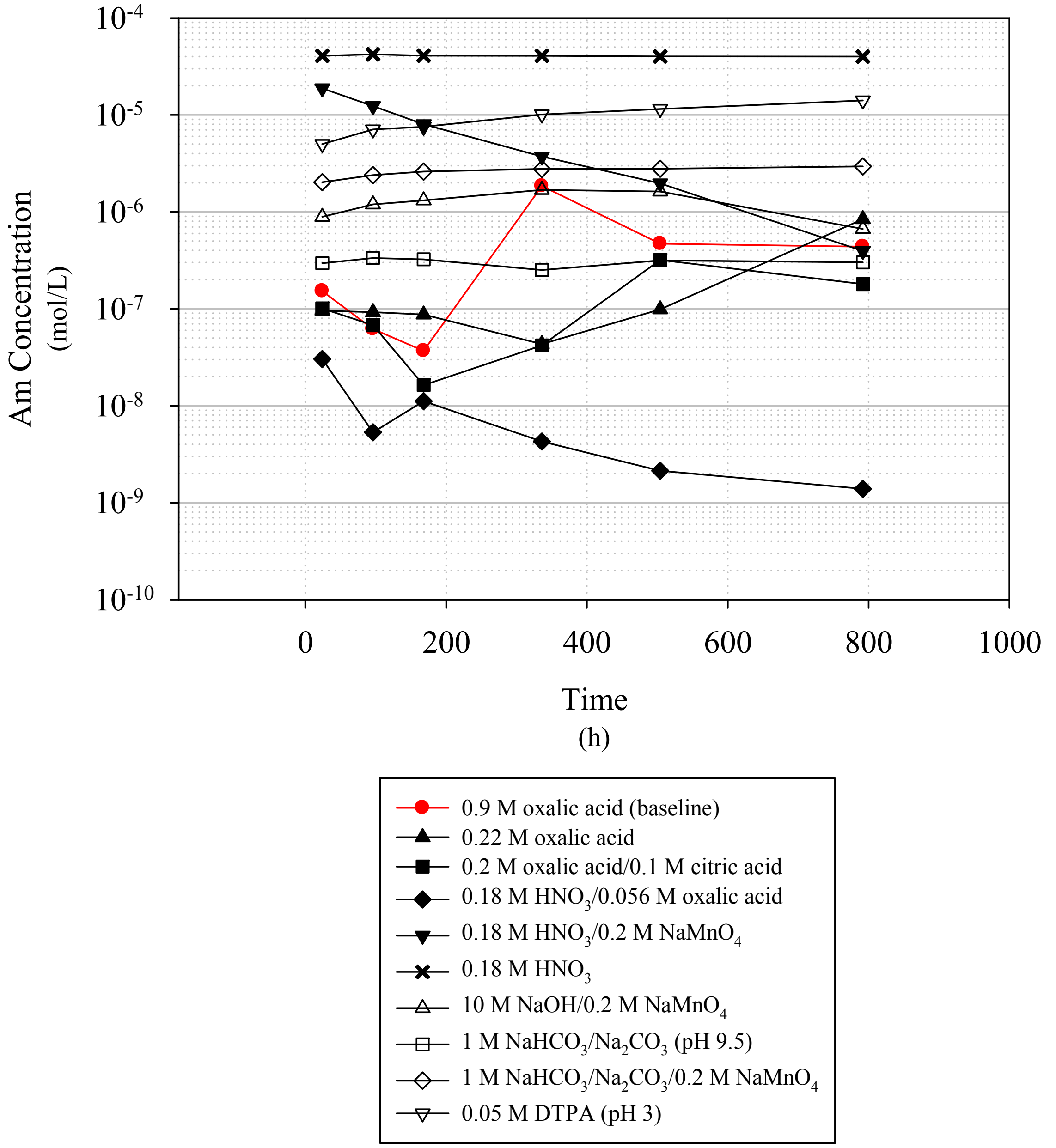

Figure 3-3. Am Concentration Over Time in ECC Test Solutions

3.1 Pu Solubility

The Pu data plotted on Figure 3-1 show that the test solutions containing 0.2 M $NaMnO_4$ resulted in the highest concentrations. The order of the solutions from the highest to the lowest concentrations achieved was:

0.18 M HNO_3/0.2 M $NaMnO_4$,
> 10 M NaOH/0.2 M $NaMnO_4$,
> 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$.

The oxidation of Pu(IV) to Pu(VI) (equation 1) in these solutions generates a Pu species with higher solubility which is consistent with Pu solubility generally increasing with increasing oxidation state.[9] The measured Pu concentrations in the solutions containing $NaMnO_4$ were also approaching the maximum concentrations based on the estimated amount of sludge added to the test solutions; therefore, it is possible that the Pu concentrations may not have been at the solubility limits. In the scouting experiments, we chose to use 0.2 M $NaMnO_4$ to ensure that an excess of the oxidant was always present. Based on equation 1, the permanganate was in excess by approximately a 11:1 ratio. In future experiments, a lower concentration can be identified, but care must be taken to ensure that loss of oxidant in acidic solutions does not reduce the solubilized Pu. Manganese dioxide (MnO_2) is produced in HNO_3 solution due to the oxidation of Mn by the small amounts of HNO_2 present in the solution (equation 2). Based on this mechanism, the solids observed in the 0.18 M HNO_3/0.2 M $NaMnO_4$ solution following preparation were assumed to be MnO_2.

As shown in Figure 3-1, the test solution containing 0.9 M oxalic acid resulted in a Pu concentration after 792 h (33 days) which was comparable to the concentrations measured in the 10 M NaOH/0.2 M $NaMnO_4$ and 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ solutions. At the completion of the experiment, no visible solids were observed in the solution remaining in the centrifuge tube. Based on the literature, the best estimate for the solubility of Pu in 0.9 M oxalic is > 8E-04 mol/L (200 mg/L).[21] The concentration measured in the test solution after 792 h (33 days) was 5.18E-03 mol/L (1240 mg/L). In contrast to the final concentration, the concentrations measured in earlier samples were lower and exhibited a somewhat cyclic behavior. We also encountered problems during the preparation of samples from the test solution. After 336 h (14 days), the samples from the 0.9 M oxalic acid solutions would not pass through a 0.02 µm disk filter indicating the presence of very fine solids. The sample was successfully filtered using a 0.1 µm filter disk. After 504 h (21 days), solids were produced when the filtered sample was combined with the 0.5-mL aliquot of 5 M HNO_3 used to acidify the sample. The solids were allowed to settle prior to removing a sample of the supernate for analysis. Based on these observations, it is clear that the complexation chemistry of the Pu (by oxalate and possibly hydroxide) was changing during the course of the experiment. The cyclic behavior of the concentration and the presence of solids could be explained by changes in the Pu speciation over time which produced both soluble and insoluble species (which were not characterized in the experiment). A potential mechanism for the generation of solids upon acidification of the sample is provided by equation 5.

$$\mathrm{Pu(C_2O_4)_3^{2-}}_{(aq)} + 2\mathrm{HNO}_{3(aq)} \rightarrow \mathrm{Pu(C_2O_4)}_{2(s)} + \mathrm{H_2C_2O}_{4(aq)} + 2\mathrm{NO}^{-}_{3(aq)} \quad (5)$$

The Pu concentrations measured in the 0.22 M oxalic acid, 0.18 M HNO_3/0.056 M oxalic acid, and 0.2 M oxalic acid/0.1 M citric acid solutions show some cyclic behavior similar to what was observed in the 0.9 M oxalic acid solution; although, the variations in the concentrations are not as large. As with the 0.9 M oxalic acid concentrations, this behavior could be explained by changes in the Pu speciation which produced soluble and insoluble species which change with time. The Pu concentrations measured after 792 h (33 days) are significantly less (i.e., approximately an order of magnitude or greater) than the final concentration measured in the 0.9 M oxalic acid solution; although, the Pu concentration in the 0.22 M oxalic acid may have been increasing at the end of the experiment. The solubility of Pu in 0.25 M oxalic acid is 1.01E-03 mol/L (242 mg/L) [21] compared to 7.22E-04 mol/L (173 mg/L) in the final 0.22 M oxalic acid sample. Therefore, it is possible that an equilibrium concentration may not have been achieved in the test solution.

The Pu concentrations measured in the 0.18 M HNO_3 were nearly two orders of magnitude less than the concentrations measured in the 0.18 M HNO_3/0.2 M $NaMnO_4$ which illustrate the importance of the oxidant for enhanced solubility. Plutonium is soluble in dilute HNO_3 solutions; however, the dissolution rate of PuO_2 can be very slow unless fluoride is added to catalyze the dissolution. For the dissolution of PuO_2 pellets in HNO_3, the Pu dissolution rate can be expressed by equation 6, [22]

$$\text{Rate (mg/min-cm}^2\text{)} = 1.1\text{E-}07\left[\text{HNO}_3\right]^4 \tag{6}$$

which shows the sensitivity of the rate of dissolution to the HNO_3 concentration. During the preparation of samples from the test solution we also encountered problems which affected the Pu solubility. None of the samples from the test solution could be filtered using a 0.02 μm filter disk indicating the presence of very fine solids; however, the samples were successfully filtered using a 0.1 μm filter disk. This was a unexpected result, since visible solids in the solution disappeared during the course of the experiment. When the filtered samples were combined with the 0.5-mL aliquot of 5 M HNO_3 used to adjust the acidity of the sample, a precipitate was produced. The precipitate was allowed to settle prior to removing a sample of the supernate for analysis. Since the test solution only contained HNO_3, the solids were likely Pu polymer. The 0.18 M HNO_3 and the visible solids produced during sample preparation were green in color which is consistent with the color of Pu polymer.[23]

The Pu concentrations measured in samples of the 10 M NaOH, 1 M $NaHCO_3$/Na_2CO_3, and 0.05 M DTPA show that these solutions are not viable candidates to improve the Pu solubility in the tanks. The Pu concentrations increased rapidly at first, but then slowed dramatically. It appears that the concentrations of Pu in the $NaHCO_3$/Na_2CO_3 and DTPA solutions were still increasing at the conclusion of the experiments which shows that equilibrium was not reached. However, the rates of dissolution were so slow that the use of these solutions is not practical. The Pu concentrations measured in the NaOH solution also increased rapidly at first and then slowed dramatically; however, the Pu concentration decreased in the final two samples. It is likely that higher solubilities could be obtained in 10 M NaOH if the solution was actively purged with air or ozone to facilitate the oxidation of Pu(IV) to Pu(VI).[8]

3.2 Np Solubility

The Np data plotted on Figure 3-2 show that the test solutions containing $NaMnO_4$ also resulted in solutions containing the highest concentrations of Np. However, in contrast to the Pu data, the solution containing 0.18 M HNO_3 also resulted in concentrations which were of the same order of magnitude as the solutions containing $NaMnO_4$. The order of the solutions from the highest to the lowest concentrations achieved after 792 h (33 days) was:

0.18 M HNO_3/0.2 M $NaMnO_4$,
= 10 M NaOH/0.2 M NaOH,
> 0.18 M HNO_3,
> 1 M $NaHCO_3$/$Na_2CO_3$0.2 M $NaMnO_4$.

In the permanganate-containing solutions, the oxidation of Np(IV) to Np(V) or Np(VI) (equations 7 and 8) generates Np species with higher solubility.

$$3Np^{4+} + MnO_4^- + 4H_2O \rightarrow 3NpO_2^+ + MnO_2 + 8H^+ \tag{7}$$

$$3Np^{4+} + 2MnO_4^- + 2H_2O \rightarrow 3NpO_2^{2+} + 2MnO_2 + 4H^+ \tag{8}$$

The increased solubility of Np in the 0.18 M HNO_3 is a result of the accessibility of the more soluble higher valence states during dissolution in contrast to Pu which prefers to remain in the less soluble 4+ valence. In addition, Np does not polymerize at low HNO_3 concentrations (like Pu) so the formation of polymeric solids will not occur. The Np concentrations measured in the test solutions containing $NaMnO_4$ and HNO_3 were at or approaching the maximum concentrations based on the estimated amount of sludge added to the test solutions; therefore, it is possible that the Np concentrations may not have been at the solubility limits.

The use of 1 M $NaHCO_3$/Na_2CO_3 was more successful in dissolving the hydrated NpO_2 than it was in dissolving the hydrated PuO_2. The improved dissolution rate can also be attributed to the accessibility of the more soluble higher valence states of Np. The concentration of Np initially increased rapidly, but slowed beyond approximately 168 h (1 week); however, it appears the concentration of Np in the solution was still increasing at the conclusion of the experiment; therefore, equilibrium was not achieved. At the conclusion of the experiment, the concentration of Np in the solution was only about a factor of two less than the Np concentration measured in the 1 $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$.

None of the test solutions containing oxalic acid were considered effective in solubilizing Np. The concentrations achieved in the test solutions were significantly less than the concentrations measured in the three solutions containing $NaMnO_4$ and the solutions containing HNO_3 and $NaHCO_3$/Na_2CO_3 (Figure 3-2). The concentrations of Np in the 0.9 M oxalic acid, 0.22 M oxalic acid, and 0.2 M oxalic acid also exhibited cyclic behavior similar to the Pu concentrations measured in these solutions. This behavior may also be explained by changes in the Np speciation which produced soluble and insoluble species which change with time. It appears the Np in the 0.18 M HNO_3/0.056 M oxalate precipitated as $Np(C_2O_4)_2$ during the course of the experiment. The concentration in the solution generally decreased with time. The Np concentration in the 792 h (33 day) sample was below than the minimum detection of the analysis (1.75E-06 mol/L (0.4 mg/L)). The estimated Np solubility in 0.18 M HNO_3/0.056 M oxalic acid is 0.8-1E-4 mol/L (20-30 mg/L).[24]

The solubility of Np in 0.05 M DTPA relative to the other test solutions was better than observed for Pu; however, it was still not effective for the dissolution of NpO_2. Other test solutions previously discussed have much higher Np solubilities. From Figure 3-2, it is also clear that 10 M NaOH was not effective for the dissolution of NpO_2. Only the concentration measured at 168 h (7 days) was above the minimum detection of the analysis.

3.3 Am Solubility

The Am concentrations measured in the test solutions (Figure 3-3) show that 0.18 M HNO_3 was the most effective solution investigated for the dissolution of the hydrated Am_2O_3. The Am_2O_3 dissolved quickly and the concentration remained constant during the course of the experiment. The Am concentration was also approaching the maximum concentration based on the estimated amount of sludge added to the test solution; therefore, it likely that the Am concentration was not at the solubility limit. At the beginning of the experiment, the next highest Am concentration was measured in the solution containing 0.18 M HNO_3/0.2 M $NaMnO_4$; however, over the course of the experiment the Am concentration decreased almost two orders of magnitude. In the presence of permanganate, it is possible that Am(III) was oxidized to Am(V) (equation 9) which subsequently coprecipitated with MnO_2. In an analogous manner, MnO_2 was used to remove Pa(V) from ^{233}U solutions during purification by a coprecipitation process.[25]

$$3Am^{3+} + 2MnO_4^- + 2H_2O \rightarrow 3AmO_2^+ + 2MnO_2 + 4H^+ \qquad (9)$$

Although the magnitude of the complexation constant for Am^{3+} and DTPA is smaller than the corresponding constants for the Pu^{4+}-DTPA and Np^{4+}-DTPA complexes (Table 1-1), DPTA was effective in solubilizing Am from the hydrated sludge. It also appears that the Am concentration was still slowly increasing at the conclusion of the experiment; therefore, equilibrium conditions were probably not achieved. It is likely that DTPA could be used to selectively dissolve Am from the other actinide oxides and if Cm^{3+} behaves similarly to Am^{3+}, it may be possible to separate the minor actinides from the lanthanide elements by selectively dissolving Am_2O_3 and Cm_2O_3 from the lanthanide oxides using DTPA.

The next most effective test solutions in solubilizing the Am_2O_3 were the remaining solutions containing 0.2 M $NaMnO_4$. The 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$ (which was more effective than the 10 M NaOH/0.2 M $NaMnO_4$) produced an initial increase in the Am concentration during the first 168 h (first week) which became more gradual as the experiment progressed. It does not appear that an equilibrium concentration was reached. The Am concentration in the 10 M NaOH/0.2 M $NaMnO_4$ solution also showed an initial increase which then slowed after 168 h (1 week); however, the Am concentration started to decrease after 336 h (2 weeks). It also does not appear that an equilibrium concentration was reached. It is unclear why the Am concentrations in these solutions behaved differently. The Am species in the NaOH solution may change with time due to reaction with the permanganate to produce Am(V) (equation 9) which coprecipitates with other solids in the test solution. The 0.2 M $NaMnO_4$ in the 1 M Na_2HCO_3/Na_2CO_3 clearly had an effect on the Am solubility. The concentration of Am was greater than an order of magnitude higher in the solution containing $NaMnO_4$ than it was in the 1 M $NaHCO_3$/Na_2CO_3. In this case, the presence of permanganate did not result in a decrease in the Am concentration with time. The Am concentration in the 1 M $NaHCO_3$/Na_2CO_3 was also relatively constant which suggests that the measured values were near the equilibrium concentration in this solution.

As observed with the other actinides, none of the test solutions containing oxalic acid were effective in solubilizing Am. The highest Am concentration was obtained with the 0.22 M oxalic acid where the concentrations decreased during the first 168 h (1 week) and subsequently increased during the remainder of the experiment. The final concentration was slightly greater than the final concentration measured in the 10 M NaOH/0.2 M $NaMnO_4$ solution. The Am concentrations in the 0.9 M oxalic acid and 0.2 M oxalic acid/0.1 M citric acid solutions exhibited cyclic behavior similar to the Pu and Np concentrations in these solutions. This behavior may be due to changes in the Am-oxalate complexes with time which results in the formation of soluble and insoluble species. The Am in the 0.18 M HNO_3/0.056 M oxalic acid appeared to precipitate as $Am_2(C_2O_4)_3$. The Am concentration generally decreased with time. The Am concentration in the 792 h (33 day) sample was 1.39E-09 mol/L (3.35E-04 mg/L) compared to an estimated solubility of approximately 4E-06 mol/L (1 mg/L) in 0.18 HNO_3/0.056 M oxalic acid.[26]

Americium was essentially insoluble in the 10 M NaOH solution. The concentration in all samples was below the minimum detection of analysis which ranged from 1.1-2.8E-10 mol/L (2.6-6.7E-05 mg/L).

4.0 Conclusions

The concentrations of Pu, Np, and Am were measured as a function of time in a series of alkaline and mildly acidic test solutions to provide a direct comparison of the efficiency of each solution in solubilizing the actinide elements from a surrogate sludge. Although the composition of the sludge was limited to hydrated PuO_2 and tracer level amounts of hydrated Np, and Am oxides produced by neutralization with NaOH (and did not contain other components of demonstrated importance), the results of the study provides guidance for the selection of solutions which should be evaluated in subsequent tests with a more realistic surrogate sludge and actual tank waste.

The test solutions containing 0.2 M $NaMnO_4$ were highly effective in solubilizing the Pu. The order of the solutions from the highest to the lowest concentrations achieved was:

0.18 M HNO_3/0.2 M $NaMnO_4$,
> 10 M NaOH/0.2 M $NaMnO_4$,
> 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$.

The concentrations after 792 h (33 days) fell in the range of 0.4-2.0E-02 mol/L (1.0-4.8 g/L); although, the Pu in each solution was at or near its maximum concentration after 168 h (1 week). The concentrations of Pu in these solutions were higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (5.2E-03 mol/L or 1.2 g/L) except for the concentration in $NaHCO_3$/Na_2CO_3/$NaMnO_4$ solution which was slightly lower.

The three solutions containing $NaMnO_4$ and the 0.18 M HNO_3 solution were highly effective in solubilizing the hydrated NpO_2 in the surrogate sludge. The order of the solutions from the highest to the lowest concentrations achieved after 792 h (33 days) was:

0.18 M HNO_3/0.2 M $NaMnO_4$,
= 10 M NaOH/0.2 M $NaMnO_4$,
> 0.18 M HNO_3,
> 1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$.

The concentrations in the final samples fell in the range of 3.2-4.6E-04 mol/L (0.08-0.10 g/L). The Np in these solutions was also at or near its maximum concentration after only 168 h (1 week). The concentrations were all significantly higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (6.5E-05 mol/L or 0.015 g/L).

The high concentrations of Pu and Np in the test solutions containing permanganate were due to the oxidation of the Pu(IV) and Np(IV) to higher and more soluble valences (i.e., Pu(VI) and Np(V)/Np(VI)). The increased solubility of Np in the 0.18 M HNO_3 is a result of the accessibility of the more soluble higher valence states during dissolution in contrast to Pu which prefers to remain in the less soluble 4+ valence.

The Am concentrations measured in the test solutions show that 0.18 M HNO_3 was the most effective solution investigated for the dissolution of the hydrated Am_2O_3. The Am_2O_3 dissolved quickly and the concentration remained constant during the course of the experiment. The final concentration after 792 h (33 days) was 4.0E-05 mol/L (0.01 g/L). The concentration of Am in the HNO_3 solution was nearly two order of magnitude higher than the concentration measured in the baseline 0.9 M oxalic acid solution at the conclusion of the experiments (4.4E-07 mol/L or 0.00011 g/L). At the beginning of the experiment, the next highest Am concentration was measured in the solution containing 0.18 M HNO_3/0.2 M $NaMnO_4$; however, over the course of the experiment the Am concentration decreased almost two orders of magnitude. The decrease in the concentration is attributed to the oxidation of Am(III) to Am(V) and coprecipitation with MnO_2. The next most effective solutions in solubilizing the Am were 0.05 DTPA and the two remaining solutions containing $NaMnO_4$; although, the Am concentration in the 10 M NaOH/0.2 M $NaMnO_4$ started to decrease after 336 h (2 weeks), perhaps due to reaction with the permanganate to produce Am(V) which coprecipitated with other solids in the test solution.

The remaining solutions evaluated in the experiments were generally not effective in solubilizing the Pu, Np, and Am from the surrogate sludge. One notable exception was the 0.9 M oxalic acid. The Pu concentration after 792 h (33 days) was comparable to the concentrations measured in the 10 M NaOH/0.2 M $NaMnO_4$ solution; however, the concentrations measured in the earlier samples were lower and exhibited a somewhat cyclic behavior. The actinide concentrations in other solutions containing oxalic acid (0.22 M oxalic acid and 0.2 M oxalic acid/0.1 M citric acid) also showed similar behavior. This behavior could be explained by changes in the actinide speciation which produced soluble and insoluble species which change with time. The solution containing 0.18 M HNO_3/0.056 M oxalic acid was an effective precipitant for Np and Am oxalates. The use of 1 M $NaHCO_3$/Na_2CO_3, 0.05 M DTPA (except for Am), and 10 M NaOH were inferior choices to solubilize the actinides from the surrogate sludge. It is likely that higher Pu and Np solubilities could be obtained in 10 M NaOH if the solution was actively purged with air or ozone to facilitate the oxidation of Pu(IV) and Np(IV) to higher valences.

5.0 Recommendations for Future Work

Solubility experiments performed as part of this study identified three solutions containing $NaMnO_4$ which were highly effective in dissolving hydrated Pu and Np oxides from a surrogate sludge. Based on these results, we recommend performing additional studies to evaluate the use of a dilute HNO_3 solution containing $NaMnO_4$ and the use of a basic solution (either NaOH or $NaHCO_3$/Na_2CO_3) containing $NaMnO_4$ as potential reagents for enhancing the solubility of the actinide elements during waste tank cleaning. These studies should be performed using a surrogate sludge with a chemical composition similar to real waste. The studies should also include solubility experiments with actual SRS waste. The surrogate sludge (and actual waste) should be pretreated and washed to simulate the sludge dissolution which will be performed in the SRS waste tanks prior to chemical cleaning. Future studies should consider the use of a higher concentration of NaOH containing permanganate near the end of the Al dissolution process as a means to improve actinide solubility. The effect of acidic solutions containing permanganate on the corrosion of the carbon steel waste tanks and the effect of the carbon steel on the actinide solubility should also be considered. The future studies should determine the minimum concentrations of $NaMnO_4$ required in the solutions to solubilize the actinide elements in a simulated or actual sludge heel.

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Appendix A Preparation of Actinide Sludge

Chemical Reagents

A 50 wt % (19.4 M) NaOH solution procured from Fisher Scientific was used to neutralize and adjust the hydroxide concentration of the actinide solution.

Neutralization of Actinide Solution

The reaction stoichiometry for the neutralization of the actinides and HNO_3 in the solution used to prepare the sludge for the solubility experiments are given by equations A.1-A.4.

$$Pu(NO_3)_{4\,(aq)} + 4NaOH_{(aq)} \rightarrow Pu(OH)_{4\,(s)} + 4NaNO_{3\,(aq)} \tag{A.1}$$

$$NpO_2(NO_3)_{(aq)} + NaOH_{(aq)} \rightarrow NpO_2(OH)_{(s)} + NaNO_{3\,(aq)} \tag{A.2}$$

$$Am(NO_3)_{3\,(aq)} + 3NaOH_{(aq)} \rightarrow Am(OH)_{3\,(s)} + 3NaNO_{3\,(aq)} \tag{A.3}$$

$$HNO_{3\,(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + NaNO_{3\,(aq)} \tag{A.4}$$

To calculate the volume of 19.4 M NaOH required to neutralize the actinide solution and adjust the excess hydroxide concentration to 1.2 M, the total moles of each element and HNO_3 in the solution were initially calculated. The calculations are summarized in Table A-1.

Table A-1. Actinide Elements and HNO_3 Requiring Neutralization

Element	Concentration	Volume	HNO_3	Actinide	HNO_3
	(g/L)	(mL)	(M)	(moles)	(moles)
Pu	29.4	75	3.63	9.21E-03	2.72E-01
Np	31.9	1.5	1.5	2.02E-04	2.25E-03
Am	0.055	75	3.63	1.70E-05	NA

The amounts of 19.4 M NaOH required to neutralize the actinides and the HNO_3 are provided in Table A-2. The table also provides the amount of water produced from equation A.4 which is from the neutralization of the HNO_3 in the Pu and Np stock solutions.

Table A-2. HNO_3 Required to Neutralize Actinide Solution

Actinide	Required NaOH		Water
	Actinide	HNO_3	Produced
	Neutralization	Neutralization	
	(mol)	(mol)	(mol)
Pu	3.69E-02	2.72E-01	2.72E-01
Np	2.02E-04	2.25E-03	2.25E-03
Am	5.11E-05	NA	NA

The volume increase due to the generation of water (by equation A.4) was 4.94 mL. The volume was calculated from the total moles of water produced (Table A-2) assuming the density of water was 1.0 g/mL. The amount of NaOH required to neutralize the actinides and HNO_3 was 0.312 mol (or 16.1 mL of 19.4 M NaOH). This value was calculated using the individual amounts of NaOH provided by Table A.2 for the neutralization of each solution component and the stoichiometry of equations A.1-A.4. The estimated volume of the neutralized solution was approximately 97.5 mL (i.e., 75 mL (Pu stock solution) + 1.5 mL (Np stock solution) + 16.1 mL

(19.4 M NaOH) + 4.94 mL (water produced)). Based on this volume, a total of 6.45 mL of 19.4 M NaOH were required to adjust the excess hydroxide concentration to 1.2 M; therefore, the total volume of NaOH required to neutralize the solution and achieve the excess concentration was 22.55 mL. This value was rounded-up to 23 mL when the neutralization/adjustment was performed.

Appendix B Preparation of Test Solutions

Chemical Reagents

The manufacturer and purity information for the chemicals used to prepare the test solutions for the actinide solubility experiments are provided in Table B.1.

Table A-1. Chemical Manufacturer and Purity Information

Chemical	Manufacturer	Concentration	Purity
oxalic acid dihydrate	Fisher Scientific		Certified A.C.S.
citric acid	Aldrich		Certified A.C.S.
HNO_3	Fisher Scientific	15.0 M	(1)
$NaMnO_4 \cdot H_2O$	Acros Organics		97%
NaOH	Fisher Scientific		Certified A.C.S.
$Na_2CO_3 \cdot H_2O$	J. T. Baker		99.8%
DTPA	Aldrich		97%

(1) Analyzed by titration.

Solution Preparation

The preparation of each test solution used in the solubility experiments is described in the following sections.

0.9 M oxalic acid

A 0.9 M oxalic acid solution was prepared by initially transferring 11.3462 g of oxalic acid dihydrate to a 150 mL beaker. The solids were dissolved in approximately 90 mL of deionized water by heating to 70 °C and stirring with a magnetic stir bar. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with deionized water. The final calculated oxalic acid concentration was 1.00 M.

0.22 M oxalic acid

A 0.22 M oxalic acid solution was prepared by initially transferring 2.7734 g of oxalic acid dihydrate to a 150 mL beaker. The solids were dissolved in approximately 60 mL of deionized water by stirring with a magnetic stir bar. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with deionized water. The final calculated oxalic acid concentration was 0.220 M.

0.2 M oxalic acid/0.1 M citric acid

A 0.2 M oxalic acid/0.1 M citric acid solution was prepared by initially transferring 2.5227 g of oxalic acid dihydrate and 2.1041 g of citric acid to a 150 mL beaker. The solids were dissolved in approximately 60 mL of deionized water. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with deionized water. The final calculated solution concentration was 0.200 M oxalic acid/0.100 M citric acid.

0.18 M HNO_3

To prepare a 0.18 M HNO_3 solution, a 6-mL aliquot of 15.0 M HNO_3 was transferred to a 500 mL volumetric flask containing deionized water. The flask was subsequently diluted to volume with deionized water. The final HNO_3 concentration was 0.180 M.

0.18 M HNO_3/0.056 M oxalic acid

A 0.18 M HNO_3/0.056 M oxalic acid solution was prepared by initially transferring 0.7066 g of oxalic acid dihydrate to a 100 mL beaker. The solids were dissolved in approximately 60 mL of 0.18 M HNO_3. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with 0.18 M HNO_3. The final calculated solution concentration was 0.180 M HNO_3/0.056 M oxalic acid.

0.18 M HNO_3/0.2 M $NaMnO_4$

A 0.18 M HNO_3/0.2 M $NaMnO_4$ solution was prepared by initially transferring 3.1993 g of $NaMnO_4 \cdot H_2O$ to a 150 mL beaker. The solids were dissolved in approximately 60 mL of 0.18 M HNO_3 by heating at 75 °C and stirring with a magnetic stir for several hours. The beaker was covered with a watch glass containing water to reduce the evaporation rate. When the solution was transferred to a 100 mL volumetric flask, solids remained in the beaker. The solids were slurried into the volumetric flask which was diluted to volume with 0.18 M HNO_3. When the solution was transferred from the volumetric flask to a plastic bottle, it appeared that the solids had dissolved. Since the solution could potentially contain undissolved $NaMnO_4$, a sample of the solution was analyzed for Mn by ICP-ES to determine the actual concentration. The Mn analysis is given in Table 2-6 and discussed in Section 2.2.

10 M NaOH

A 10 M NaOH solution was prepared by initially transferring 100.1016 g of NaOH into a 250 mL beaker. The solids were dissolved in approximately 150 mL of deionized water by breaking-up the solids with a stirring rod and subsequent stirring with a magnetic stir bar. The solution was transferred to a 250 mL volumetric flask which was diluted to volume with deionized water. The final calculated NaOH concentration was 10.0 M.

10 M NaOH/0.2 M NaMnO4

A 10 M NaOH/0.2 M $NaMnO_4$ solution was prepared by initially transferring 3.1998 g of $NaMnO_4 \cdot H_2O$ to a 150 mL beaker. The solids were dissolved in approximately 80 mL of 10 M NaOH by agitating with a magnetic stir bar. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with deionized water. The final concentration based on the mass of $NaMnO_4 \cdot H_2O$ dissolved was 0.200 M. The Mn concentration of the solution was also analyzed by ICP-ES for comparison. The Mn analysis is given in Table 2-6 and discussed in Section 2.2.

1 M $NaHCO_3$/Na_2CO_3 (pH 9.5)

Since the desired pH of the 1 M $NaHCO_3$/Na_2CO_3 solution was 9.5, it was necessary to initially prepare a more concentrated Na_2CO_3 solution to account for dilution when the pH was adjusted. Following the preparation of an approximate 1 M Na_2CO_3 solution and adjustment to pH 9.5, the estimated volume increase during the adjustment was approximately 13 mL. Based on this value, a 1.052 M Na_2CO_3 solution was initially prepared. The 1.052 M Na_2CO_3 solution was prepared by transferring 32.6228 g of Na_2CO_3 to 250 mL beaker and dissolving in approximately 150 mL of deionized water. The solids were broken-up using a stirring rod and agitated using a stirring bar until dissolution was achieved. The solution was transferred to a 250 mL volumetric flask which was diluted to volume with deionized water. The final calculated Na_2CO_3 concentration was 1.052 M.

The pH of the solution was adjusted using an Accumet® AB15 pH meter which was calibrated with pH 3, 6, and 10 buffer solutions. The initial pH of the solution was 11.47. The solution was neutralized with 15 M HNO_3 until the pH was 9.50. The estimated volume of acid required to perform the neutralization was 13.8 mL. Based on this value, the final calculated $NaHCO_3/Na_2CO_3$ concentration was 1.00 M.

1 M $NaHCO_3/Na_2CO_3$/0.2 M $NaMnO_4$ at pH 9.5

A 1 M $NaHCO_3/Na_2CO_3$/0.2 M $NaMnO_4$ solution at pH 9.5 was prepared by initially transferring 3.1991g of $NaMnO_4 \cdot H_2O$ to a 150 mL beaker. An attempt was made to dissolve the solids in approximately 75 mL of 1 M $NaHCO_3/Na_2CO_3$ at pH 9.5. The solution was heated at 75 °C and agitated with a stirring bar for approximately 2 h. A watch glass containing water was placed on the beaker to reduce evaporation losses. When the contents of the beaker were transferred to a 100 mL volumetric flask solids were observed. The contents of the beaker were completely transferred to the volumetric flask using 1 M $NaHCO_3/Na_2CO_3$. The flask was allowed to sit overnight without diluting to volume. On the following day, the flask was diluted to volume with 1 M $NaHCO_3/Na_2CO_3$. When the solution was transferred from the volumetric flask to a plastic bottle, solids were observed. The solids were transferred to the plastic bottle by transferring solution back to the volumetric flask with a transfer pipette. Since complete dissolution was not achieved, a sample of the solution was analyzed for Mn by ICP-ES to determine the actual concentration. The Mn analysis is given in Table 2-6 and discussed in Section 2.2.

0.05 M DTPA at pH 2-4

A 0.05 M DTPA solution at pH 2-4 was prepared by initially transferring 1.9667 g of DTPA to a 150 mL beaker. Approximately 60 mL of deionized water and a stirring bar were added to the beaker. The beaker was placed on a hot plate and heated at 75 °C while stirring. A watch glass containing water was placed on the beaker to reduce the evaporation rate. The DTPA did not completely dissolve following 1.5 h at this temperature. To dissolve the remainder of the DTPA, it was necessary to adjust the pH to a higher value. A 4.85 M NaOH solution was prepared by performing a 1:3 dilution of 19.4 M NaOH with deionized water. While heating at 75 °C and stirring the solution, the 4.85 M NaOH was added in a drop-wise manner. The addition of approximately 1.5 mL of base was required to completely dissolve the DTPA. The DTPA was transferred to a 100 mL volumetric flask which was diluted to volume with deionized water. The pH of the solution was measured using an Accumet® AB15 pH meter which was calibrated with pH 3, 6, and 10 buffer solutions. The pH of the solution was 2.97; therefore, no adjustment was performed.

0.18 M HNO_3 blank

The 0.18 M HNO_3 solution prepared for the solubility experiment was also used as the blank.

10.0 M NaOH blank

The 10.0 M NaOH solution prepared for the solubility experiment was also used as the blank.

1 M $NaHCO_3/Na_2CO_3$ *at pH 9.5 blank*

The 1 M $NaHCO_3/Na_2CO_3$ solution at pH 9.5 prepared for the solubility experiment was also used as the blank.

Appendix C Measured Actinide Concentrations

Measured Actinide Concentrations

The activities of ^{238}Pu, $^{239/240}$Pu, ^{237}Np, and ^{241}Am measured in the samples from each test solution are provided in Tables C-1 – C-6.

Table C-1. Actinide Activities Measured in 1 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	3.50E+05	4.98	6.73E+06	4.65
0.22 M oxalic acid	2.70E+05	4.89	5.16E+06	4.87
0.2 M oxalic acid/0.1 M citric acid	6.81E+05	5.05	1.32E+07	5.04
0.18 M HNO_3/0.056 M oxalic acid	1.07E+05	4.93	2.07E+06	4.89
0.18 M HNO_3/0.2 M $NaMnO_4$	3.38E+07	5.25	6.00E+08	5.13
0.18 M HNO_3	4.91E+05	4.92	9.28E+06	4.90
10 M NaOH	1.10E+03	7.97	2.20E+04	5.00
10 M NaOH/0.2 M $NaMnO_4$	2.79E+06	6.27	4.99E+07	5.03
1 M $NaHCO_3$/Na_2CO_3	1.33E+04	5.15	2.57E+05	4.85
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	2.58E+06	6.98	4.52E+07	5.22
0.05 M DTPA	1.46E+04	5.56	2.73E+05	5.21
0.18 M HNO_3 blank	2.96E+02	15.5	7.53E+03	5.66
10.0 M NaOH blank	<6.09E+01	MDA	1.77E+03	6.90
1 M $NaHCO_3$/Na_2CO_3 blank	1.60E+02	19.3	3.86E+03	6.08

MDA-minimum detection of analysis

Table C-1. continued

Solution Composition	Np	1 sigma	Am	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	1.46E+04	5.00	1.87E+05	5.00
0.22 M oxalic acid	3.64E+04	5.00	1.17E+05	5.00
0.2 M oxalic acid/0.1 M citric acid	3.66E+04	20.0	1.24E+05	5.00
0.18 M HNO_3/0.056 M oxalic acid	5.33E+04	5.00	3.72E+04	5.00
0.18 M HNO_3/0.2 M $NaMnO_4$	1.59E+05	5.00	2.30E+07	5.00
0.18 M HNO_3	7.50E+04	6.03	4.99E+07	5.00
10 M NaOH	<1.49E+02	MDA	<5.08E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	3.45E+04	8.87	4.08E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	1.79E+04	5.11	2.72E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.75E+04	8.53	1.86E+06	5.00
0.05 M DTPA	1.00E+04	5.00	6.15E+06	5.00
0.18 M HNO_3 blank	<1.49E+02	MDA	9.03E+02	11.8
10.0 M NaOH blank	<1.13E+02	MDA	<2.48E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<1.23E+02	MDA	<3.93E+02	MDA

MDA-minimum detection of analysis

Table C-2. Actinide Activities Measured in 4 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	3.22E+06	5.22	6.05E+07	5.19
0.22 M oxalic acid	3.18E+05	5.09	5.96E+06	5.07
0.2 M oxalic acid/0.1 M citric acid	9.22E+05	5.45	1.78E+07	5.45
0.18 M HNO_3/0.056 M oxalic acid	1.28E+05	4.93	2.42E+06	4.89
0.18 M HNO_3/0.2 M $NaMnO_4$	3.29E+07	5.61	6.15E+08	5.46
0.18 M HNO_3	7.51E+05	5.49	1.42E+07	5.48
10 M NaOH	3.08E+03	6.15	5.50E+04	4.98
10 M NaOH/0.2 M $NaMnO_4$	4.35E+06	5.80	8.38E+07	5.05
1 M $NaHCO_3$/Na_2CO_3	3.12E+04	5.25	5.77E+05	5.10
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.25E+06	6.51	6.13E+07	5.34
0.05 M DTPA	4.31E+04	6.11	7.93E+05	5.97
0.18 M HNO_3 blank	1.60E+02	32.7	2.32E+03	7.19
10.0 M NaOH blank	1.15E+02	36.7	2.95E+03	6.78
1 M $NaHCO_3$/Na_2CO_3 blank	6.88E+01	39.5	1.87E+03	7.06

Table C-2. continued

Solution Composition	Np	1 sigma	Am	1 sigma
		Uncert.		Uncert.
	(%)	(dpm/mL)	(dpm/mL)	(%)
0.9 M oxalic acid	5.10E+03	16.2	7.59E+04	5.00
0.22 M oxalic acid	1.34E+04	9.10	1.13E+05	5.00
0.2 M oxalic acid/0.1 M citric acid	1.35E+04	8.64	8.30E+04	5.00
0.18 M HNO_3/0.056 M oxalic acid	3.34E+04	6.3	6.51E+03	15.4
0.18 M HNO_3/0.2 M $NaMnO_4$	1.72E+05	5.00	1.51E+07	5.00
0.18 M HNO_3	8.12E+04	5.16	5.18E+07	5.00
10 M NaOH	<2.10E+02	MDA	<2.05E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	4.66E+04	9.37	5.50E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	2.53E+04	5.40	3.07E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.09E+04	9.00	2.20E+06	5.00
0.05 M DTPA	1.56E+04	5.00	8.69E+06	5.00
0.18 M HNO_3 blank	<3.53E+02	MDA	<5.74E+02	MDA
10.0 M NaOH blank	<1.32E+02	MDA	<3.84E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<2.46E+02	MDA	<8.25E+02	MDA

MDA-minimum detection of analysis

Table C-3. Actinide Activities Measured in 7 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	2.64E+05	5.48	4.99E+06	5.47
0.22 M oxalic acid	1.50E+05	5.04	2.82E+06	5.01
0.2 M oxalic acid/0.1 M citric acid	9.03E+04	4.98	1.69E+06	4.93
0.18 M HNO_3/0.056 M oxalic acid	7.07E+04	5.17	1.33E+06	5.10
0.18 M HNO_3/0.2 M $NaMnO_4$	3.01E+07	5.44	5.62E+08	5.28
0.18 M HNO_3	4.70E+05	5.04	8.68E+06	5.03
10 M NaOH	3.84E+03	6.25	7.28E+04	5.17
10 M NaOH/0.2 M $NaMnO_4$	5.24E+06	6.15	9.27E+07	5.24
1 M $NaHCO_3$/Na_2CO_3	4.80E+04	5.39	8.91E+05	5.29
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.73E+06	6.35	6.75E+07	5.22
0.05 M DTPA	5.66E+04	5.34	1.07E+06	5.25
0.18 M HNO_3 blank	5.85E+01	28.3	1.11E+03	9.59
10.0 M NaOH blank	7.75E+01	32.4	1.01E+03	8.22
1 M $NaHCO_3$/Na_2CO_3 blank	1.07E+02	19.9	2.20E+03	6.80

Table C-3. continued

Solution Composition	Np	1 sigma	Am	1 sigma
		Uncert.		Uncert.
	(%)	(dpm/mL)	(dpm/mL)	(%)
0.9 M oxalic acid	5.04E+03	9.58	4.51E+04	5.00
0.22 M oxalic acid	1.71E+04	5.00	1.07E+05	5.00
0.2 M oxalic acid/0.1 M citric acid	2.03E+03	12.1	2.00E+04	5.00
0.18 M HNO_3/0.056 M oxalic acid	4.00E+04	5.00	1.37E+04	5.00
0.18 M HNO_3/0.2 M $NaMnO_4$	1.57E+05	5.00	9.81E+06	5.00
0.18 M HNO_3	1.08E+05	5.00	5.01E+07	5.00
10 M NaOH	2.24E+02	24.5	<3.04E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	4.49E+04	8.78	6.05E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	2.29E+04	5.00	2.97E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	5.28E+04	5.00	2.39E+06	5.00
0.05 M DTPA	1.70E+04	5.00	9.27E+06	5.00
0.18 M HNO_3 blank	<1.49E+02	MDA	4.55E+02	18.3
10.0 M NaOH blank	<1.23E+02	MDA	<1.19E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<1.01E+02	MDA	<3.19E+02	MDA

MDA-minimum detection of analysis

Table C-4. Actinide Activities Measured in 14 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	2.66E+06	4.78	5.02E+07	4.74
0.22 M oxalic acid	1.39E+05	5.29	3.13E+06	5.22
0.2 M oxalic acid/0.1 M citric acid	1.32E+05	5.83	2.41E+06	5.79
0.18 M HNO_3/0.056 M oxalic acid	1.24E+05	5.47	2.29E+06	5.42
0.18 M HNO_3/0.2 M $NaMnO_4$	2.55E+07	5.20	5.85E+08	5.00
0.18 M HNO_3	7.43E+05	5.28	1.40E+07	5.27
10 M NaOH	4.54E+03	6.49	8.23E+04	5.33
10 M NaOH/0.2 M $NaMnO_4$	7.01E+06	5.63	1.28E+08	5.13
1 M $NaHCO_3$/Na_2CO_3	6.55E+04	5.52	1.22E+06	5.44
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.43E+06	6.36	7.76E+07	5.46
0.05 M DTPA	9.87E+04	5.87	1.88E+06	5.80
0.18 M HNO_3 blank	<1.57E+02	UL	<3.88E+03	UL
10.0 M NaOH blank	<6.25E+01	UL	<9.64E+02	UL
1 M $NaHCO_3$/Na_2CO_3 blank	1.66E+04	6.07	3.21E+05	5.49

UL-upper limit

Table C-4. continued

Solution Composition	Np	1 sigma	Am	1 sigma
		Uncert.		Uncert.
	(%)	(dpm/mL)	(dpm/mL)	(%)
0.9 M oxalic acid	3.09E+04	5.00	2.26E+06	5.00
0.22 M oxalic acid	3.10E+03	16.3	5.30E+04	5.00
0.2 M oxalic acid/0.1 M citric acid	5.36E+03	7.84	5.13E+04	5.00
0.18 M HNO_3/0.056 M oxalic acid	7.84E+03	6.13	5.24E+03	6.81
0.18 M HNO_3/0.2 M $NaMnO_4$	1.62E+05	5.00	4.57E+06	5.00
0.18 M HNO_3	9.39E+04	5.00	5.00E+07	5.00
10 M NaOH	<2.34E+02	MDA	<2.62E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	4.72E+04	9.00	7.76E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	1.98E+04	5.00	2.31E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	6.33E+04	7.34	2.55E+06	5.00
0.05 M DTPA	2.48E+04	5.00	1.24E+07	5.00
0.18 M HNO_3 blank	<1.13E+02	MDA	<3.72E+02	MDA
10.0 M NaOH blank	<1.49E+02	MDA	<1.93E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<1.23E+02	MDA	<4.42E+02	MDA

MDA-minimum detection of analysis

Table C-5. Actinide Activities Measured in 21 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	5.68E+05	4.85	1.02E+07	4.69
0.22 M oxalic acid	1.60E+05	5.12	3.07E+06	4.75
0.2 M oxalic acid/0.1 M citric acid	9.54E+05	4.87	1.82E+07	4.83
0.18 M HNO_3/0.056 M oxalic acid	8.00E+04	5.64	1.41E+06	4.99
0.18 M HNO_3/0.2 M $NaMnO_4$	2.96E+07	7.65	5.51E+08	7.39
0.18 M HNO_3	5.58E+05	4.73	1.02E+07	4.66
10 M NaOH	3.70E+03	15.6	7.70E+04	4.82
10 M NaOH/0.2 M $NaMnO_4$	6.71E+06	6.47	1.33E+08	5.55
1 M $NaHCO_3$/Na_2CO_3	8.74E+04	5.04	1.61E+06	4.56
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.06E+06	7.41	7.21E+07	5.83
0.05 M DTPA	1.37E+05	5.61	2.59E+06	5.17
0.18 M HNO_3 blank	<7.92E+02	MDA	<2.61E+03	UL
10.0 M NaOH blank	<3.80E+02	MDA	<4.76E+03	UL
1 M $NaHCO_3$/Na_2CO_3 blank	<5.60E+02	MDA	<1.93E+03	UL

MDA-minimum detection of analysis
UL - upper limit

Table C-5. continued

Solution Composition	Np	1 sigma	Am	1 sigma
		Uncert.		Uncert.
	(%)	(dpm/mL)	(dpm/mL)	(%)
0.9 M oxalic acid	1.78E+04	5.32	5.74E+05	5.00
0.22 M oxalic acid	8.56E+03	6.91	1.21E+05	5.00
0.2 M oxalic acid/0.1 M citric acid	2.82E+04	23.7	3.91E+05	5.00
0.18 M HNO_3/0.056 M oxalic acid	7.41E+02	22.0	2.62E+03	8.03
0.18 M HNO_3/0.2 M $NaMnO_4$	1.24E+05	6.46	2.41E+06	5.00
0.18 M HNO_3	8.23E+04	5.00	4.91E+07	5.00
10 M NaOH	<2.34E+02	MDA	<1.99E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	4.56E+04	8.72	7.46E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	3.19E+04	5.00	2.91E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	5.13E+04	7.39	2.56E+06	5.00
0.05 M DTPA	1.42E+04	37.7	1.41E+07	5.00
0.18 M HNO_3 blank	<1.32E+02	MDA	<3.15E+02	MDA
10.0 M NaOH blank	<1.23E+02	MDA	<4.31E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<1.41E+02	MDA	<3.15E+02	MDA

MDA-minimum detection of analysis

Table C-6. Actinide Activities Measured in 33 Day Samples

Solution Composition	^{238}Pu	1 sigma	$^{239/240}$Pu	1 sigma
		Uncert.		Uncert.
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	(1)	(1)	(1)	(1)
0.22 M oxalic acid	9.39E+05	5.54	1.84E+07	4.63
0.2 M oxalic acid/0.1 M citric acid	2.65E+05	9.41	5.05E+06	5.34
0.18 M HNO_3/0.056 M oxalic acid	6.71E+04	20.1	1.52E+06	5.13
0.18 M HNO_3/0.2 M $NaMnO_4$	2.75E+07	5.13	5.07E+08	4.99
0.18 M HNO_3	1.58E+06	5.40	2.55E+07	5.36
10 M NaOH	1.42E+04	23.4	7.49E+04	11.6
10 M NaOH/0.2 M $NaMnO_4$	3.62E+06	6.34	6.66E+07	5.21
1 M $NaHCO_3$/Na_2CO_3	1.27E+05	11.4	2.24E+06	5.02
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.43E+06	6.94	8.28E+07	5.54
0.05 M DTPA	1.92E+05	12.4	3.65E+06	5.01
0.18 M HNO_3 blank	1.05E+04	35.0	<9.71E+03	MDA
10.0 M NaOH blank	<3.15E+04	MDA	<6.09E+04	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<2.84E+04	MDA	<4.33E+04	MDA

(1) Sufficient sample was not available for the Pu TTA extraction/APHA. The concentration obtained from the GPHA for ^{239}Pu was used for this sample - ^{239}Pu = 1.07E+08 dpm/mL, 1 sigma uncertainty = 5.00%.

MDA-minimum detection of analysis

Table C-6. continued

Solution Composition	Np	1 sigma	Am	1 sigma
	(dpm/mL)	(%)	(dpm/mL)	(%)
0.9 M oxalic acid	1.61E+04	8.03	5.36E+05	5.00
0.22 M oxalic acid	3.03E+04	5.00	1.03E+06	5.00
0.2 M oxalic acid/0.1 M citric acid	2.08E+04	5.28	2.20E+05	5.00
0.18 M HNO_3/0.056 M oxalic acid	<4.31E+02	MDA	1.70E+03	12.4
0.18 M HNO_3/0.2 M $NaMnO_4$	1.14E+05	5.92	4.85E+05	5.00
0.18 M HNO_3	9.21E+04	5.99	4.89E+07	5.00
10 M NaOH	<2.15E+02	MDA	<2.05E+02	MDA
10 M NaOH/0.2 M $NaMnO_4$	4.22E+04	7.75	3.06E+05	5.00
1 M $NaHCO_3$/Na_2CO_3	3.65E+04	5.00	2.77E+05	5.00
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	6.03E+04	7.23	2.70E+06	5.00
0.05 M DTPA	3.24E+04	5.00	1.73E+07	5.00
0.18 M HNO_3 blank	<1.13E+02	MDA	3.50E+02	22.4
10.0 M NaOH blank	<1.41E+02	MDA	<1.49E+02	MDA
1 M $NaHCO_3$/Na_2CO_3 blank	<1.01E+02	MDA	<3.60E+02	MDA

MDA-minimum detection of analysis

Actinide Concentrations in Test Solutions

To calculate the concentrations of Pu, Np, and Am in the test solutions, the ^{238}Pu and $^{239/240}$Pu activities measured by the TTA extraction/APHA and the Np and Am activities measured by the GPHA were converted to a molar concentration using the specific activities given in Table C-7 and the nominal mass fractions of ^{239}Pu (0.94) and ^{240}Pu (0.06) in weapons grade Pu. The specific activity for $^{239/240}$Pu given in Table C-7 was calculated as a weighted average using the mass fractions of ^{239}Pu and ^{240}Pu as the weighting factors.

Table C-7. Specific Activities of Selected Actinide Isotopes

Isotope	Specific Activity
	(dpm/g)
^{238}Pu	4.97E+14
^{239}Pu	1.38E+11
^{240}Pu	5.04E+11
$^{239/240}$Pu	1.60E+11
^{237}Np	1.56E+09
^{241}Am	7.63E+12

The concentration of Pu, Np, and Am were calculated using equations C.1 – C.3, respectively. The equations also take into account the sample dilution which resulted from the addition of 5 M HNO_3 during sample preparation (Table 2-6).

$$\mathrm{Pu}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right)=\left(\frac{{}^{238}\mathrm{Pu}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{238}\mathrm{Pu}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}+\frac{{}^{239/240}\mathrm{Pu}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{239/240}\mathrm{Pu}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mole\ Pu}}{239.06\ \mathrm{g\ Pu}}\right)\left(\frac{1\ \mathrm{mL}}{1\ \mathrm{mL}+\mathrm{vol}\ 5\ \mathrm{M\ HNO_3(mL)}}\right) \tag{C.1}$$

$$\mathrm{Np}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right)=\left(\frac{{}^{237}\mathrm{Np}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{237}\mathrm{Np}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mole\ Np}}{237\ \mathrm{g\ Np}}\right)\left(\frac{1\ \mathrm{mL}}{1\ \mathrm{mL}+\mathrm{vol}\ 5\ \mathrm{M\ HNO_3(mL)}}\right) \tag{C.2}$$

$$\mathrm{Am}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right)=\left(\frac{{}^{241}\mathrm{Am}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{241}\mathrm{Am}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mole\ Am}}{241\ \mathrm{g\ Am}}\right)\left(\frac{1\ \mathrm{mL}}{1\ \mathrm{mL}+\mathrm{vol}\ 5\ \mathrm{M\ HNO_3(mL)}}\right) \tag{C.3}$$

There was insufficient sample prepared from the 0.9 M oxalic acid test solution following 33 days of equilibration to complete the Pu TTA extraction/APHA. For this reason, the ^{239}Pu activity obtained from the GPHA was used to calculate the Pu concentration in the test solution. The Pu concentration was calculated by equation C.4.

$$\left(\frac{1.07\mathrm{E}{+}08\dfrac{\mathrm{dpm}\ {}^{239}\mathrm{Pu}}{\mathrm{mL}}}{1.38\mathrm{E}{+}11\dfrac{\mathrm{dpm}\ {}^{239}\mathrm{Pu}}{\mathrm{g}\ {}^{239}\mathrm{Pu}}}\right)\left(\frac{1\ \mathrm{g\ Pu}}{0.94\ \mathrm{g}\ {}^{239}\mathrm{Pu}}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mol\ Pu}}{239.06\ \mathrm{g\ Pu}}\right)\left(\frac{1\ \mathrm{mL}}{1\ \mathrm{mL}+0.5\ \mathrm{mL}}\right)=5.18\mathrm{E}{-}03\frac{\mathrm{mol\ Pu}}{\mathrm{L}} \tag{C.4}$$

The concentrations of Pu, Np, and Am in the test solutions for each sample day are provided in Tables C-8 – C-13. Data recorded as NA corresponds to analyses which were less than the minimum detection of analysis or were give as an upper limit.

Table C-8. Actinide Concentrations Measured in 1 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	2.64E-04	5.92E-05	1.53E-07
0.22 M oxalic acid	2.02E-04	1.48E-04	9.54E-08
0.2 M oxalic acid/0.1 M citric acid	5.18E-04	1.48E-04	1.01E-07
0.18 M HNO_3/0.056 M oxalic acid	8.12E-05	2.16E-04	3.03E-08
0.18 M HNO_3/0.2 M $NaMnO_4$	2.35E-02	6.45E-04	1.88E-05
0.18 M HNO_3	3.64E-04	3.04E-04	4.07E-05
10 M NaOH	2.30E-06	NA	NA
10 M NaOH/0.2 M $NaMnO_4$	5.22E-03	3.73E-04	8.88E-07
1 M $NaHCO_3$/Na_2CO_3	1.34E-05	9.68E-05	2.96E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	2.36E-03	2.03E-04	2.02E-06
0.05 M DTPA	1.07E-05	4.06E-05	5.02E-06
0.18 M HNO_3 blank	2.95E-07	NA	NA
10.0 M NaOH blank	NA	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	2.02E-07	NA	NA

Table C-9. Actinide Concentrations Measured in 4 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	2.37E-03	2.07E-05	6.19E-08
0.22 M oxalic acid	2.34E-04	5.44E-05	9.22E-08
0.2 M oxalic acid/0.1 M citric acid	6.98E-04	5.48E-05	6.77E-08
0.18 M HNO_3/0.056 M oxalic acid	9.49E-05	1.36E-04	5.31E-09
0.18 M HNO_3/0.2 M $NaMnO_4$	2.41E-02	6.98E-04	1.23E-05
0.18 M HNO_3	5.57E-04	3.29E-04	4.23E-05
10 M NaOH	5.75E-06	NA	NA
10 M NaOH/0.2 M $NaMnO_4$	8.77E-03	5.04E-04	1.20E-06
1 M $NaHCO_3$/Na_2CO_3	3.02E-05	1.37E-04	3.34E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.21E-03	2.21E-04	2.39E-06
0.05 M DTPA	3.11E-05	6.33E-05	7.09E-06
0.18 M HNO_3 blank	9.10E-08	NA	NA
10.0 M NaOH blank	3.09E-07	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	9.78E-08	NA	NA

Table C-10. Actinide Concentrations Measured in 7 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	1.96E-04	2.04E-05	3.68E-08
0.22 M oxalic acid	1.11E-04	6.94E-05	8.73E-08
0.2 M oxalic acid/0.1 M citric acid	6.63E-05	8.24E-06	1.63E-08
0.18 M HNO_3/0.056 M oxalic acid	5.22E-05	1.62E-04	1.12E-08
0.18 M HNO_3/0.2 M $NaMnO_4$	2.20E-02	6.37E-04	8.00E-06
0.18 M HNO_3	3.40E-04	4.38E-04	4.09E-05
10 M NaOH	7.62E-06	2.42E-06	NA
10 M NaOH/0.2 M $NaMnO_4$	9.70E-03	4.86E-04	1.32E-06
1 M $NaHCO_3$/Na_2CO_3	4.66E-05	1.24E-04	3.23E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.53E-03	2.86E-04	2.60E-06
0.05 M DTPA	4.20E-05	6.90E-05	7.56E-06
0.18 M HNO_3 blank	4.35E-08	NA	3.71E-10
10.0 M NaOH blank	1.06E-07	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	1.15E-07	NA	NA

Table C-11. Actinide Concentrations Measured in 14 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	1.97E-03	1.25E-04	1.84E-06
0.22 M oxalic acid	1.23E-04	1.26E-05	4.32E-08
0.2 M oxalic acid/0.1 M citric acid	9.45E-05	2.17E-05	4.18E-08
0.18 M HNO_3/0.056 M oxalic acid	8.98E-05	3.18E-05	4.27E-09
0.18 M HNO_3/0.2 M $NaMnO_4$	2.29E-02	6.57E-04	3.73E-06
0.18 M HNO_3	5.49E-04	3.81E-04	4.08E-05
10 M NaOH	8.61E-06	NA	NA
10 M NaOH/0.2 M $NaMnO_4$	1.34E-02	5.11E-04	1.69E-06
1 M $NaHCO_3$/Na_2CO_3	6.38E-05	1.07E-04	2.51E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.06E-03	3.42E-04	2.77E-06
0.05 M DTPA	7.37E-05	1.01E-04	1.01E-05
0.18 M HNO_3 blank	NA	NA	NA
10.0 M NaOH blank	NA	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	1.68E-05	NA	NA

Table C-12. Actinide Concentrations Measured in 21 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	4.00E-04	7.22E-05	4.68E-07
0.22 M oxalic acid	1.20E-04	3.47E-05	9.87E-08
0.2 M oxalic acid/0.1 M citric acid	7.14E-04	1.14E-04	3.19E-07
0.18 M HNO_3/0.056 M oxalic acid	5.53E-05	3.01E-06	2.14E-09
0.18 M HNO_3/0.2 M $NaMnO_4$	2.16E-02	5.03E-04	1.97E-06
0.18 M HNO_3	4.00E-04	3.34E-04	4.01E-05
10 M NaOH	8.05E-06	NA	NA
10 M NaOH/0.2 M $NaMnO_4$	1.39E-02	4.93E-04	1.62E-06
1 M $NaHCO_3$/Na_2CO_3	8.42E-05	1.73E-04	3.17E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	3.77E-03	2.78E-04	2.78E-06
0.05 M DTPA	1.02E-04	5.76E-05	1.15E-05
0.18 M HNO_3 blank	NA	NA	NA
10.0 M NaOH blank	NA	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	NA	NA	NA

Table C-13. Actinide Concentrations Measured in 33 Day Samples

Solution Composition	Pu	Np	Am
	(mol/L)	(mol/L)	(mol/L)
0.9 M oxalic acid	5.18E-03	6.53E-05	4.37E-07
0.22 M oxalic acid	7.22E-04	1.23E-04	8.40E-07
0.2 M oxalic acid/0.1 M citric acid	1.98E-04	8.44E-05	1.79E-07
0.18 M HNO_3/0.056 M oxalic acid	5.96E-05	NA	1.39E-09
0.18 M HNO_3/0.2 M $NaMnO_4$	1.99E-02	4.63E-04	3.96E-07
0.18 M HNO_3	1.00E-03	3.74E-04	3.99E-05
10 M NaOH	7.84E-06	NA	NA
10 M NaOH/0.2 M $NaMnO_4$	6.97E-03	4.57E-04	6.66E-07
1 M $NaHCO_3$/Na_2CO_3	1.17E-04	1.97E-04	3.01E-07
1 M $NaHCO_3$/Na_2CO_3/0.2 M $NaMnO_4$	4.33E-03	3.26E-04	2.94E-06
0.05 M DTPA	1.43E-04	1.31E-04	1.41E-05
0.18 M HNO_3 blank	NA	NA	NA
10.0 M NaOH blank	NA	NA	NA
1 M $NaHCO_3$/Na_2CO_3 blank	NA	NA	NA

Appendix D Time-dependent Actinide Concentrations in Test Solutions

The concentrations of Pu, Np, and Am measured in each test solution as a function of time are plotted on Figures D-1 – D-11.

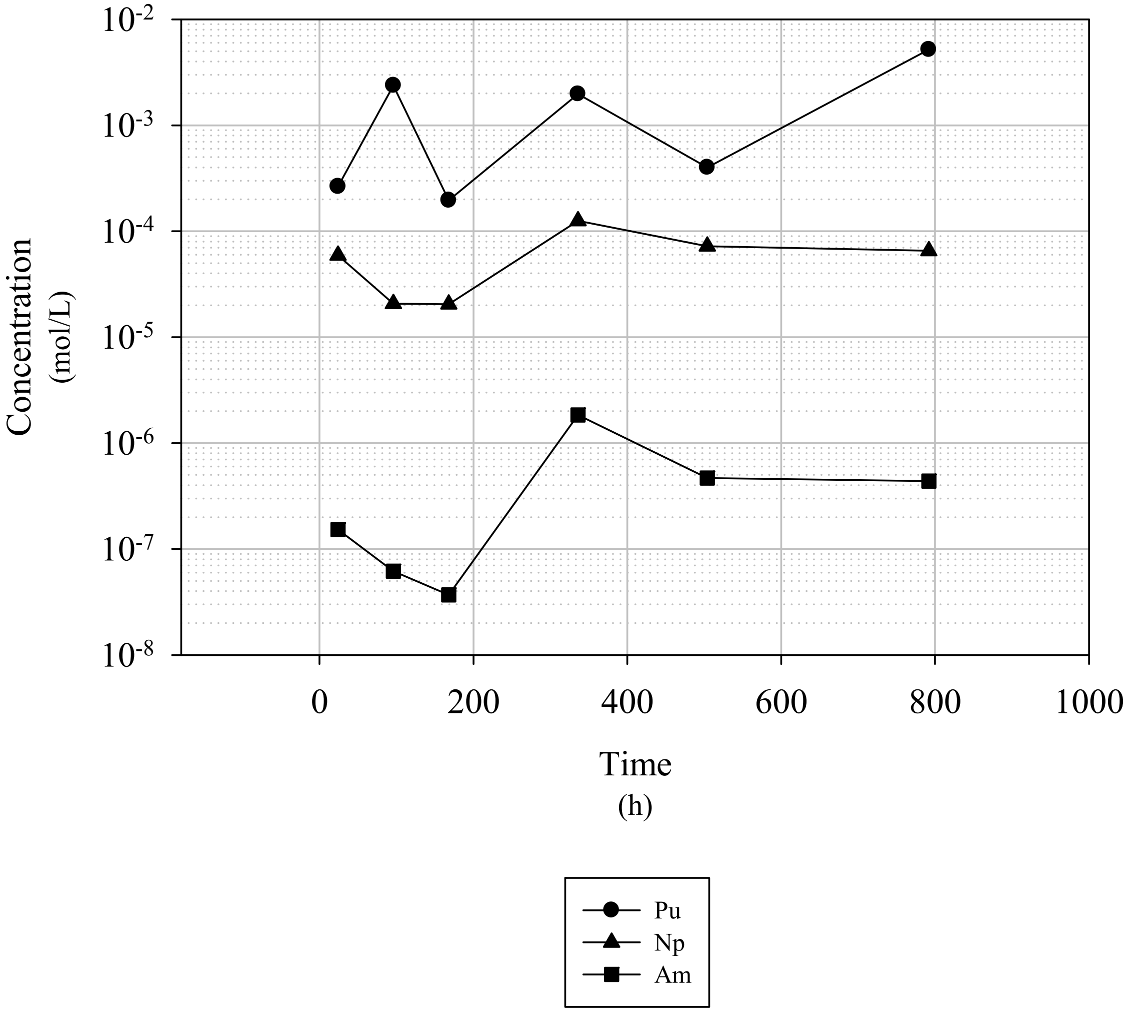

Figure D.1 Actinide Concentrations in 0.9 M Oxalic Acid

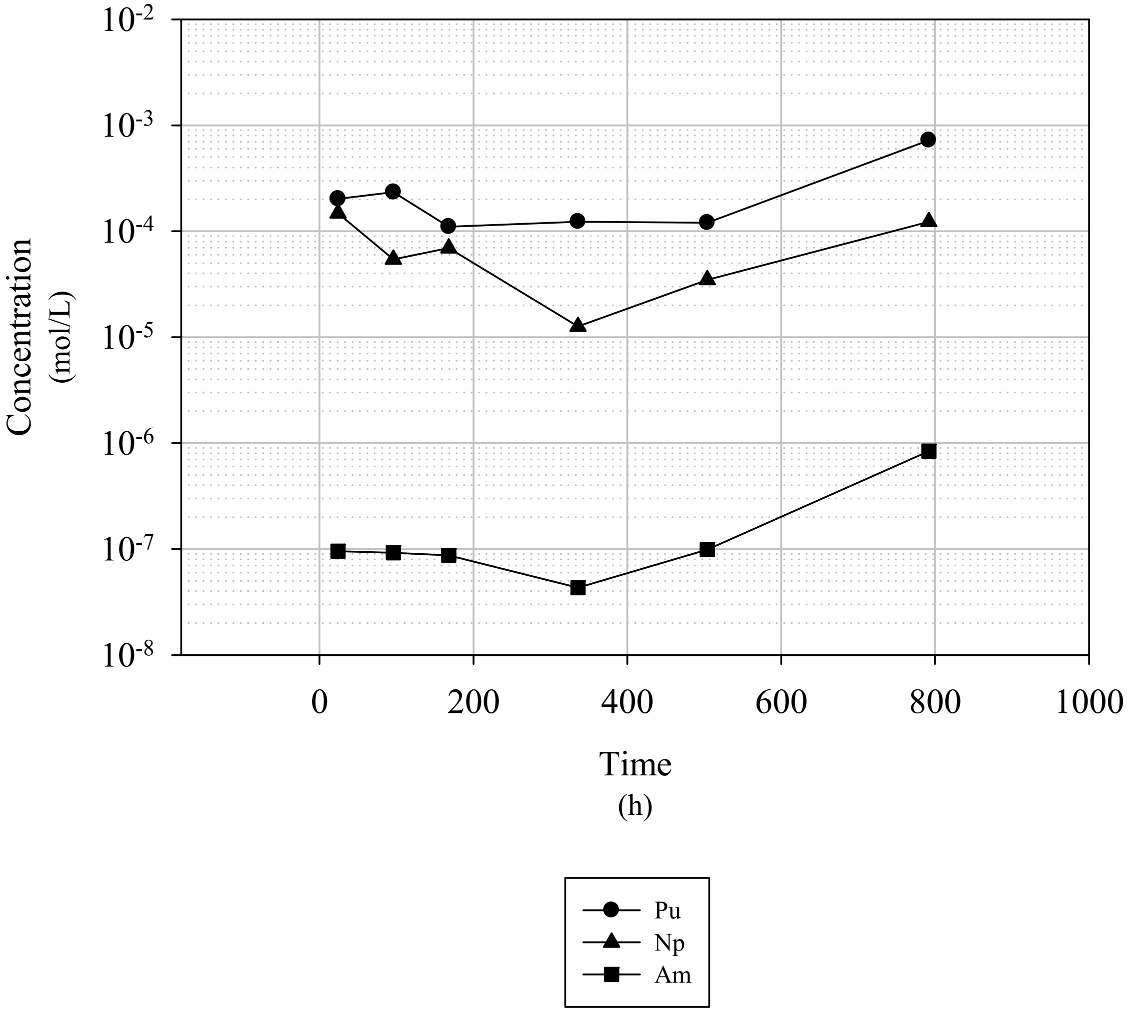

Figure D.2 Actinide Concentrations in 0.22 M Oxalic Acid

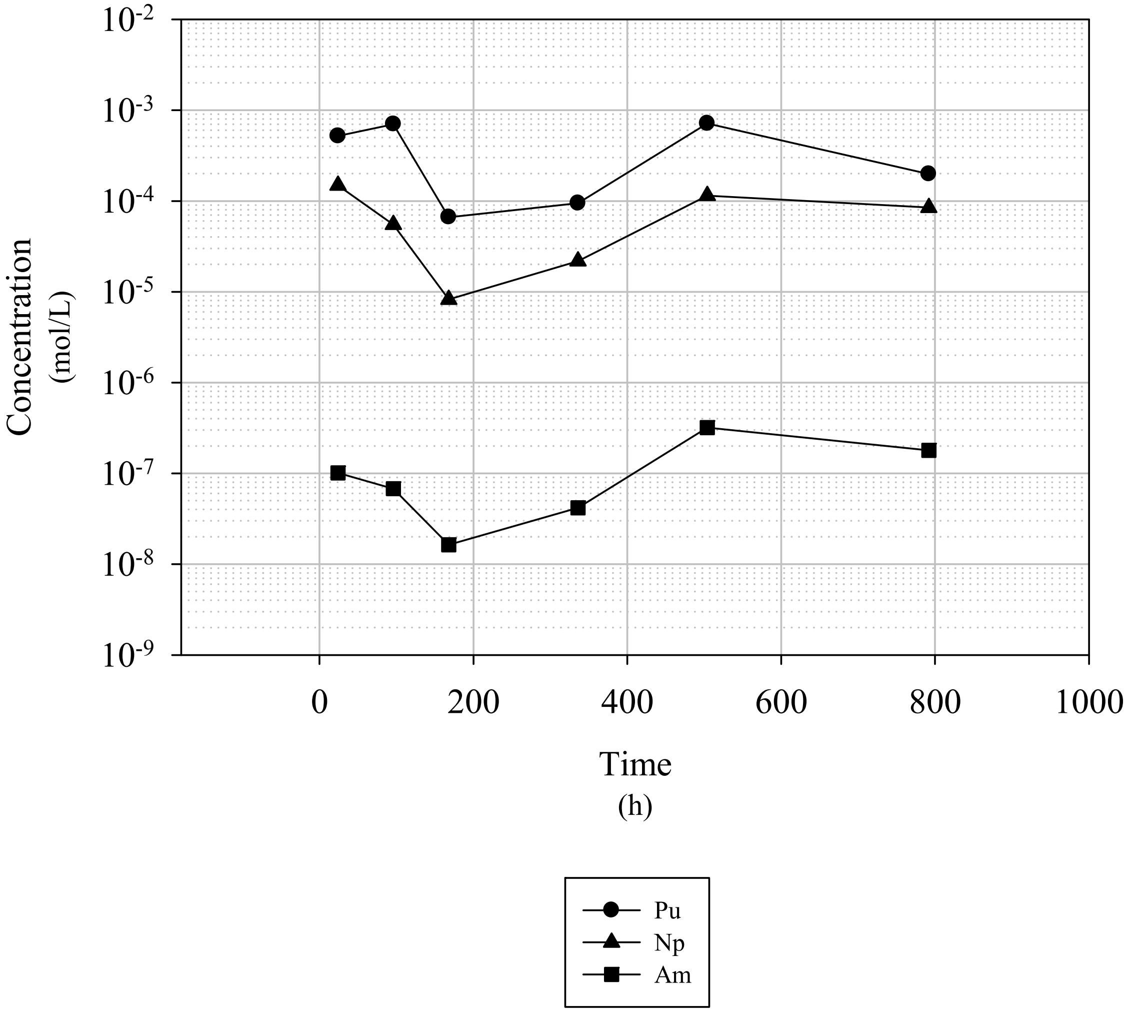

Figure D.3 Actinide Concentrations in 0.2 M Oxalic Acid/0.1 M Citric Acid

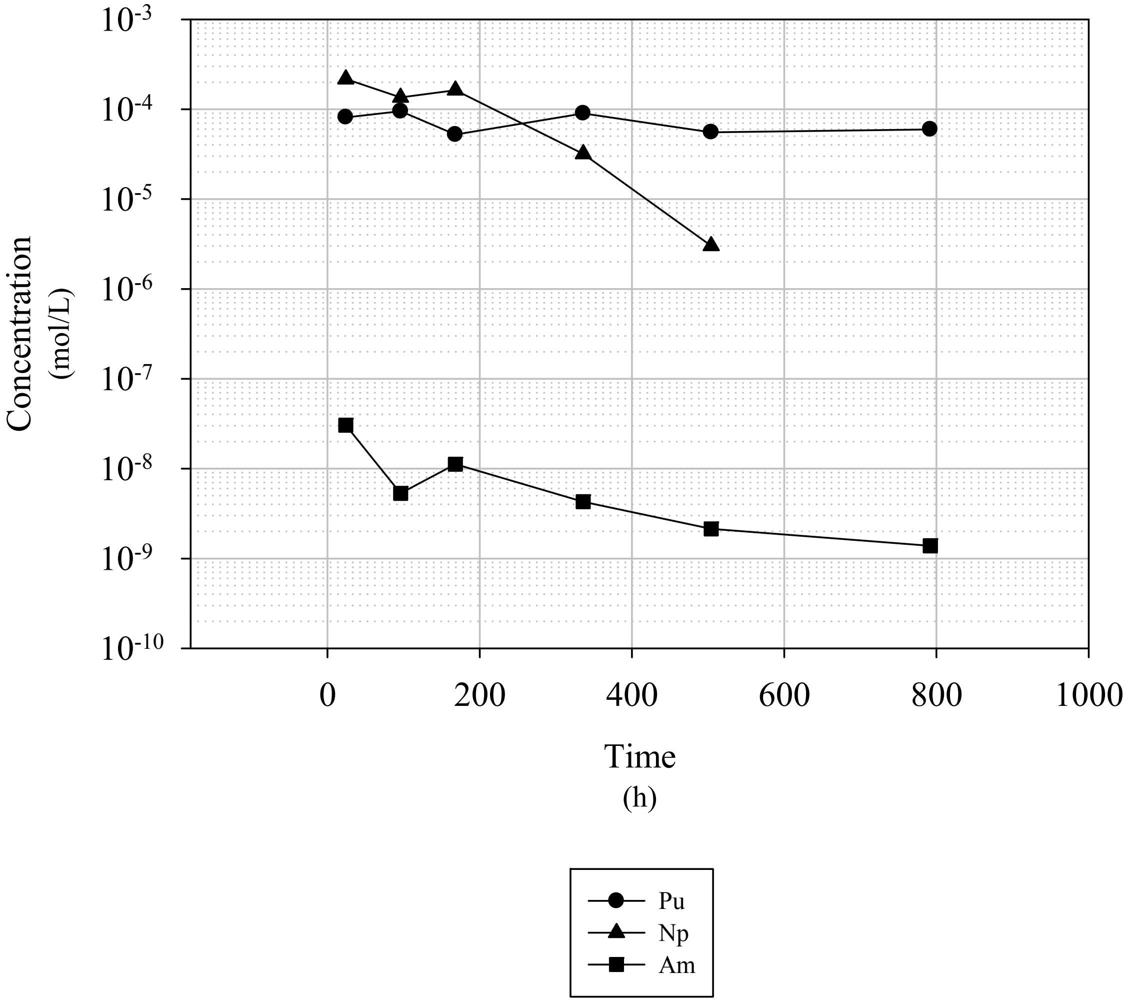

Figure D.4 Actinide Concentrations in 0.18 M HNO_3/0.056 M Oxalic Acid

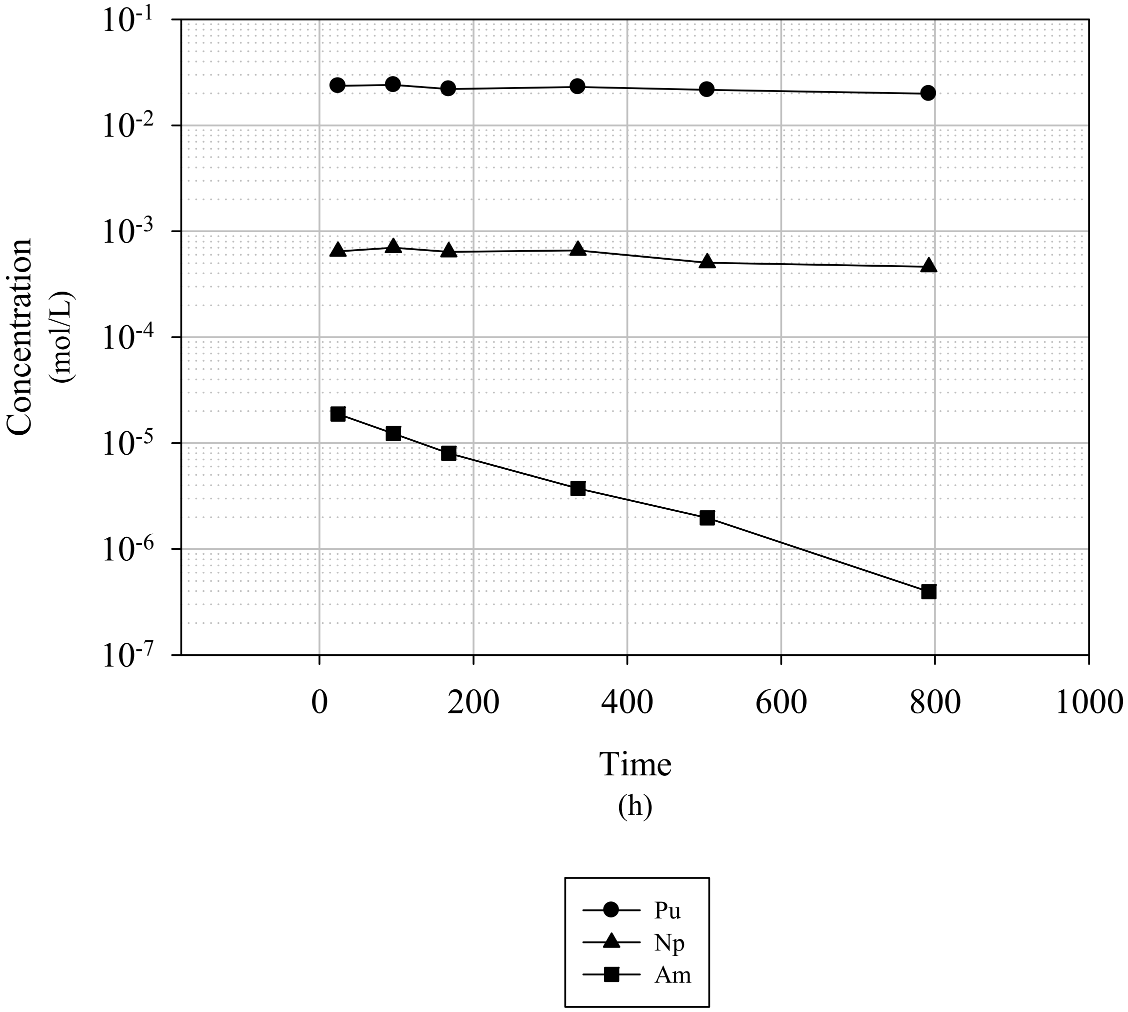

Figure D.5 Actinide Concentrations in 0.18 M HNO_3/0.2 M $NaMnO_4$

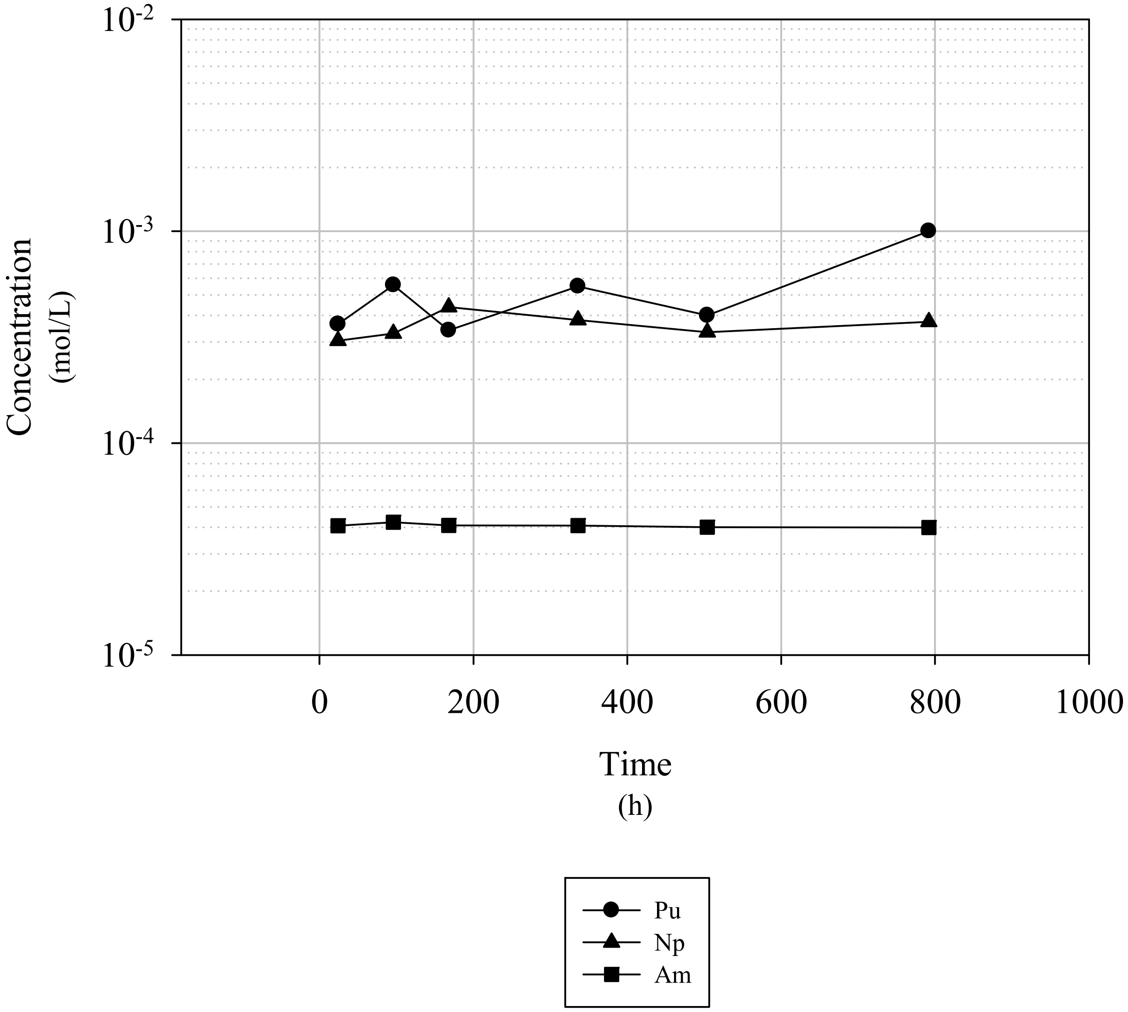

Figure D.6 Actinide Concentrations in 0.18 M HNO_3

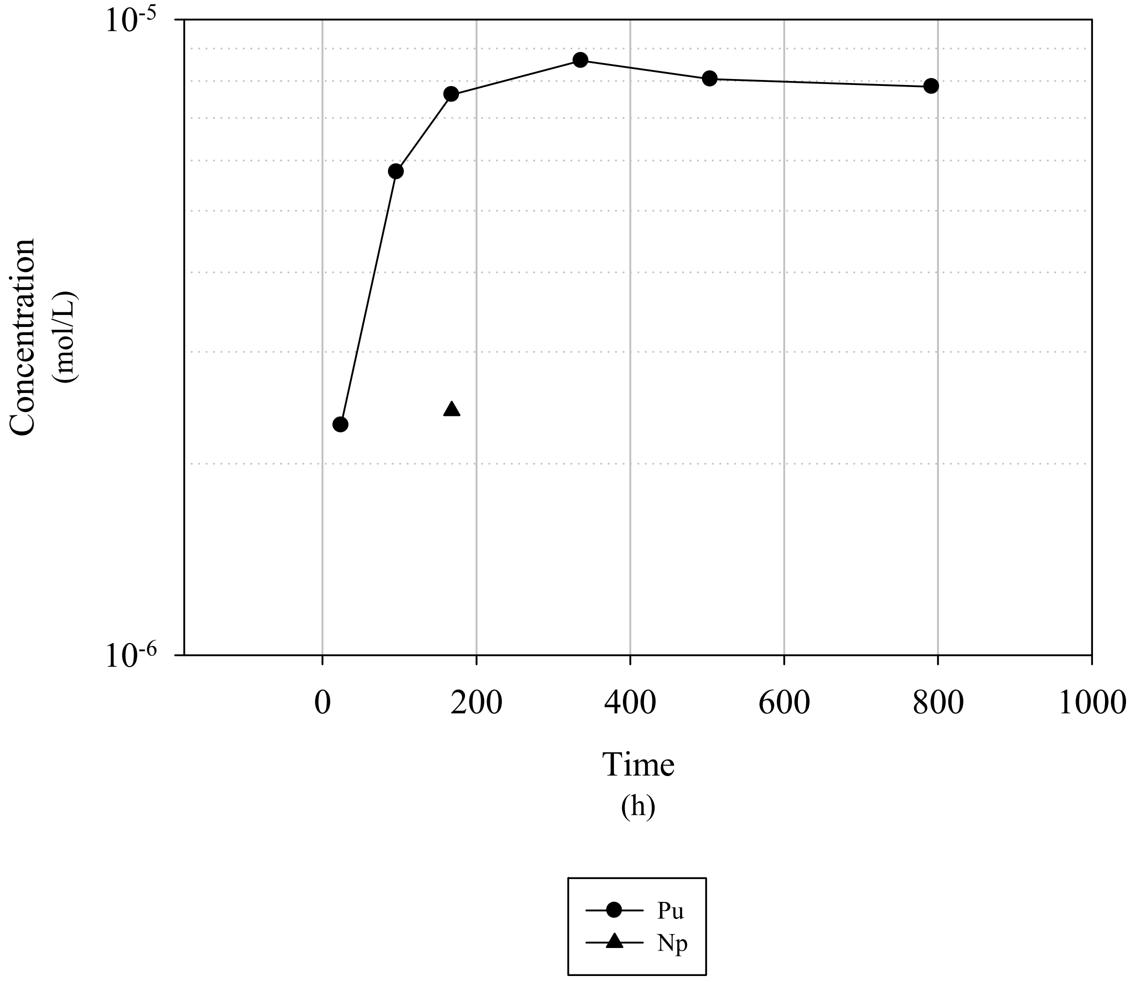

Figure D.7 Actinide Concentrations in 10 M NaOH

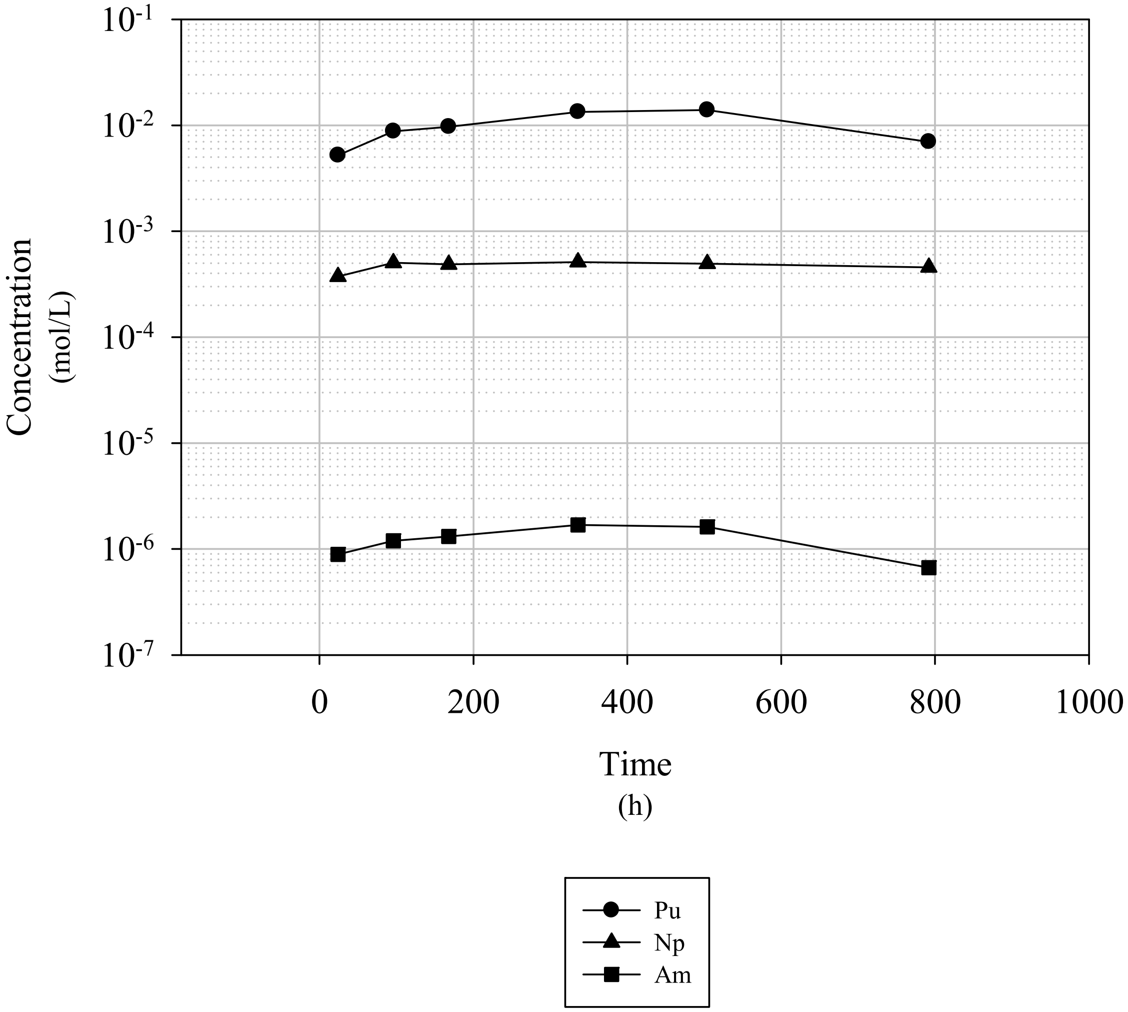

Figure D.8 Actinide Concentrations in 10 M NaOH/0.2 M $NaMnO_4$

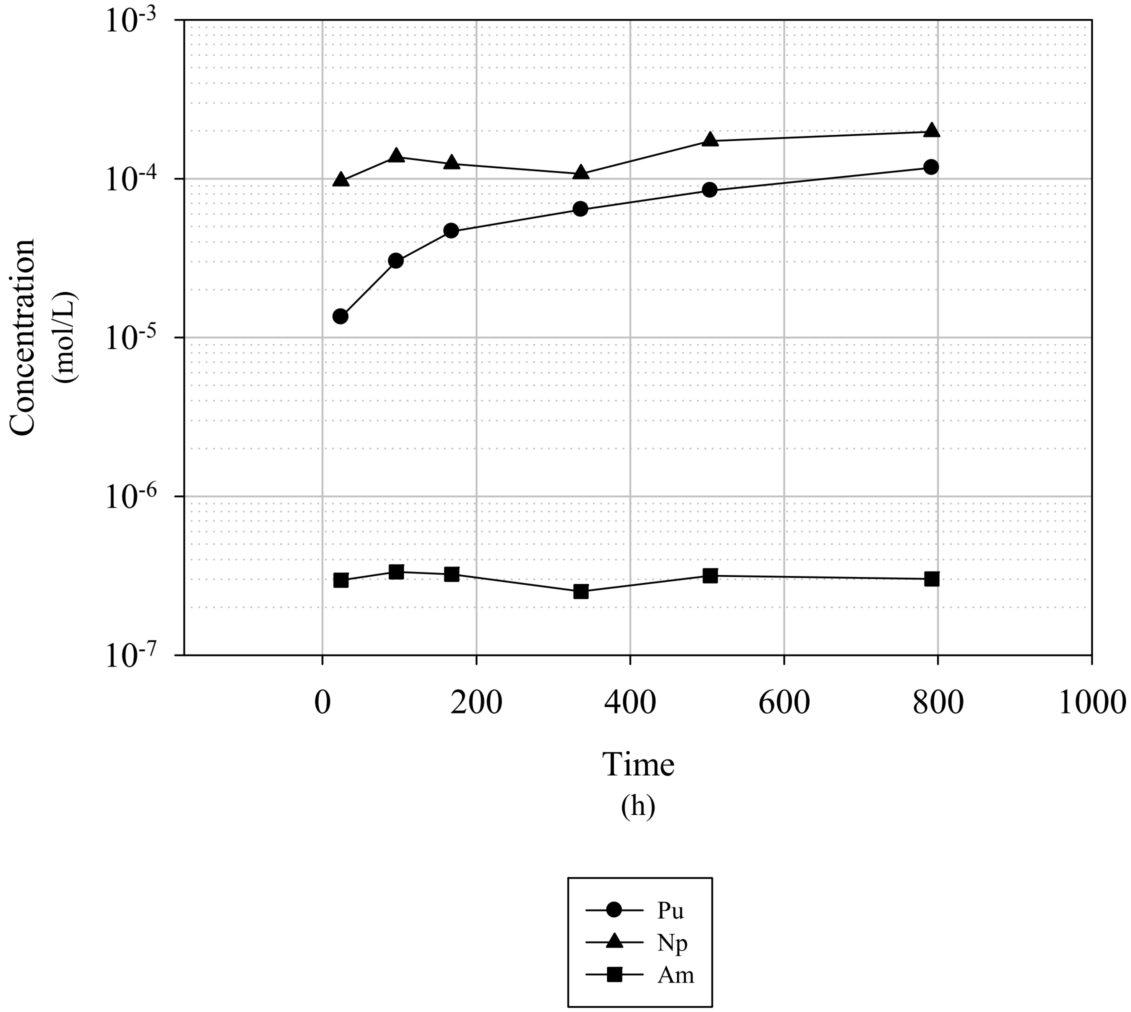

Figure D.9 Actinide Concentrations in 1 M $NaHCO_3/Na_2CO_3$

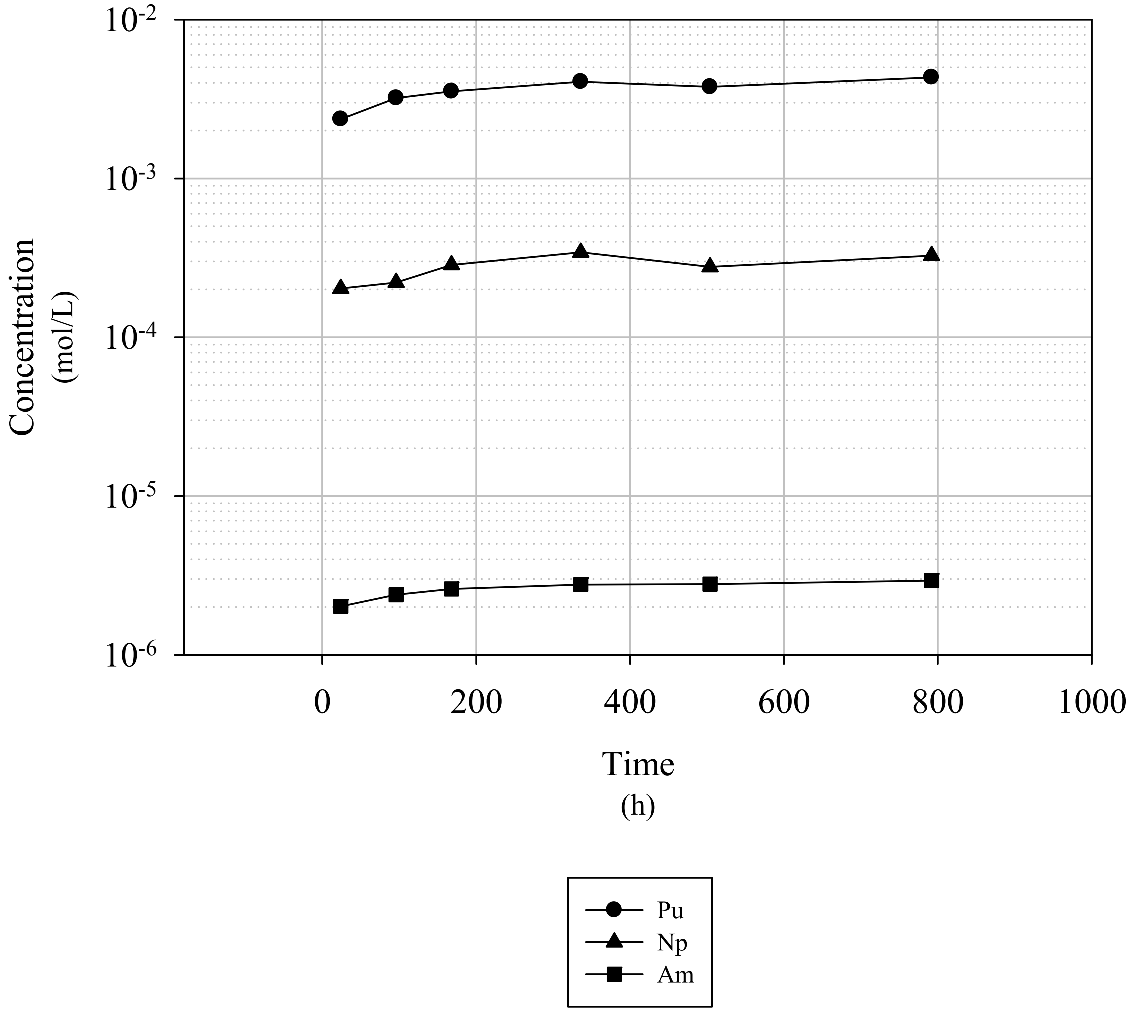

Figure D.10 Actinide Concentrations in 1 M $NaHCO_3/Na_2CO_3/0.2$ M $NaMnO_4$

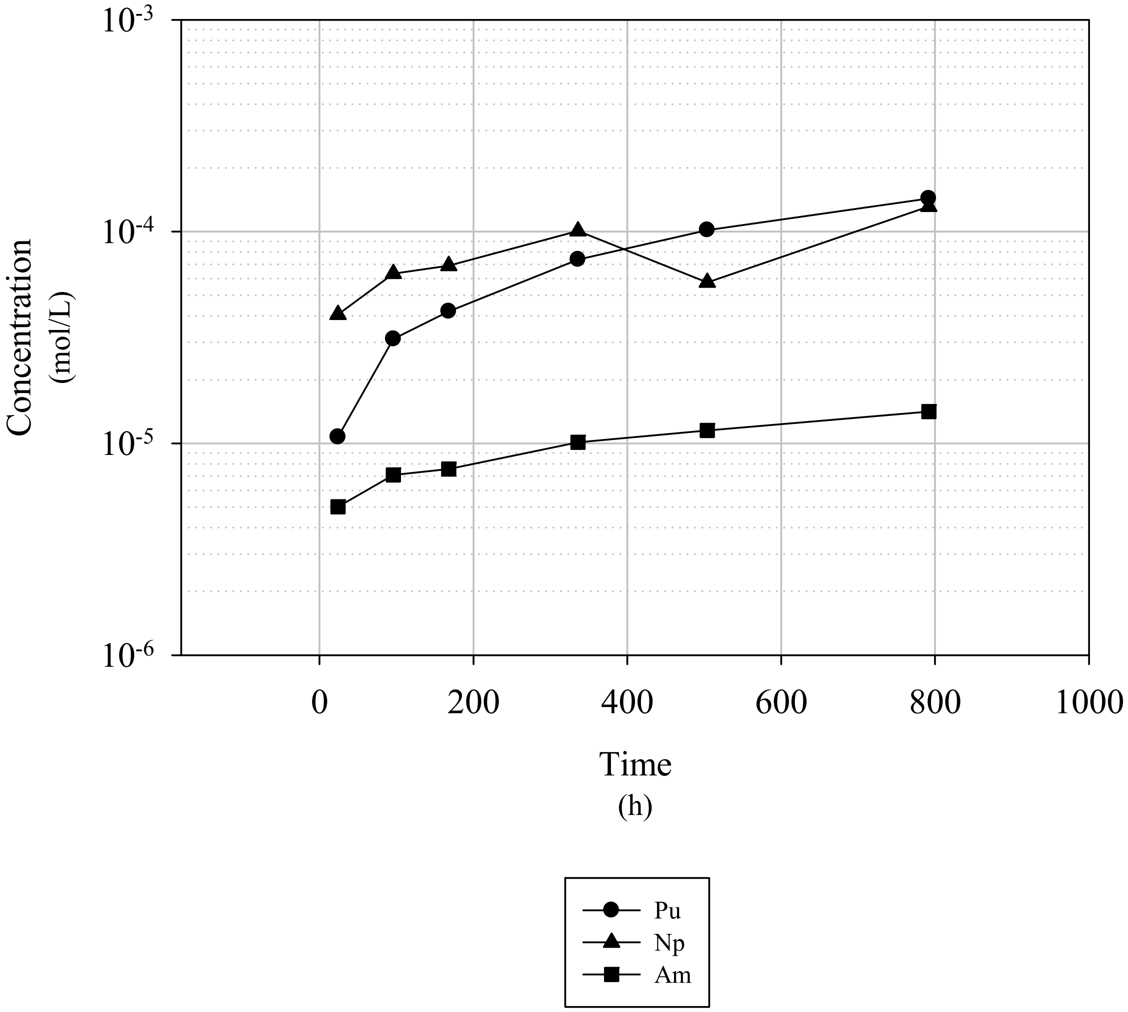

Figure D.11 Actinide Concentrations in 0.05 M DTPA