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Alternative Chemical Cleaning Methods for High Level Waste Tanks: Simulant Studies

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PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

Solubility testing with simulated High Level Waste tank heel solids has been conducted in order to evaluate two alternative chemical cleaning technologies for the dissolution of sludge residuals remaining in the tanks after the exhaustion of mechanical cleaning and sludge washing efforts. Tests were conducted with non-radioactive pure phase metal reagents, binary mixtures of reagents, and a Savannah River Site PUREX heel simulant to determine the effectiveness of an optimized, dilute oxalic/nitric acid cleaning reagent and pure, dilute nitric acid toward dissolving the bulk non-radioactive waste components. A focus of this testing was on minimization of oxalic acid additions during tank cleaning. For comparison purposes, separate samples were also contacted with pure, concentrated oxalic acid which is the current baseline chemical cleaning reagent. In a separate study, solubility tests were conducted with radioactive tank heel simulants using acidic and caustic permanganate-based methods focused on the "targeted" dissolution of actinide species known to be drivers for Savannah River Site tank closure Performance Assessments. Permanganate-based cleaning methods were evaluated prior to and after oxalic acid contact.

Based on the results, significantly more oxalic acid than necessary has likely been used in previous tank chemical cleaning campaigns. Furthermore, the baseline oxalic acid reagent is not effective for the removal of nickel and mercury simulated sludge components. The baseline method is somewhat effective at removing most simulated sludge manganese components and very effective at removing iron and aluminum (gibbsite). Dilute nitric/oxalic acid mixtures are effective for the removal of most primary (iron and aluminum) and secondary (manganese, nickel and mercury) sludge phases. Dilute, pure nitric acid is effective at removing aluminum, nickel, divalent manganese, and mercury. Dilute nitric acid should be considered for heel pre-acidification and removal of selected sludge components (aluminum, nickel, and some actinides, see below). A processing sequence involving dilute nitric acid followed by the recommended dilute nitric/oxalic acid mixture appears to be the optimal cleaning approach resulting in minimal oxalate additions. This cleaning method requires larger water addition volumes than the baseline method, which places greater demand on evaporator operations. Cleaning reagent volume increases of approximately 100% are anticipated, although decreased subsequent water additions are expected during sludge washing since minimal sodium oxalate salts should be present in the sludge heel.

Solubility tests with radioactive simulants prior to oxalic acid addition indicated that small amounts of transuranic elements can be solubilized (approximately 30% Pu, 10% Np, and 5% Am) using the caustic permanganate method relative to the acidic permanganate method. However, the measured actinide concentrations using the caustic permanganate method exceeded concentrations typically observed in waste supernate by several orders of magnitude, so there is potential for solubilizing significant amounts of actinides from tank residuals using this method. When the radioactive sludge heel simulant was contacted with acidic (HNO_3) permanganate solution, ~90% of the neptunium and plutonium components were solubilized, indicating that solubility limits were probably not reached in these tests due to depletion of these species from the residual solids. In contrast, only ~50% of the americium was solubilized, which indicates that some interaction with a component in the simulated sludge or manganese dioxide precipitate (formed from the added permanganate) resulted in decreased americium solubility. Based on the results, it appears that the treatment of waste tank sludge residuals with an acidic permanganate solution has the potential to solubilize a higher fraction of the actinides than a caustic permanganate solution, although both methods are effective.

Evaluations of the permanganate-based methods after oxalic acid contact revealed that treatment of the radioactive simulant with either the optimized or the baseline oxalic acid cleaning reagents resulted in the dissolution of a majority of the residual solids including the neptunium, plutonium, and americium. No actinides above the minimum detection of the analysis remained following contact with the optimized

oxalic/nitric acid reagent. Following treatment using the baseline oxalic acid reagent, detectable levels of actinide removal were achieved using the acidic permanganate cleaning method.

Based on the results observed with non-radioactive and radioactive simulants, actual waste testing of both alternative cleaning technologies (optimized oxalic acid cleaning using supplementary nitric acid and permanganate-based cleaning under both acidic and basic conditions) is recommended.

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LIST OF ABBREVIATIONS

AD	Analytical Development
BOAC	Bulk Oxalic Acid Cleaning
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EM	Environmental Management
HLW	High Level Waste
HM	H-Modified
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
LTAD	Low Temperature Aluminum Dissolution
PMP	Polymethylpentene
PSAL	Process Science Analytical Laboratory
PUREX	Plutonium Uranium Reduction Extraction
RPM	Revolutions per Minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
XRD	X-Ray Diffraction

1.0 Introduction

Regulatory requirements for the closure of waste tanks utilized for the storage of High Level Waste (HLW) at the Savannah River Site (SRS) in Aiken, SC include the removal of highly radioactive nuclides to the maximum extent practical. Chemical cleaning methods have been utilized in SRS HLW tanks in order to promote at least partial dissolution of the bulk non-radioactive sludge components to assist in heel removal. Chemical cleaning is conducted following the removal of water soluble waste components by washing and the exhaustion of mechanical methods for the removal of insoluble solids. The remaining radioactive sludge and insoluble salt heels are distributed on the floor and walls of large (exceeding 1 million gallons) radioactive waste tanks containing many obstructions which limit the effectiveness of mechanical removal methods.

The U. S. Department of Energy (DOE) Office of Environmental Management (EM) has tasked the Savannah River National Laboratory (SRNL) with developing alternative and improved strategies and technologies to chemically clean the tanks prior to tank closure.[1] Two chemical cleaning technologies have been implemented previously at SRS: Low Temperature Aluminum Dissolution (LTAD) and Bulk Oxalic Acid Cleaning (BOAC). Recent chemical cleaning efforts on SRS Tank 12 were very successful with regard to the removal of bulk sludge heel components (Al, Fe, and U phases) and beta/gamma radionuclide removal.[2] The Tank 12 chemical cleaning strategy utilized the following processing sequence: LTAD, washing, BOAC, and neutralization. Although chemical cleaning using these technologies has been shown to be effective, no disposition path has been identified for oxalate ion added to the waste inventory from BOAC and other SRS processes, and insoluble oxalate salts are accumulating within the SRS tank farm and waste processing facilities (evaporators, etc.).[3] Extensive sludge washing is also required to remove moderately soluble sodium oxalate salts from the waste prior to sludge vitrification in the SRS Defense Waste Processing Facility (DWPF). Such water additions to the tank farm inventory increase the waste volume requiring evaporation and management. As a result, oxalate additions to the tank farm need to be minimized.

The use of supplementary acids has been shown to assist bulk sludge dissolution in oxalic acid. Previous SRNL testing[4,5] revealed the importance of pH control (specifically maintaining low pH), recommended the use of a supplementary acid (dilute HNO_3) with dilute oxalic acid to minimize oxalate additions,[6] and indicated that manageable corrosion rates would be observed with these oxalic/nitric acid mixtures.[7] Methods to destroy the oxalate solids have also been identified[8] and evaluated, but have not been implemented. During oxalic acid cleaning of SRS Tank 12H, the heel was maintained at a low pH (~pH 2), but a supplementary acid was not utilized and oxalate additions were not minimized. Nonetheless, significant improvements in the tank cleaning methods (mechanical and chemical) were realized in the Tank 12 cleaning campaign.

Primary drivers in SRS Tank Closure Performance Assessments,[9] which evaluate the fate of tank sludge residuals on a geological timescale, are alpha-emitting radionuclides such as neptunium, plutonium, and americium. The amounts of these radionuclides remaining in tank residuals following chemical cleaning are sufficiently high based on their half-life and activity that they present the greatest dose risk to the public. As a result, there is interest in chemical cleaning methods targeting these specific minor waste constituents. Scoping studies conducted at SRNL revealed promising methods to dissolve the actinides from the HLW tank residual solids.[10] Oxidation of the actinides with permanganate in either strong caustic (10 M NaOH) or dilute acid (0.18 M HNO_3) solutions was shown to result in dissolution of simple surrogate oxy/hydroxide phases of these metals. Either of these two permanganate-based methods for alpha removal might be suitable for incorporation into a chemical cleaning flow sheet, though they would likely be utilized at different times in the waste processing sequence. Utilization of permanganate-based methods results in the addition of manganese dioxide solids to the waste, so minimization of permanganate additions is needed.

Neither LTAD nor BOAC are highly effective at removing certain secondary metal components of HLW tank residuals. Specifically, mercury, nickel, and manganese have not been effectively removed during SRS tank cleaning operations.[11] If removal of these secondary phases is needed to support tank closure efforts, then methods need to be developed to solubilize these phases. In addition, understanding the behavior of these metals in oxalic acid-based cleaning reagents is important in evaluating the effectiveness of chemical cleaning campaigns and in optimizing cleaning methods.

Testing conducted as part of the 2014-2015 Alternative Chemical Cleaning test program included:

- Non-radiological Simulant Testing - This testing focused on performance comparisons between the baseline BOAC method and the optimized oxalic acid cleaning method (utilizing supplementary nitric acid) recommended previously.[6] Additional dissolution tests were conducted using dilute nitric acid alone to evaluate the effectiveness of nitric acid for cleaning with no oxalate added. Tests were conducted using a PUREX sludge tank heel simulant containing numerous waste components (including mercury and other RCRA metals), as well as pure metal reagents believed to be representative of the iron, aluminum, nickel, and manganese phases in HLW sludge tank residuals.
- Radioactive Simulant Testing – This testing focused on permanganate-based methods for the dissolution of alpha-emitting actinide elements (neptunium, plutonium, and americium). Both the acidic and the basic permanganate methods were evaluated under flowsheet relevant conditions. The testing included solubility tests prior to and after oxalic acid and oxalic/nitric acid contacts. The tests were conducted using a simplified PUREX sludge simulant prepared by the co-precipitation of the transuranic actinides with iron, aluminum, nickel, manganese, and uranium solids.
- Corrosion Evaluations – Electrochemical and gravimetric tests were conducted to determine corrosion rates of carbon steel coupons representative of SRS HLW tanks immersed in the cleaning reagents of interest and in the presence of either PUREX or HM sludge simulants. The cleaning reagents evaluated included the optimized oxalic acid cleaning reagent (oxalic/nitric acid mixture), permanganate in dilute nitric acid, and permanganate in caustic solution. Results from these studies are provided in a separate technical report.[12]

Testing of actual SRS tank residual samples, evaluations of unique Hanford HLW sludge phases, identification of new cleaning strategies for Hanford waste, and solubility testing of SRS waste residuals in environmental solutions following chemical cleaning, were not conducted, although this testing was specified in the Task Technical and Quality Assurance Plan (TTQAP) for the experimental studies.[13] SRS actual waste evaluations are planned for future testing. Testing in environmental solutions has been conducted under a separate test program.[14] The TTQAP also indicated that results will be used to evaluate current OLI model predictions. A decision was made to use remaining funds primarily for actual waste testing since significant data comparisons to OLI model predictions were made in previous reports. As funding and time allow, data comparisons to OLI model predictions may be conducted in the next program phase.

This testing was conducted to identify alternative and improved strategies for: 1) the removal of non-radiological HLW sludge heel primary and secondary waste components with minimal oxalate additions, at least partially through the dissolution of the bulk metal species, and, 2) the targeted removal of actinide elements present at low concentrations by oxidation and dissolution. Promising alternative cleaning methods identified through simulant testing should be further evaluated with actual tank residual samples.

2.0 Experimental Procedure

2.1 Non-Radioactive Simulant Testing

2.1.1 Reagents, Supplies, and Equipment for Non-Radioactive Simulant Testing

Commercially-purchased, concentrated nitric acid (HNO_3) solution and oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$) solid were utilized for the preparation of acidic chemical cleaning solutions for testing. Analysis confirmed that the concentration of the mixed nitric/oxalic acid solution contained 0.167 M NO_3^- (92.7% of the target concentration of 0.18 M) and 0.058 M $C_2O_4^{2-}$ (104.0% of the target concentration of 0.056 M). Pure nitric and oxalic acid solutions were prepared by the same methods utilizing the same reagents and were not analyzed. Dilute NaOH solution (0.01 M; inhibited water) was prepared from commercially-purchased, concentrated reagent solution and was not analyzed.

An aged sample of PUREX waste heel residual simulant was obtained from SRNL archives. The simulant was prepared following procedures outlined in Reference 15. The measured composition of a simulant sample prepared following these procedures is provided in Table 2-1. A representative simulant sub-sample for testing was isolated from the larger archive sample by agitating and suspending the solids using an impellor and then transferring the sub-sample to a smaller bottle using a peristaltic pump. The density of the original slurry was 1.324 g/mL.

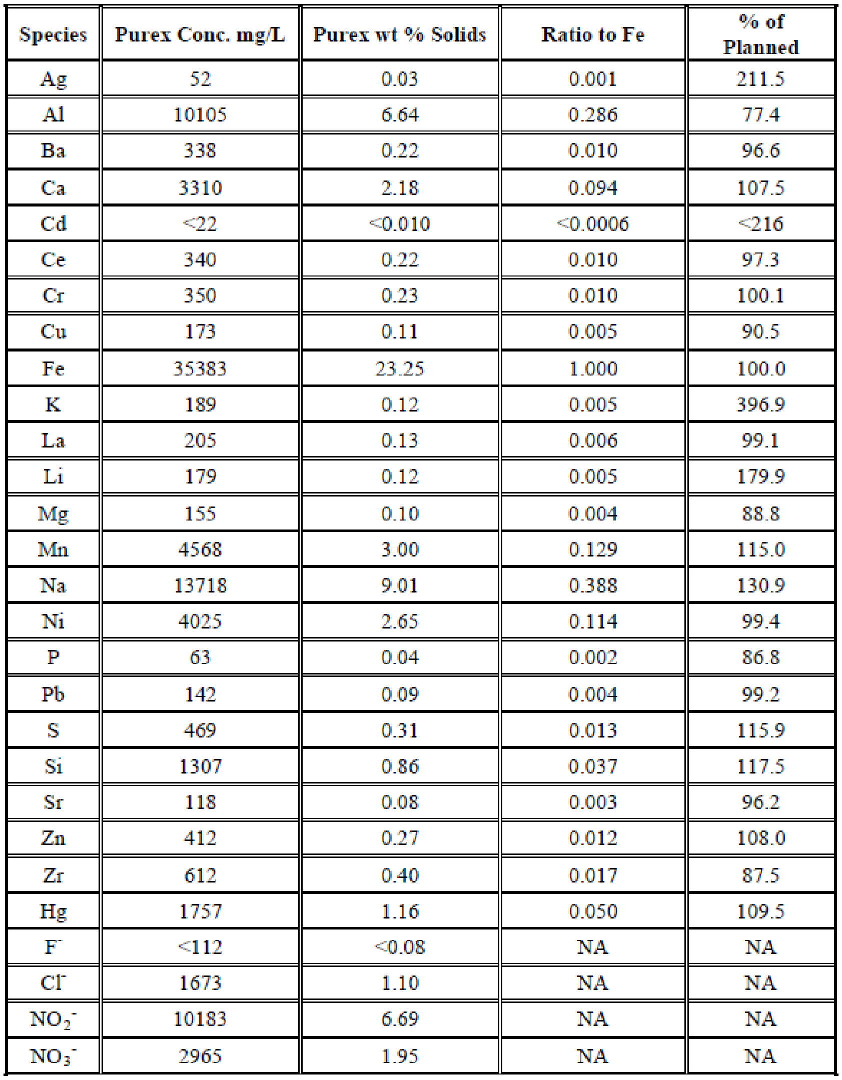
Additional non-radioactive simulant tests were conducted using the following commercially-purchased reagents: $Ni(OH)_2$ (catalogue #93-2847), MnO (catalogue #93-2515), MnO_2 (catalogue #93-2510), Fe_2O_3 (catalogue #93-2617) from Strem Chemicals, Inc., and $Al(OH)_3$ from Almatis, Inc (Bauxite, AR). Two manganese reagents were tested because the oxidation state of manganese in waste sludge is not known and mixed valency is postulated.

All dissolution tests were conducted in 125 or 250 mL polymethylpentene (PMP) bottles. Analysis samples were prepared in 15 mL polyethylene bottles. Ten milliliter polyethylene syringes (polypropylene plungers) fitted with 0.45 µm Nalgene Nylon filters were used for analysis sample filtration. Analytical balances used for the measurement of all sample and bottle weights are calibrated annually by the SRNL Standards Laboratory and checked on a daily basis with a calibrated weight set. Samples were maintained in temperature-controlled, Innova incubator shaker ovens (Models 4230 and 42) and agitated by orbital rotation.

2.1.2 Non-Radioactive Sample Handling and Pretreatment

The dissolution test matrix for non-radioactive simulant testing is provided in Figure 2-1. The solubility of various metal species was determined in three acidic solutions which were contacted with the simulant slurry or reagent solids (not shown in the figure) in three sequential cycles. The acid test solutions included: 1) 0.18 M HNO_3, 2) 0.92 M $H_2C_2O_4$ (8 wt. % BOAC baseline method), and, 3) a mixture containing both 0.18 M HNO_3 and 0.056 M $H_2C_2O_4$ (optimized oxalic acid cleaning method).

Table 2-1. Non-Radioactive PUREX Hazardous Sludge Heel Simulant As-Prepared Composition (data originally provided as Table 3-2 in Reference 15).



Species	Purex Conc. mg/L	Purex wt % Solids	Ratio to Fe	% of Planned
Ag	52	0.03	0.001	211.5
Al	10105	6.64	0.286	77.4
Ba	338	0.22	0.010	96.6
Ca	3310	2.18	0.094	107.5
Cd	<22	<0.010	<0.0006	<216
Ce	340	0.22	0.010	97.3
Cr	350	0.23	0.010	100.1
Cu	173	0.11	0.005	90.5
Fe	35383	23.25	1.000	100.0
K	189	0.12	0.005	396.9
La	205	0.13	0.006	99.1
Li	179	0.12	0.005	179.9
Mg	155	0.10	0.004	88.8
Mn	4568	3.00	0.129	115.0
Na	13718	9.01	0.388	130.9
Ni	4025	2.65	0.114	99.4
P	63	0.04	0.002	86.8
Pb	142	0.09	0.004	99.2
S	469	0.31	0.013	115.9
Si	1307	0.86	0.037	117.5
Sr	118	0.08	0.003	96.2
Zn	412	0.27	0.012	108.0
Zr	612	0.40	0.017	87.5
Hg	1757	1.16	0.050	109.5
F^-	<112	<0.08	NA	NA
Cl^-	1673	1.10	NA	NA
NO_2^-	10183	6.69	NA	NA
NO_3^-	2965	1.95	NA	NA

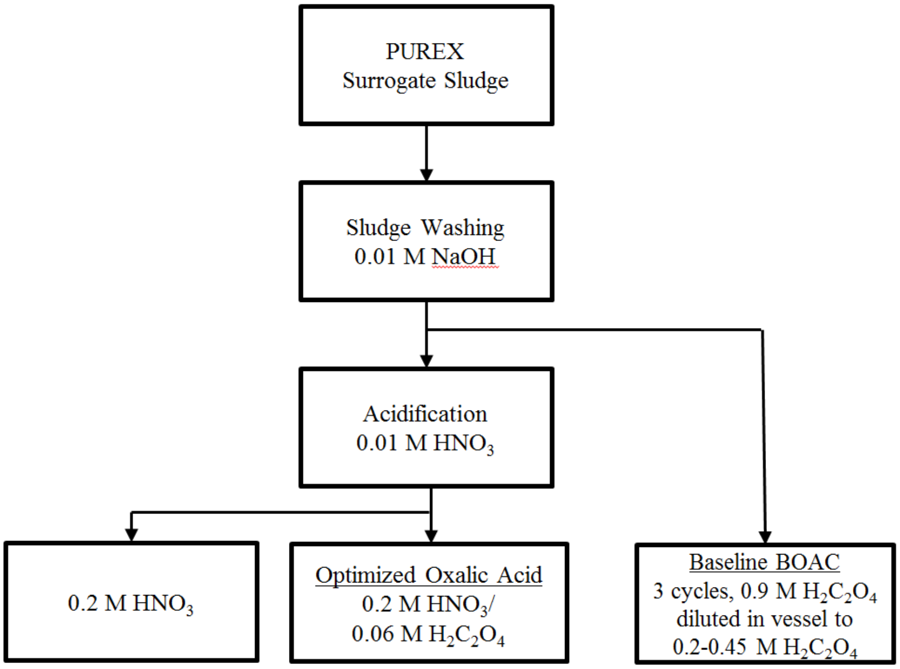


Figure 2-1. Non-Radioactive PUREX Sludge Heel Simulant Solubility Test Matrix.

An inhibited water wash pretreatment step was performed for all PUREX simulant tests as described below. A 175 mL representative sample of the original PUREX simulant slurry was pretreated by mixing the slurry with 250 mL of 0.01 M NaOH. Approximately 75% of the liquid was decanted from the settled solids following pretreatment to give a washed simulant slurry containing: 27.51 wt. % insoluble solids, 0.85 wt. % soluble solids, and 28.37 wt. % total solids. For comparison, the as-prepared PUREX simulant was reported to contain 3.05 wt. % soluble solids and 0.01 M NaOH contains 0.04 wt. % soluble solids. Representative sub-samples (~10 g each) of the washed simulant slurry were transferred to separate PMP bottles for dissolution testing. Analysis results for a sub-sample of the washed simulant slurry following acid digestion are provided in Table 2-2. Results indicate that the washed and decanted PUREX sludge simulant sample was concentrated by a factor of 1.8 relative to the original recipe formulation provided in Table 2-1. The mercury analysis result is lower than expected. Based on the above concentration factor, the mercury content was expected to be 2.1 wt. %. The dry solid reagent samples were not pretreated with dilute NaOH for any tests.

Table 2-2. Pretreated Non-Radioactive PUREX Sludge Simulant Composition.

Element	Wt. %
Al	10.70
Ba	0.33
Ca	3.29
Cr	0.45
Cu	0.24
Fe	34.97
K	0.05
Li	<0.10
Mg	0.18
Mn	4.62
Na	2.03
Ni	4.21
P	<0.10
Pb	0.10
S	<0.10
Si	1.29
Zn	0.40
Zr	0.63
Hg	0.99

The testing with pure nitric acid and mixed nitric/oxalic acid solutions assumed an idealized treatment strategy not currently in use, where the waste was pre-acidified with 0.01 M nitric acid prior to chemical cleaning in more concentrated acids. It was anticipated that some of the pure reagents and simulant components would partially dissolve in dilute nitric acid and it was unknown whether the as-received reagents contained any residual base equivalents. Acid pretreatment involved contacting the samples (PUREX simulant and selected pure phase reagents) with 0.01 M HNO_3 with agitation. Volume-based phase ratios near 10 (acid:simulant slurry) were used for the PUREX simulant samples. Mass-based phase ratios near 50:1 (acid:dry reagent) were used for the pure reagents. The pH was measured during acid pretreatment with the goal of achieving a stable pH $\leq$2.5. This was achieved with all of the pure phase reagents after acid contact, except for the nickel hydroxide reagent, which produced a pH between 5 and 6.5 even after three contact cycles. The green color of the solution and the high pH measured for these samples indicated reagent dissolution. Similarly, the PUREX simulant samples contacted with 0.01 M HNO_3 produced solution pH values $\geq$6 even after four acid contact cycles. The nickel hydroxide and the simulant samples were used for subsequent testing without further acidification in 0.01 M HNO_3. Approximately 75% of the pretreatment liquid was removed from all test samples prior to use in subsequent tests. In order to emulate the baseline BOAC treatment, which does not include pre-acidification, simulant samples and pure phase reagents in this test group were not pre-acidified.

2.1.3 Non-Radioactive Solubility Testing

Following pretreatment, solubility tests were conducted on the PUREX simulant samples in nitric acid and mixed oxalic/nitric acid solutions by transferring known cleaning reagent amounts to the PMP bottles containing the pre-acidified samples. Sample and bottle weights were obtained using analytical balances. Samples were maintained in temperature-controlled incubator shaker ovens, continually agitated at a rotation rate of 250 RPM, and maintained at a temperature of 55 ºC. Dissolution tests were also conducted with the pre-acidified nickel hydroxide and manganese oxide reagents and with 50:50 (mass-based) mixtures of hematite (Fe_2O_3) and gibbsite ($Al(OH)_3$). Tests with pure phase reagents (~1.5 g per sample) were conducted at mass phase ratios of 50±2:1 (liquid:solid; ~75 g liquid reagent). For simulant samples, a volume ratio of 19±3:1 (reagent liquid:simulant slurry; ~150 mL reagent:~8 mL simulant) was used. Solubility tests involved three sequential 14-day contact cycles with the reagent solutions. After 14 days, the agitation was stopped to allow the solids to settle. Sample dilution bottles were prepared using 3 M HNO_3 acid. Sub-samples of the liquid phase were collected from each test bottle and transferred through 0.45 µm Nalgene Nylon syringe filters directly into the acid diluent (approximately 7 mL of sample diluted into 7 mL of diluent). The analysis samples were shaken and stored in the dark until analysis. Storing the samples in the dark was found in previous testing to avoid light-induced precipitation of iron oxalates. Dilution factors for each sample were calculated using the measured masses and assumed densities of diluent and sample. After the completion of sub-sampling, approximately 75% of the liquid was removed from each sample and fresh solution of the same volume as the original reagent solution was added. The pH was measured for each sample at the conclusion of each contact cycle using an Oakton pH 110 Series probe calibrated with pH 4.0, 7.0, and 10.0 buffer solutions. The probes were lightly wiped clean and rinsed with water between pH measurements on separate samples to avoid cross-contamination.

Testing with pure oxalic acid reagent was also conducted to emulate the baseline BOAC process used at SRS. The most recent SRS chemical cleaning campaign was conducted on Tank 12H. The simulant testing approach was generally based on this cleaning campaign. Tank 12H BOAC involved the addition of 8 wt. % (0.92 M) oxalic acid to the tank followed by a 24 hour contact period with no agitation. Water was subsequently added to the HLW tank to provide sufficient volume for mixing. The typical total acid contact time per cycle was 1 week. Three contact cycles were used following this approach. The volume-based phase ratio for the first cycle with Tank 12H was 15:1 (acid:original sludge) with a final oxalic acid concentration of 4 wt. %. The volume-based phase ratios for the second and third cycles were each 5:1 (acid:original heel volume) with a final oxalic acid concentration of 2 wt. %. A similar approach was used for simulant testing with pure oxalic acid, except that lower volume-based phase ratios were used for each 1-week cycle (8.9 for the first cycle and 3.0 for the second and third cycles). As was the case in the SRS Tank 12H Chemical Cleaning Campaign, water was added after one day to dilute the oxalic acid concentrations to 4 wt. % for Cycle 1 and 2 wt. % for Cycles 2 and 3. Sub-samples were collected and test sample pH values were measured at the conclusion of each acid contact cycle as described above for the nitric acid and mixed nitric/oxalic acid samples.

2.1.4 Sample Analysis for Non-Radioactive Simulant Testing

Reagent and sample analyses were conducted by the Process Science and Analytical Laboratory (PSAL) and the SRNL Analytical Development (AD) section. Analysis methods included Inductively Coupled Emission Spectroscopy (ICP-ES), Ion Chromatography (IC) Anion, and X-ray Diffraction (XRD). All liquid phase concentration results were corrected for dilution based on the masses of the nitric acid diluent and sample added to each bottle.

2.2 Radioactive Simulant Testing

A series of solubility experiments was performed to measure the efficiency of acidic and basic permanganate solutions in solubilizing neptunium, plutonium, and americium in a simulated sludge. The sludge was prepared by co-precipitating the actinides with major components found in sludge generated by the neutralization of waste from the PUREX process. Prior to performing the solubility tests, samples of the sludge were pretreated to simulate current and proposed waste tank cleaning processes. The preparation of the sludge and descriptions of the waste tank cleaning processes and solubility experiments are provided in following sections.

2.2.1 Sludge Preparation for Radioactive Simulant Testing

A simulated (acidic) PUREX waste solution was prepared generally targeting the compositional bases selected by Eibling for nonradioactive simulated sludge heels based on an analysis of sludge from Tank 8F.[15] Secondary and minor sludge components in the Eibling recipe were excluded. Actinide materials, including uranium, neptunium, plutonium, and americium were added to the simulated waste. The concentrations of uranium and plutonium were based on the analysis of archived SRS sludge samples, also from Tank 8F.[16] The target concentrations of neptunium and americium were based on the masses required to provide sufficient activity in the sludge for analysis which were successfully used by Rudisill et al. in previous solubility studies.[10] The target composition of the acidic simulated waste solution based on the recipe is provided in Table 2-3.

Table 2-3. Target Composition of Simulated Acidic Radioactive PUREX Waste Solution.

Element	PUREX HAW
	(g/L)
U	66
Np	0.65
Pu	0.075
Am	0.055
Fe	111
Al	41
Ni	13
Mn	12

The concentration of weapons grade plutonium given in Table 2-3 would likely not provide sufficient activity to measure the plutonium concentration in the solubility samples. Therefore, an aliquot of a solution containing plutonium-238 was added to the surrogate waste solution to increase the alpha activity to nominally 10^9 dpm/mL. The composition of the neptunium, weapons grade plutonium, americium, and plutonium-238 solutions used to prepare the acidic PUREX waste solution are given in Table 2-4.

Table 2-4. Actinide Stock Solutions Used to Prepare Acidic Radioactive PUREX Simulant and Resulting Solution Concentrations.

	Actinide Stock Solutions		Acidic PUREX Waste Solution(1)	
	Concentration	Volume Added	Concentration	Concentration
		(mL)	(g/L)	(dpm/mL)
^{237}Np Solution		1.5		
^{237}Np	48.5 g/L		7.28E-01	1.13E+06
^{238}Pu	0.18 g/L		2.69E-03	1.03E+08
HNO_3	1.5 M			
$^{239/240}$Pu Solution		0.2		
$^{239/240}$Pu	39.8 g/L		7.95E-02	1.27E+07
HNO_3	0.48 M			
^{241}Am Solution		4.5		
^{241}Am	1.20 g/L		5.40E-02	4.12E+08
HNO_3	1.57 M			
^{238}Pu Solution		9.0		
^{238}Pu	0.26 g/L		2.36E-02	9.00E+08
HNO_3	1.5 M			

(1) Concentration based on 100 mL total volume

The PUREX waste solution was prepared by dissolving nominally the target amount of each non-radioactive starting material (Table 2-5) in approximately 50 mL of 0.5 M nitric acid. The solution was transferred to a 100 mL volumetric flask which was diluted to volume with 0.5 M nitric acid. One-half of the iron was added as hematite (Fe_2O_3) and one-half of the aluminum was added as boehmite (AlOOH). The required masses of hematite and boehmite were transferred to a 250 mL plastic bottle. The solution containing the dissolved iron, aluminum, nickel, and manganese was then transferred to the bottle, which was subsequently placed in a radioactive glovebox for the addition of the actinide materials. The neptunium, weapons grade plutonium, americium, and plutonium-238 were added as the solutions described in Table 2-4 and at the concentrations indicated in the table (based on a 100 mL total solution volume). The uranium was added directly to the simulated waste solution as uranyl nitrate hexahydrate.

Table 2-5. Starting Reagents Used to Prepare Acidic Radioactive PUREX Waste Slurry.

Waste Component	Starting Material
Fe (soluble)	$Fe(NO_3)_3 \cdot 9H2O$
Fe (insoluble)	Fe_2O_3
Al (soluble)	$Al(NO_3)_3 \cdot 9H_2O$
Al (insoluble)	AlO(OH)
Ni	$Ni(NO_3)_2 \cdot 6H_2O$
Mn	$Mn(NO_3)_2 \cdot 5H2O$
U	$UO_2(NO_3)_2 \cdot 6H_2O$

The PUREX waste solution was neutralized using 50.5 wt % (19.4 M) sodium hydroxide. A magnetic stirring bar was added to the plastic bottle to agitate the precipitate slurry during neutralization. The moles of sodium hydroxide required to neutralize the waste solution were calculated based on the actual amount of each element added to the simulant and the stoichiometry provided in Equations 1-9.

$$Fe(NO_3)_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaNO_3 \quad (1)$$

$$Al(NO_3)_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaNO_3 \quad (2)$$

$$Ni(NO_3)_2 + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3 \quad (3)$$

$$Mn(NO_3)_2 + 2NaOH \rightarrow Mn(OH)_2 + 2NaNO_3 \quad (4)$$

$$2UO_2(NO_3)_2 + 6NaOH \rightarrow Na_2U_2O_7 + 4NaNO_3 + 3H_2O \quad (5)$$

$$Np(NO_3)_4 + 4NaOH \rightarrow Np(OH)_4 + 4NaNO_3 \quad (6)$$

$$Pu(NO_3)_4 + 4NaOH \rightarrow Pu(OH)_4 + 4NaNO_3 \quad (7)$$

$$Am(NO_3)_3 + 3NaOH \rightarrow Am(OH)_3 + 3NaNO_3 \quad (8)$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \quad (9)$$

The total volume of the neutralized solution (168 mL) was calculated as the sum of the initial volume (115 mL), the volume of 19.4 M sodium hydroxide added (51 mL), and the water produced during neutralization (2 mL). Sufficient sodium hydroxide was added to achieve a 1.2 M excess. Following neutralization, the bottle was approximately three-quarters full of a thick precipitated slurry. The supernate layer on top of the sludge was only a few millimeters thick. Little settling of the solids occurred following neutralization.

2.2.2 Radioactive Sludge Simulant Pretreatment Processes

Prior to performing the solubility experiments, the sludge produced from the simulated PUREX waste solution was treated to simulate current and proposed waste tank cleaning processes. A flowchart describing the treatment processes and the solubility experiments is provided in Figure 2-2. The original plans for this study proposed a series of 12 solubility experiments. Prior to starting work, the scope of the study was reduced due to availability of funding; however, the experiment numbers in Figure 2-2 are still consistent with the original work planning documentation.[13]

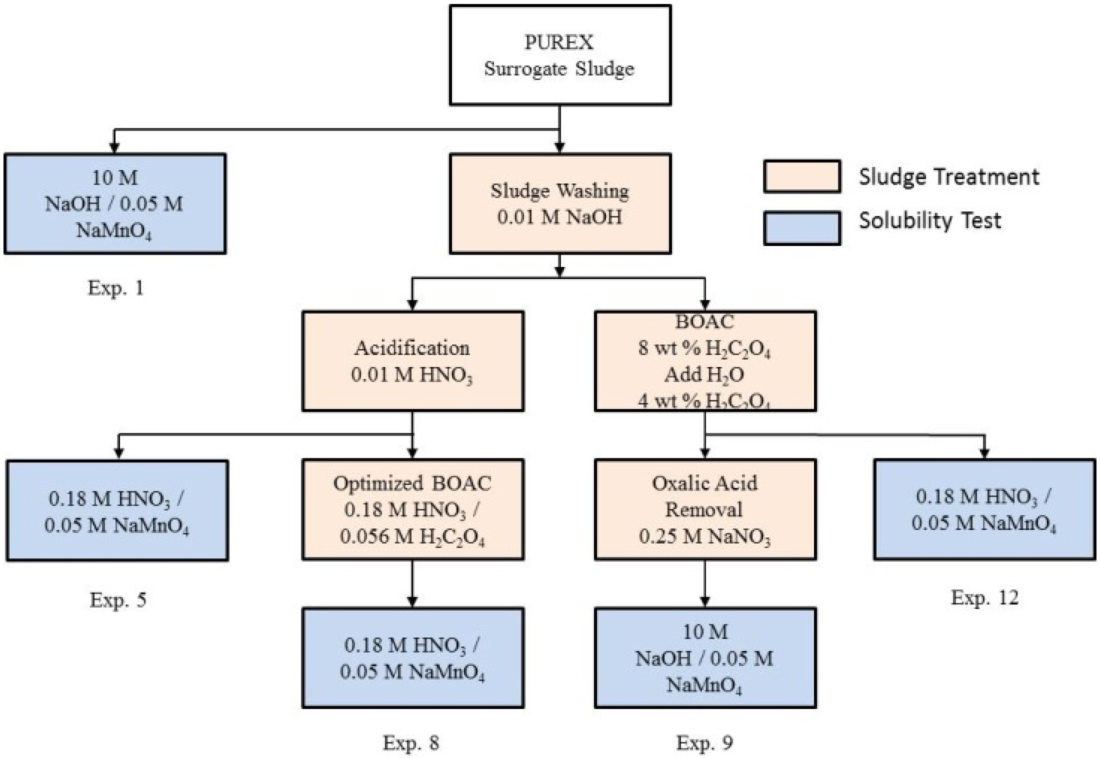


Figure 2-2. Radioactive Simulant Solubility Experiments using PUREX HLW Sludge.

2.2.2.1 Radioactive Sludge Simulant Washing

The neutralized PUREX waste simulant was allowed to age for one week prior to washing the sludge with 0.01 M sodium hydroxide in preparation for the acidification/optimized BOAC and traditional BOAC treatment processes. Prior to sludge washing, approximately 20 mL of the neutralized sludge were transferred (while stirring) using a transfer pipette into a 60 mL plastic bottle for use in solubility Experiment 1. A 300 mL aliquot of 0.01 M sodium hydroxide was used to wash the remaining sludge from the 250 mL plastic bottle into a 1 L beaker. Practically all of the sludge was removed from the bottle. The sludge was stirred for approximately 2 h. The beaker was covered with Parafilm™ to prevent evaporation. The sludge was inspected 10 days later. Following this time, the sludge had separated into layers of approximately equal volumes containing the solids and clear supernate. A 200 mL aliquot of the supernate was removed from the 1 L beaker. Initially a large transfer pipette (3-5 mL capacity) was used to remove the supernate until the suction of the supernate began to disturb the solids. At this point in the transfer, a small transfer pipette (1-2 mL capacity) was used to transfer the remaining 40-50 mL. The volume of supernate was measured using a graduated cylinder. Once the transfer was complete, the supernate was transferred to a 1 L plastic bottle.

Following the supernate removal, a second 300 mL aliquot of 0.01 M sodium hydroxide was added to the 1 L beaker. The contents of the beaker were stirred for approximately 2 h and the beaker was covered with Parafilm™ to prevent evaporation. The sludge was inspected the following day. The contents of the beaker had separated into a layer containing solids and a layer of clear supernate. A 300 mL aliquot of the supernate was removed from the 1 L beaker using the same procedure as described for the first wash cycle. The supernate was combined with the supernate removed during the first wash cycle in the 1 L plastic bottle. The sludge washing including the estimated final sodium hydroxide concentration is summarized in Table 2-6.

Table 2-6. Precipitated Radioactive Sludge Simulant Slurry Washing Summary.

Wash Step	Initial Volume (mL)	Volume Removed (mL)	Remaining Volume (mL)	Wash Volume (mL)	Total Volume (mL)	NaOH Conc. (M)
1	168	0	168	300	468	0.44
2	468	200	268	300	568	0.21

2.2.2.2 Radioactive Sludge Simulant Acidification

Prior to performing the optimized BOAC treatment, our plan was to acidify an aliquot of the washed sludge to a pH of nominally 2 to prevent partial neutralization of the acid used in the treatment process. Approximately 125 mL of the washed sludge was transferred (while stirring) to a 600 mL beaker using a large transfer pipette. The volume of sludge was approximated using a mark placed on the beaker when 125 mL of water were placed in the beaker. The sludge was initially acidified using 0.3 M nitric acid. The acid was added slowly to the beaker using a transfer pipette while stirring. The volume of 0.3 M nitric acid required to neutralize 125 mL of 0.21 M sodium hydroxide is 87.5 mL. Approximately 81 mL of acid were added. The pH was periodically checked using pH paper during the acidification; however, the pH remained strongly basic. Rather than over-shoot the desired pH of 2 during the acidification, the addition of 0.3 M nitric acid was stopped and a 300 mL aliquot of 0.01 M nitric acid was added to the beaker. The beaker was stirred for 1 h and covered with Parafilm™ to prevent evaporation.

When inspected on the following day, the sludge had settled leaving a clear supernate with a pH of 5. A 340 mL aliquot of the supernate was removed from the beaker using the same technique as used for removing the supernate during sludge washing. Although the sludge was highly colored (due to the insoluble hematite), the pH could be measured due to the wicking action of the solution when the pH paper was held in the slurry. An additional 19 mL of 0.3 M nitric acid was added to beaker while periodically checking the pH. The paper indicated the pH was between 4 and 5. An additional 80 mL of 0.3 M nitric acid was subsequently added to the beaker. After the addition of the acid, the pH was 3. A 300 mL aliquot of 0.01 M nitric acid was then added to the beaker. The beaker was stirred for approximately 4 h and was covered with Parafilm™ to prevent evaporation.

The acidified sludge was inspected the following day with the intent of removing excess supernate, adjusting the pH closer to a value of 2, and washing a third time with 0.01 M nitric acid; however, the sludge had not settled. The pH of a very thin layer of supernate was approximately 4. The suspension of the solids was likely caused by the peptization of the amorphous sludge. When salt concentrations are low in solution, flocculent solids are easily dispersed. The solids do not agglomerate due to repulsion of like charge on the metal ions and instead remain suspended in solutions.[17] It may be possible to increase the suspension of solids in SRS waste tanks by lowering the ionic strength of the supernate and increasing the suspension of the solids by peptization. The inability to reduce the pH of the supernate during the acidification of the sludge was likely due to the dissolution of boehmite which buffered the solution in a pH range of 3 to 4.

Two experiments were performed to determine if an increase in the ionic strength of the slurry or the addition of the optimized BOAC solution (0.18 M nitric acid/0.056 M oxalic acid) would facilitate settling of the solids. In the first experiment, 25 mL of sludge were added to a glass jar using a transfer pipette. To increase the ionic strength, 0.53 g of sodium nitrate were added to the jar resulting in a concentration of 0.25 M based on a total volume of 25 mL. In the second experiment, 10 mL of sludge were added to a second glass jar. A 33 mL aliquot of a 0.22 M nitric acid/0.069 M oxalic acid solution was then added to the jar. The concentrations of the nitric and oxalic acids in the solution were based on a sludge to acid volume ratio of 18:1 and achieving final concentrations of 0.18 M and 0.056 M, respectively, after accounting for the excess volume in the acidified sludge. The two jars were left undisturbed until the following day. When inspected, the solids in both jars had settled to the bottom. Based on these results, the decision was made to proceed with the optimized BOAC using a 0.22 M nitric acid solution containing 0.069 M oxalic acid for the first sludge contact. The observation of reversible peptization is important with regard to the potential application of this method for sludge suspension and removal from the tanks. Based on the results, increasing the ionic strength of the slurry results in the formation of a sludge material which settles more easily. Sludge dewatering operations (decantation) in the tank farm are dependent upon the settling of the sludge solids.

2.2.2.3 Radioactive Sludge Simulant Optimized Oxalic Acid Treatment

The baseline optimized BOAC process for this study utilized an 18:1 volume ratio (of sludge to acid) and a contact solution containing 0.18 M nitric acid and 0.056 M oxalic acid. Three, one week contacts were planned with periodic heating at 50 °C while agitating the acidic sludge mixture. To perform the optimized BOAC treatment, a 308 mL aliquot of the acidified sludge was transferred to a 2 L beaker. The sludge was initially transferred to a 250 mL graduated cylinder using a large transfer pipette. The beaker containing the remaining sludge was covered with Parafilm™ until the sludge was used in solubility Experiment 5 (Figure 2-2). Once the desired volume was obtained, a 1022 mL aliquot of 0.22 M nitric acid/0.069 M oxalic acid solution was added to the beaker. The volume of the acidic solution was measured using the 250 mL graduated cylinder and was used to wash the remaining sludge from the cylinder. The volume and concentration of the acidic solution were based on the 18:1 sludge to solution volume ratio, a planned (concentrated) sludge volume of 70 mL, and the dilution of the nitric and oxalic acid concentrations to the desired values (0.18 M and 0.056 M, respectively) by the excess volume in the acidified sludge. The level of the slurry in the beaker was marked with a pen so water could be added to the beaker to account for evaporation losses if necessary.

The sludge remained in contact with the nitric/oxalic acid solution for 19 days. On days 1, 2, and 19, the beaker containing the slurry was heated using a hot plate at 50 °C while stirring for 6, 7, and 7 h, respectively. The temperature of the hot plate was controlled using a thermocouple placed in the sludge. A watch glass was placed on top of the beaker to slow evaporation losses. To prepare for the second cycle of the optimized BOAC, a 1260 mL aliquot of supernate was removed from the beaker. The volume of supernate removed was equal to the volume of 0.18 M nitric acid/0.056 M oxalic acid which would have been added to a 70 mL aliquot of (concentrated) acidified sludge. The supernate was removed using a large transfer pipette and collected in a plastic bottle. For the second cycle of the optimized BOAC, a 1260 mL aliquot of 0.18 M nitric acid/0.056 M oxalic acid was added to the sludge in the 2 L beaker. The volume level was marked with a pen on the beaker so water could be added to account for evaporation losses. The second cycle of the optimized BOAC was performed over an eight day period. The heat treatments used for the second BOAC cycle are summarized in Table 2-7.

Table 2-7. Heat Treatments During Second Cycle of Optimized BOAC During Radioactive Simulant Testing.

Day	Temperature	Stirring	Time	Comments
	(° C)	(rpm)	(h)	
1	50	200	5	
2	50	200	10	
3	50	200	10	
4	50	200	9.75	Added 10-15 mL water
5	50	200	10	

Following completion of the second cycle of the optimized BOAC, a decision was made to forego the third cycle due to schedule and funding constraints. A 902 mL aliquot of supernate was removed from the beaker using a glass trap and vacuum pump. When the level of solution had dropped almost to the level of the solids, a large transfer pipette was used to remove additional supernate. The supernate removed from the beaker was combined with the supernate removed during the first cycle of the BOAC treatment. The beaker was covered with Parafilm™ until the sludge was used in solubility Experiment 8 (Figure 2-2).

2.2.2.4 Radioactive Sludge Simulant BOAC Treatment

The baseline BOAC process for this study utilized a 9:1 volume ratio (of sludge to acid) in the initial contact and a solution containing 8 wt % (0.92 M) oxalic acid. Following one day of a week-long contact period, dilution of the oxalic acid from 8 wt % to 4 wt % (0.46 M) was planned. Three, one week contacts were planned with periodic heating at 50 °C while agitating the acidic sludge mixture. To perform the BOAC treatment, 75 mL of the washed sludge were transferred to a 2 L beaker. The sludge was initially transferred to a 250 mL graduated cylinder using a large transfer pipette. Once the desired volume was transferred to the beaker, a 675 mL aliquot of 8 wt % (0.92 M) oxalic acid was added. The volume of oxalic acid was measured using the 250 mL graduated cylinder and was used to wash the remaining sludge from the cylinder. The level of the slurry in the beaker was marked using a pen so water could be added to account for evaporation losses if necessary.

The sludge remained in contact with oxalic acid for a total of 19 days at the planned phase ratio. On the initial day of the contact period, the beaker containing the slurry was heated using a hot plate at 50 °C while stirring for 6 h. The temperature of the hot plate was controlled using a thermocouple placed in the sludge. A watch glass was placed on top of the beaker to slow evaporation losses. On the following day, a 675 mL aliquot of deionized water was added to the beaker to dilute the oxalic acid to 4 wt % (0.46 M). The heating cycle was then repeated for an additional 7 h. On the final day of the contact period, the acidic sludge was heated and stirred for 7 h. To prepare for the second cycle of the BOAC, removal of nominally 1350 mL of supernate were planned. After removing the initial 500 mL of solution, the beaker was bumped which caused the sludge to re-suspend in the supernate. No additional supernate could be removed without the entrainment of solids. The transfer of additional supernate was delayed for six days when the remaining volume was removed from the beaker. A total of 1348 mL of supernate were removed and stored in a plastic bottle.

During the second cycle of the BOAC treatment, the sludge to oxalic acid volume ratio was reduced to 3:1 requiring the addition of a 225 mL aliquot of 8 wt % (0.92 M) oxalic acid to the beaker. The volume of oxalic acid was based on the initial volume of sludge (i.e., 75 mL). The dilution of the oxalic acid from 8 wt % to 4 wt % (0.46 M) was performed on the second day of the contact period. The volume level was marked with a pen on the beaker so water could be added to account for evaporation losses. The entire cycle was completed over an eight day period. The heat treatments used for the second BOAC treatment are summarized in Table 2-8.

Table 2-8. Heat Treatments During Second Cycle of BOAC Treatment During Radioactive Simulant Testing.

Day	Temperature (° C)	Stirring (rpm)	Time (h)	Comments
1	50	200	5	
2	50	200	10	Added 225 mL deionized water
3	50	200	10	
4	50	200	9.75	Added 10-15 mL deionized water
5	50	200	10	

Following completion of the second cycle of the BOAC, a decision was made to forego the third cycle due to schedule and funding constraints. A 435 mL aliquot of supernate was removed from the beaker using a glass trap and vacuum pump. An additional 34 mL aliquot was subsequently removed from the beaker using a large transfer pipette. The beaker was covered with Parafilm™ until a portion of the sludge was washed to remove oxalic acid and a second portion was used in solubility Experiment 12 (Figure 2-2).

2.2.2.5 Oxalic Acid Removal

The original plans for the sludge following the BOAC included washing a portion of the sludge with 0.01 M sodium hydroxide to neutralize and remove a majority of the oxalic acid in preparation for an actinide solubility experiment (Experiment 9) using a 10 M sodium hydroxide solution containing 0.05 M sodium permanganate. However, we were concerned that the low ionic strength of the supernate could lead to peptization of solids and prevent settling similar to the phenomenon that occurred during acidification of the sludge (see Section 2.2.2.2). Therefore, the oxalic acid was washed from a portion of the sludge using 0.25 M sodium nitrate. Our intent was to transfer nominally 50 mL of the slurry remaining from the BOAC to another beaker for oxalic acid removal. However, only 16 mL of sludge could be transferred to a graduated cylinder for use in the treatment process. The sludge was slurried back into the beaker using 34 mL of the BOAC supernate. A 30 mL aliquot of the slurry was then transferred to a 2 L beaker for the oxalic acid removal process leaving an estimated 30 mL of the slurry in the BOAC treatment beaker for use in solubility Experiment 12. The beaker was covered with Parafilm™ until the sludge was used in the solubility experiment.

The 30 mL of sludge treated by the BOAC process was washed with 900 mL of 0.25 M sodium nitrate solution. For a 30 mL aliquot of 0.46 M oxalic acid, 900 mL of wash solution would reduce the oxalate concentration to less than 0.015 M. The resulting slurry was stirred for approximately 2 h, covered with a watch glass, and allowed to settle overnight. The following day, an 885 mL aliquot of supernate was removed from the beaker using a combination of the vacuum pump and glass trap and a large transfer pipette. The solution was transferred to a plastic bottle for storage until analysis. The beaker containing the remaining sludge was covered with Parafilm™ until it was used in solubility Experiment 8.

2.2.3 Radioactive Sludge Simulant Solubility Experiments

2.2.3.1 Preparation for Radioactive Simulant Solubility Experiments

Sludge samples from the treatment processes were contacted with either acidic (0.18 M nitric acid) or basic (10 M sodium hydroxide) solutions containing 0.05 M sodium permanganate to evaluate the potential for increasing the solubility of transuranic actinides in residual waste tank sludge. The pathway through the sludge treatment processes leading to each solubility experiment is shown in Figure 2-2.

Two hundred milliliter stock solutions containing 0.05 M sodium permanganate in 0.18 M nitric acid and 10 M sodium hydroxide, respectively, were prepared by dissolving the permanganate in nitric acid and sodium hydroxide solutions of the desired concentration. The 0.18 M nitric acid was prepared by diluting concentrated (15.7 M) nitric acid with deionized water. A 10 M sodium hydroxide solution was prepared by diluting 50 wt % (19.4 M) sodium hydroxide with deionized water. To prepare the acidic and basic sodium permanganate solutions, the target mass of sodium permanganate hydrate was transferred to 400 mL beakers. The permanganate was dissolved in nominally 150 mL of the 0.18 M nitric acid and 10 M sodium hydroxide solutions, respectively, by stirring and heating at 50-60 °C. The concentrated solutions were transferred to 200 mL volumetric flasks which were diluted to volume with the appropriate solution.

The solubility experiments were performed using 50 mL (plastic) centrifuge tubes. To agitate the tubes, a Thermo Scientific Labquake™ Tube Shaker was placed in a radioactive SRNL glovebox. Prior to beginning the solubility experiments, it was necessary to re-suspend the sludge remaining from the BOAC and oxalic acid removal treatment processes (for solubility Experiments 9 and 12, respectively). To re-suspend the sludges, 70 mL of the supernate removed during the treatment processes were added back to the beakers. The beakers were stirred and the sludges were easily re-suspended.

For each experiment a 3 mL aliquot of the (sludge) slurry was added to a centrifuge tube. Initially, a 3 mL aliquot of water was added to the tube and the level marked with a pen. Sludge was then added to the tube using a transfer pipette until the mark was reached. The volume of the acidic or basic sodium permanganate solution was based on a 1:12 volume ratio; therefore 36 mL of the appropriate solution were added to each centrifuge tube. The volume of permanganate solution was measured using a 50 mL graduated cylinder. After filling, the centrifuge tubes were placed on the tube shaker. The motion of the shaker was set to slowly rotate the tubes with stops every one-eighth turn where the tubes were shaken.

2.2.3.2 Sampling Radioactive Simulant Solubility Experiments

Samples of the supernate were periodically removed from the centrifuge tubes for neptunium, plutonium, and americium analyses. The samples were taken at nominally 72, 168, and 360 h (3, 7, and 15 days). Initially the centrifuge tubes were removed from the tube shaker 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 nitric acid. 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.

To prepare the samples for analysis, we targeted a nitric acid concentration of 1 to 2 M in the filtered solutions. Five molar nitric acid was used to acidify the samples. Neutralization of the samples containing 10 M sodium hydroxide was based on Equation 10. Nitric acid was also added to the permanganate solution containing 0.18 M nitric acid to obtain a final free acid concentration in the 1 to 2 M range.

$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O \tag{10}$$

The 5 M nitric acid (Table 2-9) was added to 1 or 2 dram sample vials using a 100 to 1000-µL Rainin EDP3-Plus electronic pipette prior to placing the vials in the glovebox where the solubility experiments were performed.

Table 2-9. Volume of Nitric Acid Required to Acidify Solubility Samples During Radioactive Simulant Testing.

Experiment	Composition of Solution	Vial Size	Vol. 5 M HNO_3
		(dram)	(mL)
1	10 M NaOH/0.05 M $NaMnO_4$	2	3.0
5	0.18 M HNO_3/0.05 M $NaMnO_4$	1	0.5
8	0.18 M HNO_3/0.05 M $NaMnO_4$	1	0.5
9	10 M NaOH/0.05 M $NaMnO_4$	2	3.0
12	0.18 M HNO_3/0.05 M $NaMnO_4$	1	0.5

To complete the sample preparation, a 1-mL aliquot of the filtered solutions was transferred to the prepared sample vials using a Rainin FSL-1000 fixed volume pipette. After the sampling was complete, the centrifuge tubes were returned to the tube shakers for continued mixing. The solutions were analyzed for plutonium-238, neptunium-237 and americium-241 by gamma pulse height analysis (GPHA).

The solutions removed during the sludge treatment processes (Figure 2-2) were sampled and analyzed to aid in interrupting the solubility data. To prepare the samples for analysis, the solutions were filtered and acidified with nitric acid. The samples were removed from the storage bottles using a disposable 10-mL plastic syringe. A 2-3 mL sample of solution was removed from the bottle using a 4-in piece of Teflon® tubing attached to the syringe. The tubing was removed and the syringe was fitted with a disposable 0.02-µm filter disk. The solution was expelled from the syringe into a 1 dram vial.

The samples were prepared for analysis by targeting a nitric acid concentration of 1-2 M in the filtered solution. Five molar nitric acid was used to acidify the samples. Neutralization of the sludge wash solution was based on the estimated sodium hydroxide concentration given in Table 2-6. (i.e., 0.21 M) and Equation 10. The 5 M nitric acid (Table 2-10) was added to 1 dram vials using a 100 to 1000-µL Rainin EDP3-Plus electronic pipette prior to placing the vials in the glovebox. The solutions were analyzed for plutonium-238, neptunium-237 and americium-241 by GPHA.

Table 2-10. Volume of Nitric Acid Required to Acidify Sludge Treatment Solution Samples During Radioactive Simulant Testing.

Solution Sample	Vial Size	Vol. 5 M HNO_3
	(dram)	(mL)
Sludge Wash	1	0.5
Acidification	1	0.5
BOAC	1	0.5
Optimized BOAC	1	0.5
Oxalic Acid Removal	1	0.5

3.0 Results and Discussion

3.1 Non-radioactive Simulant Testing

Non-radioactive PUREX sludge heel simulant and pure metal oxide/hydroxide reagent solubility tests were conducted in dilute nitric acid, concentrated oxalic acid, and dilute nitric/oxalic acid mixtures. The sludge simulant sample was washed with 0.01 M NaOH prior to testing to dilute soluble salt concentrations in the supernatant solution. For pure nitric acid and nitric/oxalic acid blend tests, the samples (sludge and pure reagents) were pre-acidified with 0.01 M HNO_3 prior to testing. Solution pH data for each sample following pre-acidification and at the conclusion of each of the three acidic cleaning reagent contact cycles are provided in Table 3-1 along with visual observations. Photographs of the sample test bottles following pre-acidification and at the conclusion of the third acidic cleaning reagent contact cycle are provided in Figures 3-1 through 3-5. Photographs of residual solids isolated following the third contact cycle are provided in Figure 3-6.

Table 3-1. Measured Solution pH Data and Observations Following Sample Pre-Acidification and Each Succeeding Acid Contact Cycle – Non Radioactive Simulant Testing.

	Pre-Acidification	**Cleaning Reagent Contact Cycle**				
	0.01 M HNO_3	**1**	**2**	**3**	**Cleaning Reagent**	**Observations After Cycle 3**
PUREX #1	6.1	1.4	1.1	1.1	0.18 M HNO_3/ 0.056 M $H_2C_2O_4$	yellow solution, brown solids
PUREX #2	6.1	2.1	1.1	1.1	0.18 M HNO_3	little indication of dissolution
PUREX #3	---	0.8	0.8	0.8	0.92 M $H_2C_2O_4$	yellow solution, green solids
$Al(OH)_3/Fe_2O_3$ #1	2.1	1.2	1.1	1.1	0.18 M HNO_3/ 0.056 M $H_2C_2O_4$	yellow solution, brown solids
$Al(OH)_3/Fe_2O_3$ #2	2.1*	1.0	1.1	1.1	0.18 M HNO_3	little indication of dissolution
$Al(OH)_3/Fe_2O_3$ #3	---	0.6	0.7	0.8	0.92 M $H_2C_2O_4$	solids dissolved by Cycle 3, dilute yellow solution
$Ni(OH)_2$ #1	6.6	4.7	1.0	1.0	0.18 M HNO_3/ 0.056 M $H_2C_2O_4$	more green solids than initial
$Ni(OH)_2$ #2	6.6*	5.1	6.1	1.1	0.18 M HNO_3	solids dissolved by Cycle 3, green solution
$Ni(OH)_2$ #3	---	0.7	0.8	0.8	0.92 M $H_2C_2O_4$	more green solids than initial
MnO #1	2.8	5.2	5.8	1.3	0.18 M HNO_3/ 0.056 M $H_2C_2O_4$	black solids turned white and nearly all dissolved
MnO #2	2.8*	4.8	4.1	1.3	0.18 M HNO_3	black solids turned brown but did not dissolve
MnO #3	---	0.7	0.8	0.9	0.92 M $H_2C_2O_4$	black solids turned white but did not dissolve
MnO_2 #1	2.1	1.1	1.3	1.2	0.18 M HNO_3/ 0.056 M $H_2C_2O_4$	no color change, little indication of dissolution
MnO_2 #2	2.1*	0.8	1.0	1.1	0.18 M HNO_3	no color change, little indication of dissolution
MnO_2 #3	---	0.8	0.9	1.0	0.92 M $H_2C_2O_4$	black solids changed to white

*not measured, assumed same as sample #1

Figure 3-1. Photographs of the Gibbsite/Hematite Reagent Test Bottles After Acidification (left) and Following Contact Cycle 3 – Non-Radioactive Simulant Testing.

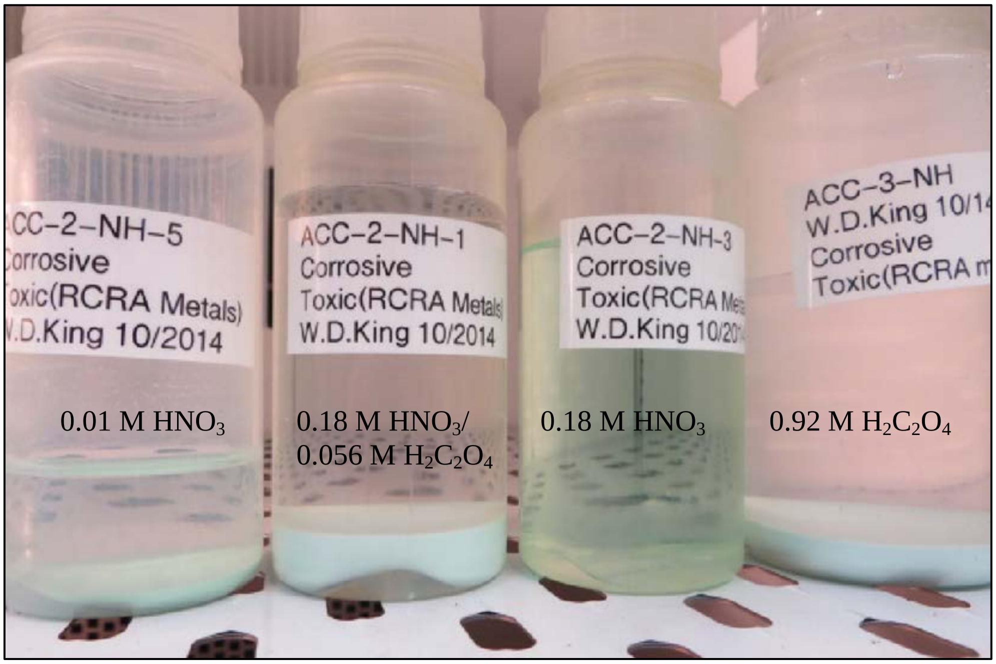


Figure 3-2. Photographs of the Nickel Hydroxide Reagent Test Bottles After Acidification (left) and Following Contact Cycle 3 Non-Radioactive Simulant Testing.

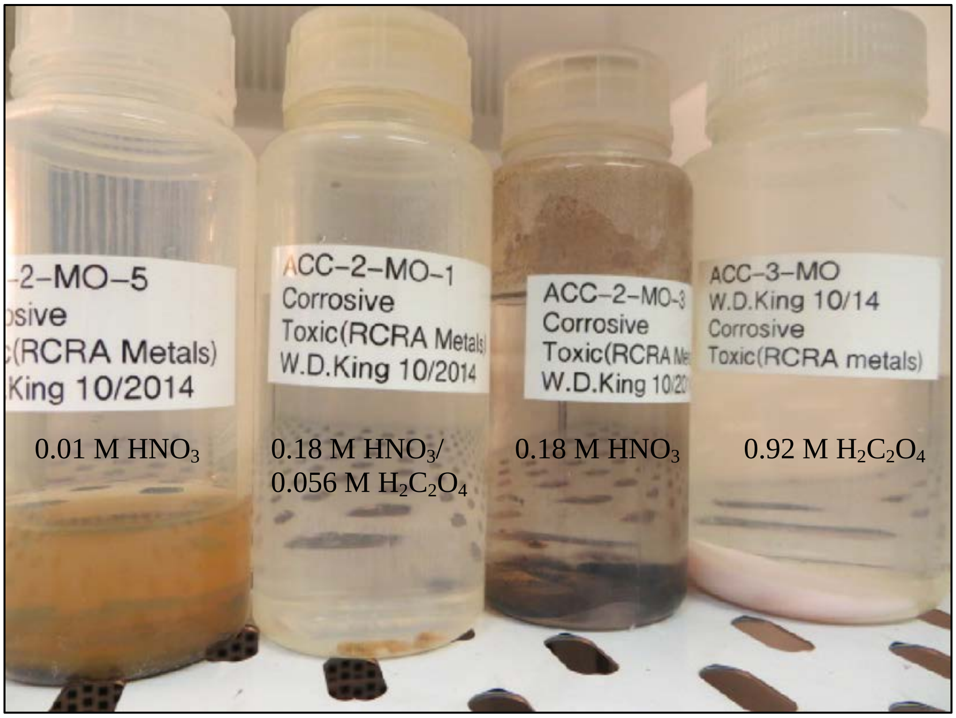


Figure 3-3. Photographs of the Manganese Oxide (MnO) Reagent Test Bottles After Acidification (left) and Following Contact Cycle 3 – Non-Radioactive Simulant Testing.

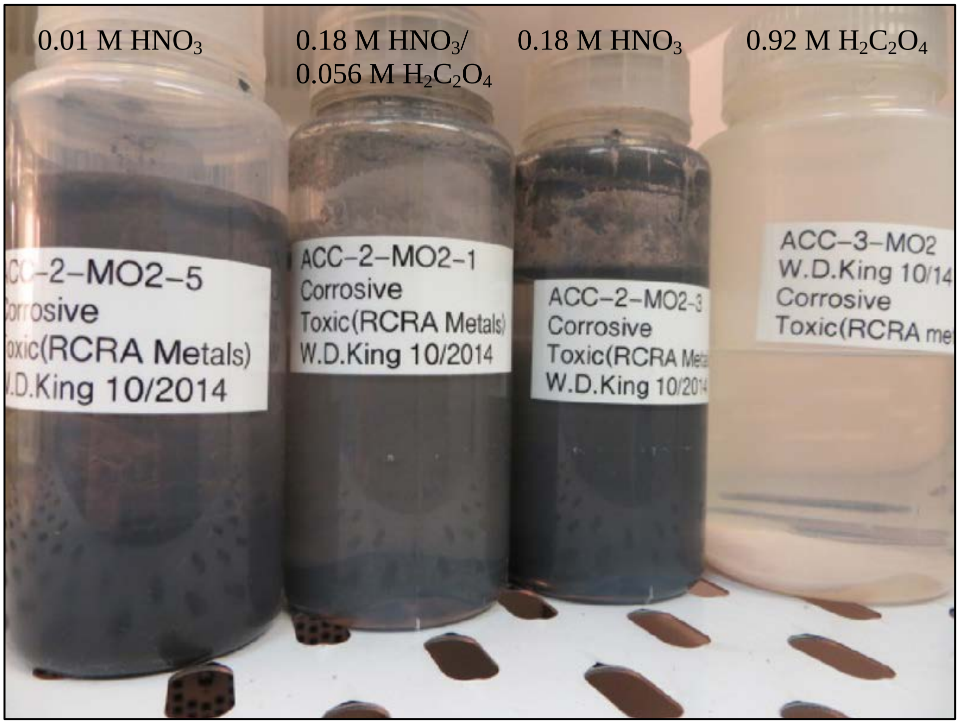


Figure 3-4. Photographs of the Manganese Dioxide (MnO_2) Reagent Test Bottles After Acidification (left) and Following Contact Cycle 3 – Non-Radioactive Simulant Testing.

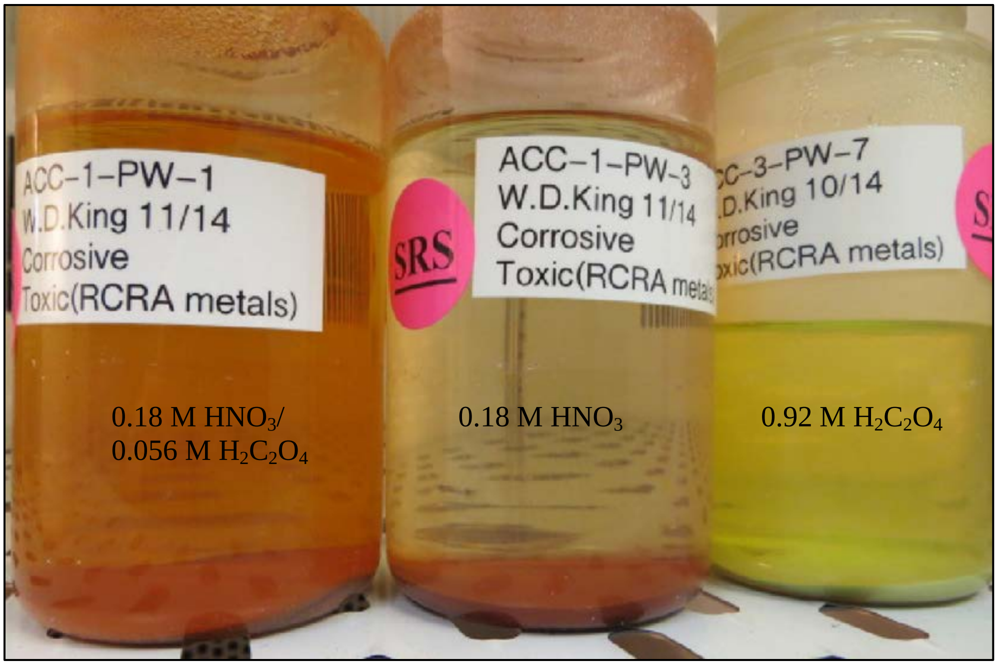


Figure 3-5. Photographs of the PUREX Simulant Test Bottles Following Contact Cycle 3 – Non-Radioactive Simulant Testing.

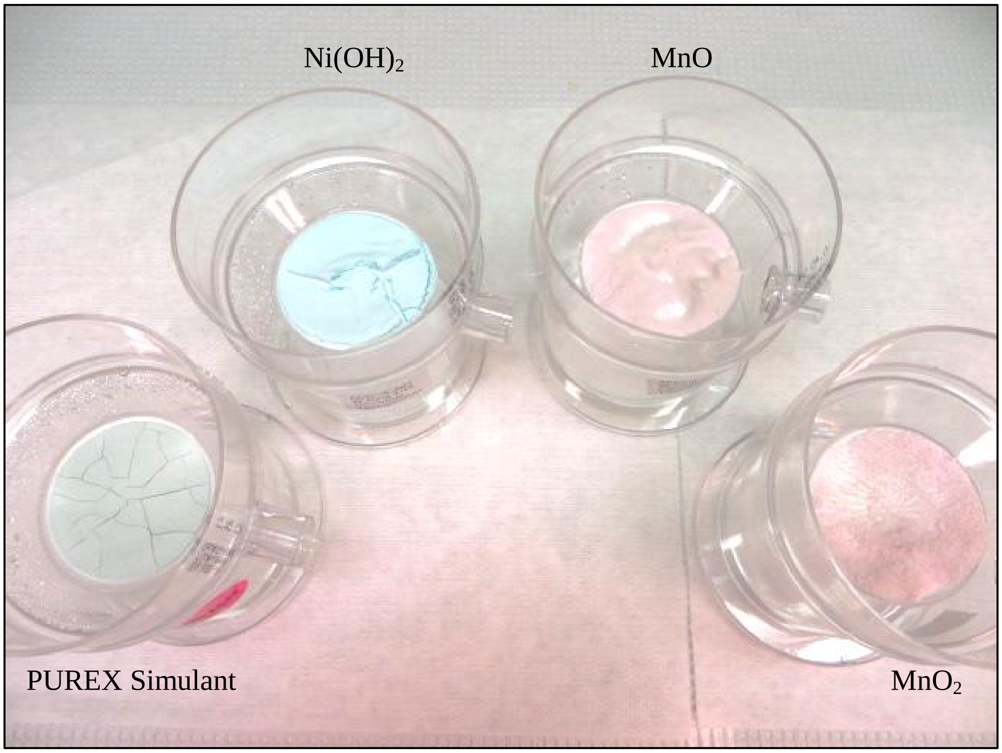


Figure 3-6. Photographs of the Residual Solids Isolated Following 0.92 M Oxalic Acid Contact Cycle 3 (original reagents indicated) – Non-Radioactive Simulant Testing.

Based on the pH measurements during pre-acidification (Table 3-1), both the nickel hydroxide reagent and PUREX sludge heel simulant react with and partially neutralize dilute (0.01 M) nitric acid. During pre-acidification, the nickel hydroxide reagent also appeared to partially dissolve, based on the light green color of the solution (Figure 3-2, left bottle). There was also evidence of reaction of manganese (II) oxide reagent with nitric acid as indicated by reagent color changes (Figure 3-3, left bottle) and a slightly elevated (approaching pH 3) solution pH during pre-acidification.

Solubility tests were conducted in 0.18 M HNO_3 because it was anticipated that some HLW sludge components (such as gibbsite, nickel hydroxide, and some actinide species) would be soluble in nitric acid. Heel acidification without the addition of a complexant such as oxalate may also assist in mechanical sludge removal by promoting partial sludge dissolution and attrition of larger sludge particles and agglomerates. Nitric acid should also be useful for heel pretreatment prior to oxalic acid contact. Nitric/oxalic acid blends were evaluated due to the known effectiveness of oxalic acid at dissolving iron and other sludge components and the fact that the addition of a supplementary acid like nitric acid serves to minimize the oxalic acid required for dissolution. Tests were also conducted with concentrated oxalic acid (initial concentration: 8 wt. %, 0.92 M with subsequent dilution to 2-4 wt. % $H_2C_2O_4$) following prototypical cleaning methodologies, primarily as a reference for comparison to evaluate the performance of the other cleaning reagents.

As was observed during sample pre-acidification in 0.01 M HNO_3, there was indication of reaction and dissolution of the nickel hydroxide and the manganese (II) oxide reagents in 0.18 M HNO_3. With nickel hydroxide reagent, the solution pH remained high (5-6) for the first and second acid contact cycles, then quickly dropped to near 1 for the third cycle (Table 3-1) and no solid remained at this point (Figure 3-2, 2nd bottle from right). Similarly, with MnO reagent, the solution pH remained elevated (4-5) for the first and second acid contact cycles then dropped to near 1.5 for the third cycle (Table 3-1) and significant solids had dissolved (Figure 3-3, 2nd bottle from right). There was little visual indication of reaction of the other pure reagents (Fe_2O_3, $Al(OH)_3$, and MnO_2) and PUREX simulant with 0.18 M HNO_3. Acidification of the PUREX simulant appeared complete following the first acid contact cycle (solution pH 2.1). The simulant slurry pH in both the second and third nitric acid contact cycles was 1.1 (theoretical reagent pH ~0.8). The solution color after the third contact cycle with PUREX simulant was slightly yellow (Figure 3-5, middle bottle).

With the 0.18 M nitric acid/0.056 M oxalic acid mixture, visual observations and pH measurements indicated reaction, but little dissolution of the nickel hydroxide reagent. A pH near 5 was observed for the first contact cycle with lower pH values (near 1) for the remaining two cycles (Table 3-1). In addition, the appearance of the solids changed to a lighter green color and the volume of the solids increased (Figure 3-2, second bottle from left). The MnO reagent also appeared to react with the nitric/oxalic acid mixture, based on visual observations and pH measurements. In this case, the solids nearly completely dissolved over three acid contact cycles (Figure 3-3, second bottle from left) and the pH was high (5-6) during the first two cycles. Measured solution pH values for the other reagents and the PUREX simulant in the nitric/oxalic mixture were all low (≤2.1). For samples containing iron (hematite/gibbsite blend and PUREX simulant), the solution color following acid contact was orange or red after all acid contacts, which is indicative of iron dissolution (Figure 3-1, second bottle from left; Figure 3-5, left bottle).

Solution pH measurements at the end of the each acid contact cycle in pure 0.9 M oxalic acid solutions were all low (≤1.0), as shown in Table 3-1. As was observed in the nitric/oxalic mixture, the nickel hydroxide reagent solids were observed to increase in volume and change to a lighter blue/green color (Figure 3-2, right bottle). The residual solids from this test were isolated and washed with cold water at the conclusion of Cycle 3 (Figure 3-6). XRD analysis (Figure 3-7) indicated conversion of the nickel hydroxide solids to phase-pure nickel (II) oxalate dihydrate ($NiC_2O_4 \cdot 2H_2O$). Exposure of both manganese (II) oxide and manganese (IV) oxide to oxalic acid solution results in the disappearance of the initial black solids and the formation of white or light pink solids (Figures 3-3 and 3-4, right bottles). The residual solids from these tests were isolated and washed with cold water at the conclusion of Cycle 3 (Figure 3-6). XRD analysis (Figure 3-8) indicated essentially complete conversion of both the MnO and the MnO_2 solids to phase-pure manganese (II) oxalate dihydrate ($MnC_2O_4 \cdot 2H_2O$). Formation of manganese (II) oxalate from MnO_2 requires a two-electron reduction of the manganese. Oxalic acid is apparently sufficiently reductive under these conditions to reduce manganese (IV). The nitric/oxalic acid mixture (see comments above) did not appear to promote manganese reduction and oxalate precipitation. This is likely due to the lower oxalic acid concentration and the presence of nitric acid oxidant, resulting in a less reducing oxidation-reduction potential for this reagent.

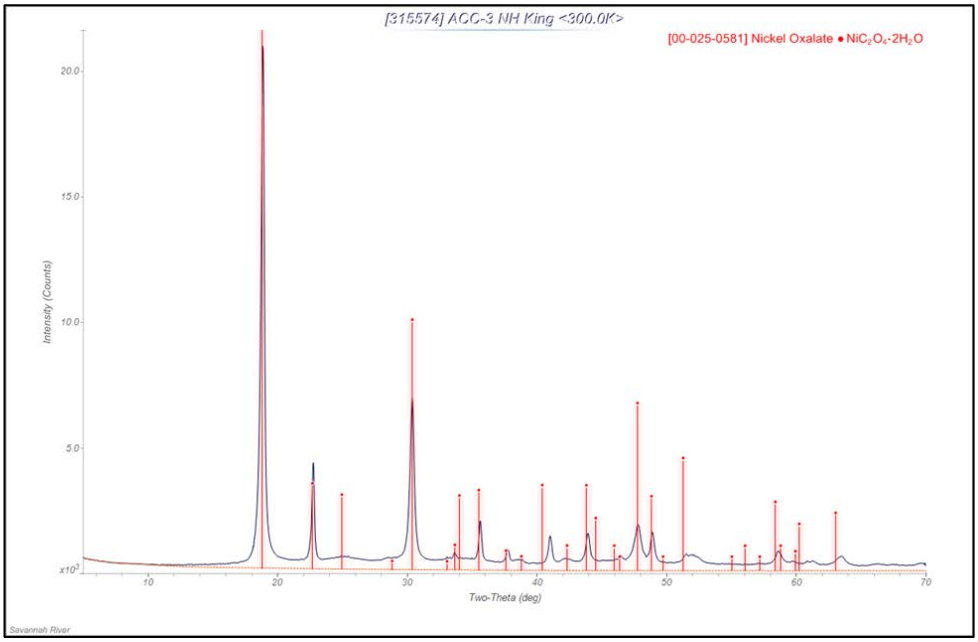


Figure 3-7. XRD Pattern Observed for Residual Solids Isolated Following $Ni(OH)_2$ Contact with 0.92 M Oxalic Acid (3 Cycles) – Non-Radioactive Simulant Testing.

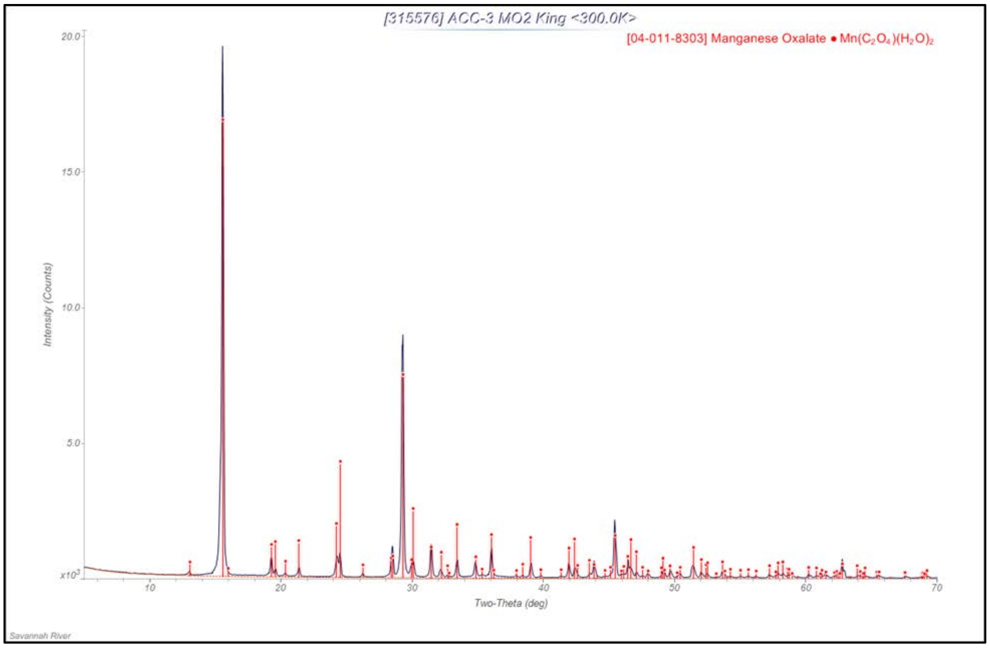


Figure 3-8. XRD Pattern Observed for Residual Solids Isolated Following MnO_2 Contact with Oxalic Acid (3 Cycles). Identical pattern observed for MnO Residuals Following Oxalic Acid Contact – Non-Radioactive Simulant Testing.

As was observed for iron-containing reagents (hematite and PUREX simulant) in nitric/oxalic acid blends the solution color was yellow to orange following contact of these solids with pure oxalic acid solutions (Figures 3-1 and 3-5, right bottles). In oxalic acid, all of the solids were observed to dissolve in the mixed hematite/gibbsite samples over the course of three contact cycles with little color being observed in solution by Cycle 3. Contact of PUREX simulant with pure oxalic acid resulted in the formation of a yellow solution with green solids after Cycle 3. The appearance of the solids was very similar to the above-mentioned nickel oxalate solids. The residual solids from the tests with PUREX simulant were isolated and washed with cold water at the conclusion of Cycle 3 (Figure 3-6). XRD analysis (Figure 3-9) indicated that the major crystalline phase in the PUREX simulant residue was nickel (II) oxalate dihydrate. Secondary phases observed included Al_2O_3 and SiO_2, each of which were added during simulant production. Minor diffraction peaks were also observed which were consistent with $HgCl_2$ and $Na_2C_2O_4$. Acid digestion of the damp PUREX residue (sample not dried due to possible presence of mercury oxalate compounds) following oxalic acid contact revealed that nickel was the dominant metal present, accounting for 64 wt. % of all metals (quantitative wt. % total solids not obtained since sample not dried). Manganese was the second most abundant metal (14 wt. % of total metals). Ca, Zn, Ce, La, and Cu were all present at wt. % total metal values ranging from 1-10%. Fe, Al, Na, Hg, Pb, and Sn were only present at trace levels (<0.5 wt. % total metals) and Cr was below detectable limits.

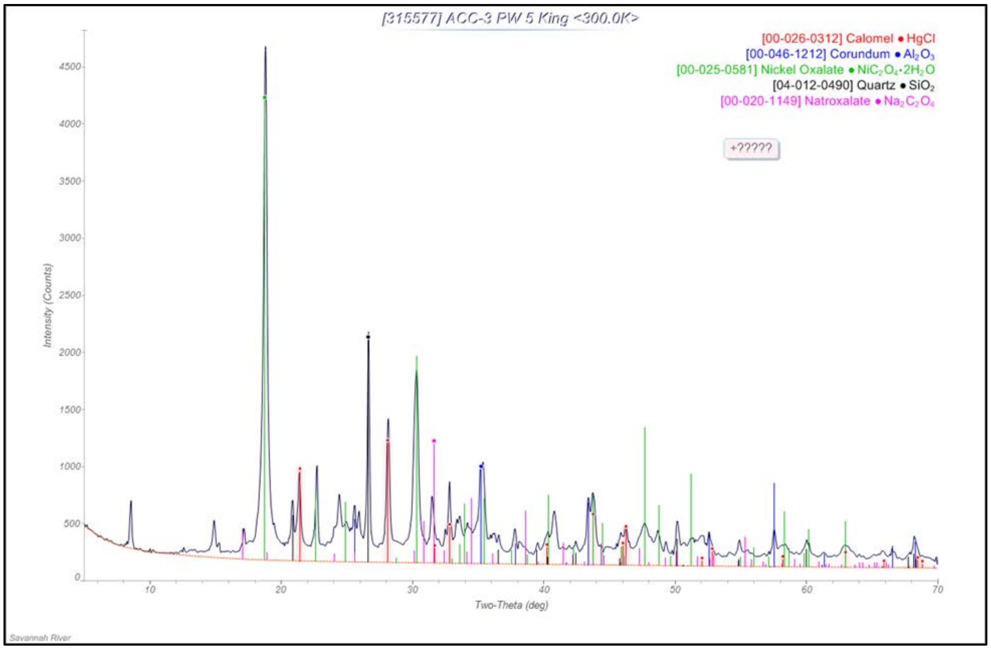


Figure 3-9. XRD Pattern Observed for Residual Solids Isolated Following PUREX Sludge Heel Simulant Contact with 0.92 M Oxalic Acid (3 Cycles) – Non-Radioactive Simulant Testing.

Analysis of liquid sub-samples collected from the test bottles at the conclusion of each acid contact cycle during the solubility experiments provided the concentrations of soluble metals in each cleaning reagent (see Appendix A). The maximum soluble iron concentration observed for PUREX simulant in contact with the oxalic/nitric acid mixture of 1.7 g/L (0.03 M) occurred in Cycle 3. The maximum iron concentration observed for PUREX simulant in pure oxalic acid of 4.5 g/L (0.08 M) occurred in Cycle 1. Minimal iron dissolution was observed in pure nitric acid. The maximum aluminum concentrations for all three cleaning reagents were observed in Cycle 1. Aluminum concentrations of 1.3, 1.4, and 1.0 g/L (ranging from 0.04-0.05 M) were observed in the oxalic/nitric acid mixture, pure oxalic acid, and pure nitric acid, respectively. It should be noted that (in contrast to iron) significant aluminum dissolution occurred in nitric acid in the absence of oxalate complexant.

Since only a portion of the cleaning reagent and the dissolved metals were removed between cycles during sample decant operations, the measured metal concentrations were used to calculate the percentage removal of each metal during each cycle and the total metal removed in all cycles. For Contact Cycles 1 and 2, solution volume removal was tracked by measuring the bottle masses and for Cycle 3 the volume of solution that could be removed without transferring the solids was estimated based on the Cycle 2 decant volumes. Approximately 75% of the solution was removed by decantation at the conclusion of each acid contact cycle. Metal weight percent removal values for the solid reagents are provided for each cleaning solution in Table 3-2 and Figures 3-10 through 3-14. Metal weight percent removal values for the PUREX simulant samples are provided for each cleaning solution in Table 3-3 and Figures 3-15 through 3-19.

Table 3-2. Percent Removal of Selected Metals from Solid Reagents in Each Cleaning Solution – Non Radioactive Simulant Testing.

Contact Cycle	% Metal Removed from Reagents Indicated					Cleaning Solution
	MnO	MnO_2	Fe_2O_3*	$Al(OH)_3$*	$Ni(OH)_2$	
1	24.7	19.7	13.2	37.4	33.3	0.056 M $H_2C_2O_4$/0.18 M HNO_3
2	28.8	19.9	21.5	26.4	5.2	0.056 M $H_2C_2O_4$/0.18 M HNO_3
3	23.5	22.4	24.1	16.8	0.2	0.056 M $H_2C_2O_4$/0.18 M HNO_3
Cumulative	77.0	62.0	58.8	80.6	38.7	0.056 M $H_2C_2O_4$/0.18 M HNO_3
1	22.8	1.1	0.9	18.5	33.8	0.18 M HNO_3
2	27.3	1.8	1.4	13.7	38.5	0.18 M HNO_3
3	19.9	2.0	1.7	10.9	15.2	0.18 M HNO_3
Cumulative	70.0	5.0	4.0	43.0	87.6	0.18 M HNO_3
1	8.3	11.8	78.6	73.4	0.06	0.92 M $H_2C_2O_4$
2	6.6	10.2	17.1	20.3	0.03	0.92 M $H_2C_2O_4$
3	6.0	9.2	3.7	4.8	0.05	0.92 M $H_2C_2O_4$
Cumulative	21.0	31.3	99.4	98.5	0.14	0.92 M $H_2C_2O_4$

*percent removal from 50:50 mass-based mixture of hematite and gibssite

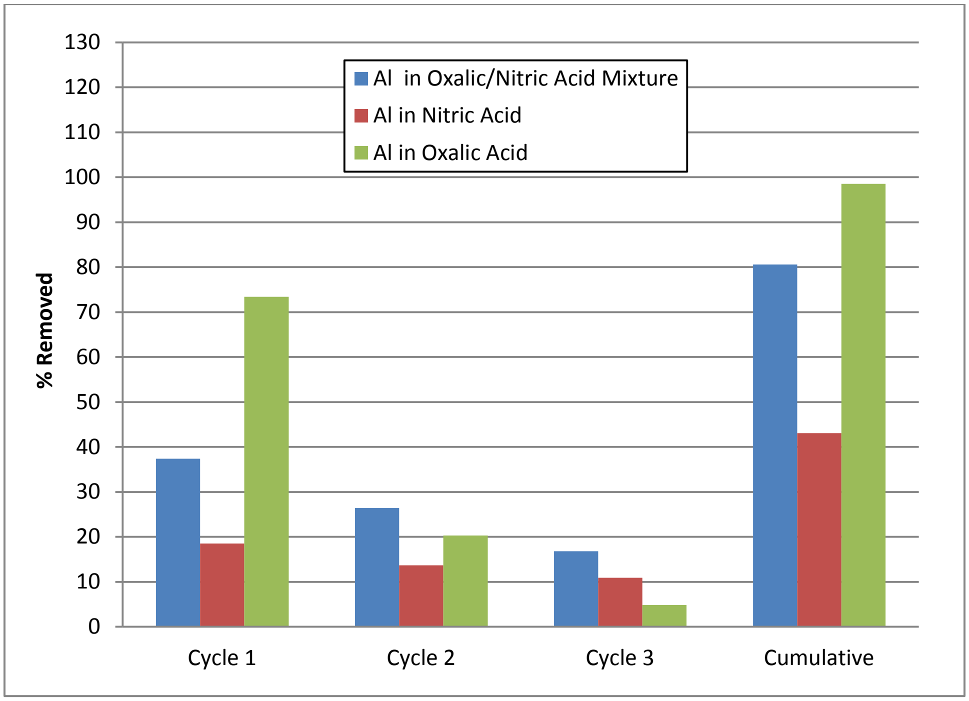


Figure 3-10. Aluminum Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Gibbsite/Hematite Reagent Mixture Non-Radioactive Simulant Testing.

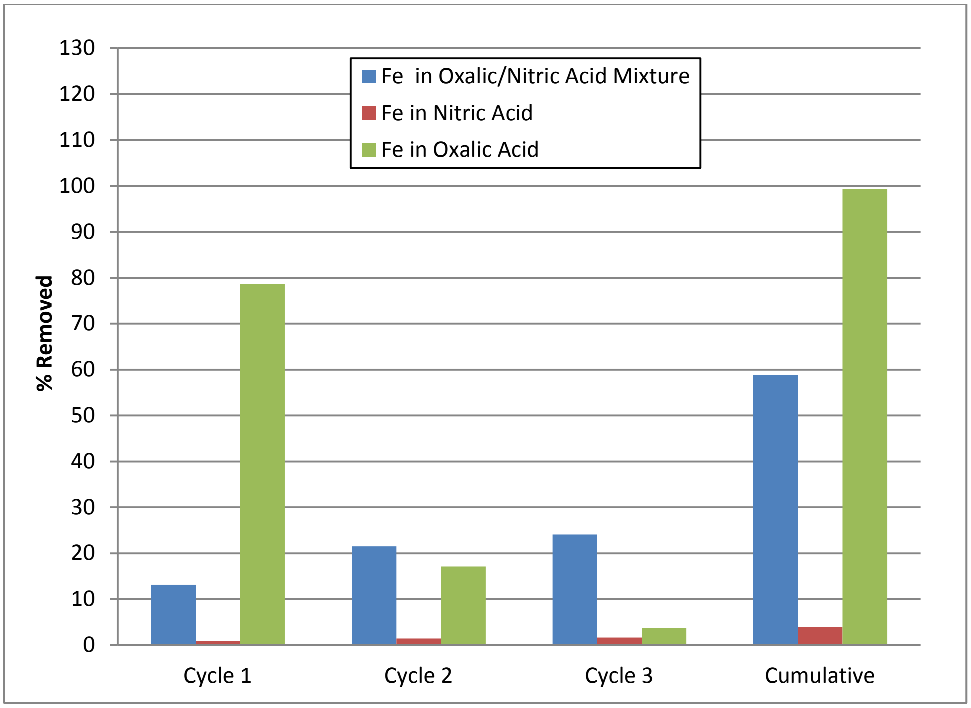


Figure 3-11. Iron Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Gibbsite/Hematite Reagent Mixture – Non-Radioactive Simulant Testing.

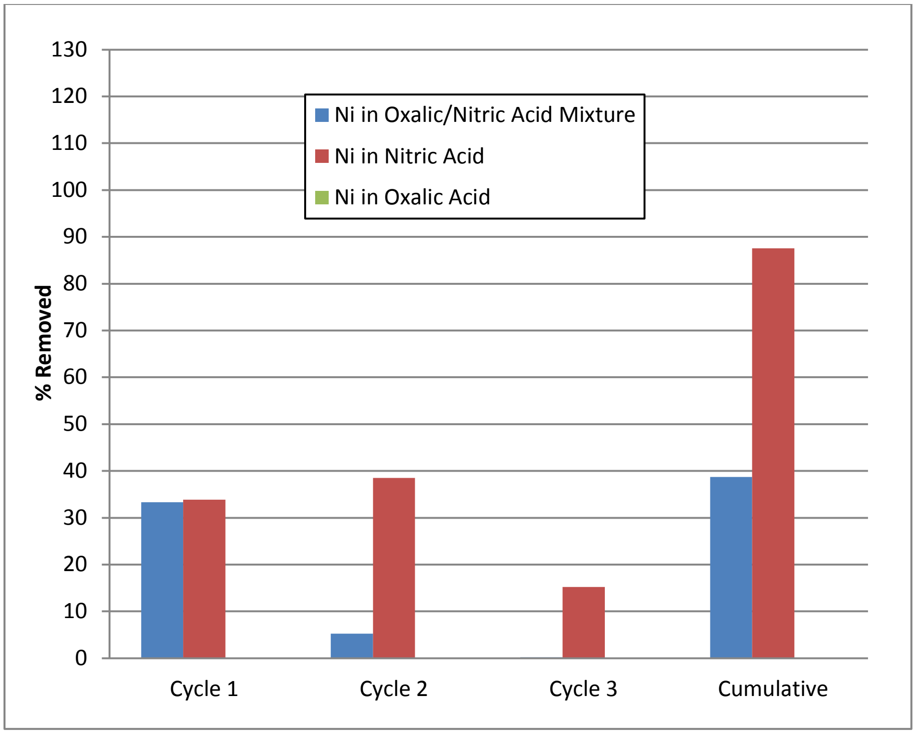


Figure 3-12 Nickel Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Nickel (II) Hydroxide Reagent – Non-Radioactive Simulant Testing.

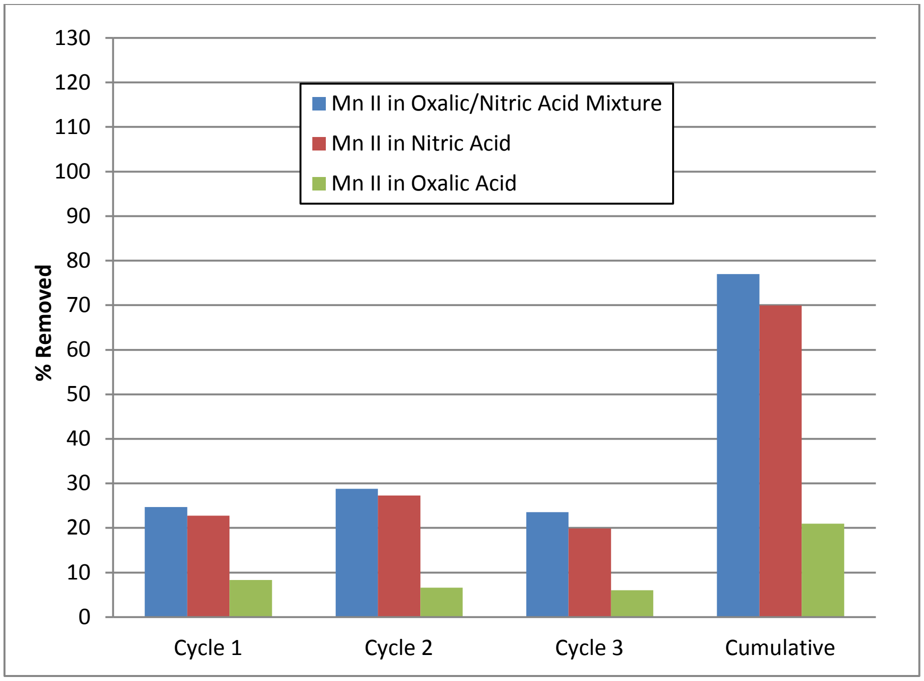


Figure 3-13. Manganese Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Manganese (II) Oxide Reagent – Non-Radioactive Simulant Testing.

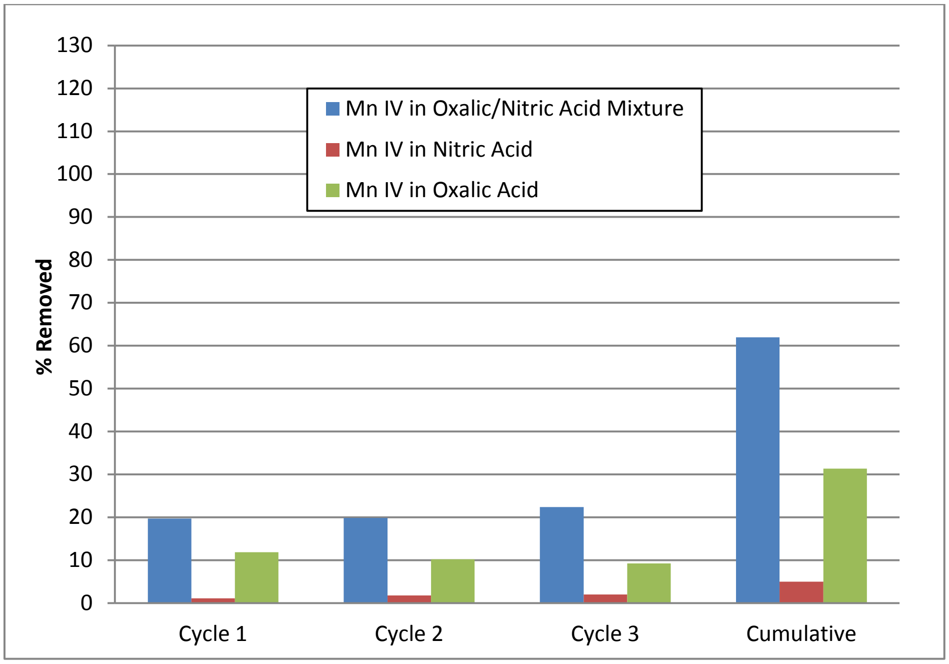


Figure 3-14. Manganese Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Manganese (IV) Oxide Reagent – Non Radioactive Simulant Testing.

Table 3-3. Percent Removal of Selected Metals from PUREX Simulant in Each Cleaning Solution – Non Radioactive Simulant Testing.

Contact Cycle	% Metal Removed						Cleaning Solution
	Al	Ca	Fe	Mn	Ni	Hg	
1	55.6	22.2	4.1	55.3	56.2	52.5	0.056 M $H_2C_2O_4$/0.18 M HNO_3
2	13.2	5.3	19.5	17.3	21.8	26.1	0.056 M $H_2C_2O_4$/0.18 M HNO_3
3	2.7	1.2	25.6	4.0	5.8	15.3	0.056 M $H_2C_2O_4$/0.18 M HNO_3
Cumulative	71.4	28.7	49.2	76.5	83.7	93.9	0.056 M $H_2C_2O_4$/0.18 M HNO_3
1	42.5	26.6	0.01	6.4	44.0	6.8	0.18 M HNO_3
2	21.5	6.9	1.88	9.5	16.0	60.0	0.18 M HNO_3
3	5.6	1.8	2.84	37.3	11.4	46.7	0.18 M HNO_3
Cumulative	69.5	35.3	4.72	53.2	71.4	113.5	0.18 M HNO_3
1	54.2	50.6	54.6	36.0	2.4	14.4	0.92 M $H_2C_2O_4$
2	12.1	10.9	19.1	14.4	0.7	9.4	0.92 M $H_2C_2O_4$
3	3.3	4.4	5.7	7.5	0.4	6.8	0.92 M $H_2C_2O_4$
Cumulative	69.6	65.9	79.3	58.0	3.5	30.6	0.92 M $H_2C_2O_4$

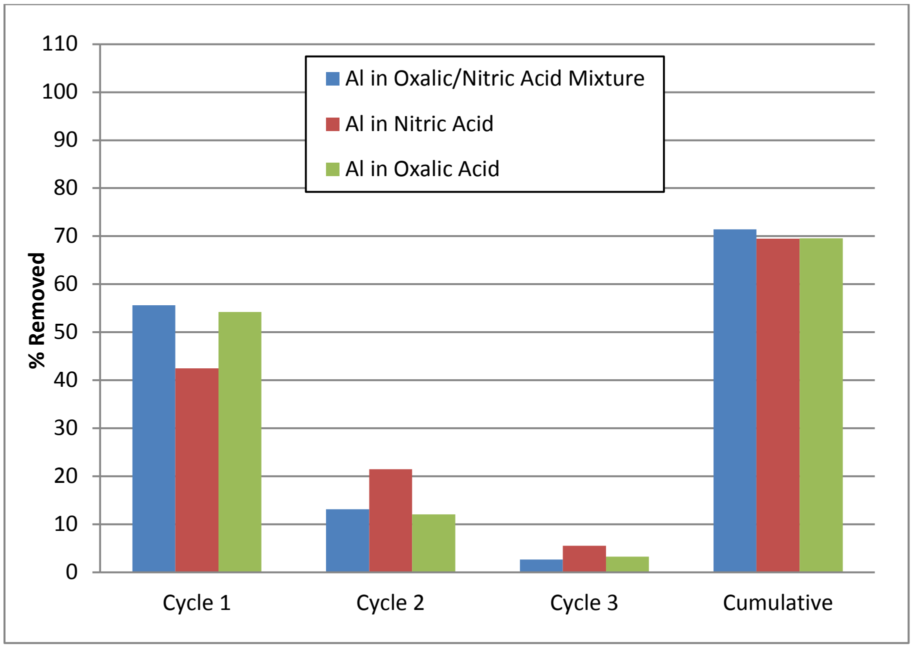


Figure 3-15. Aluminum Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant.

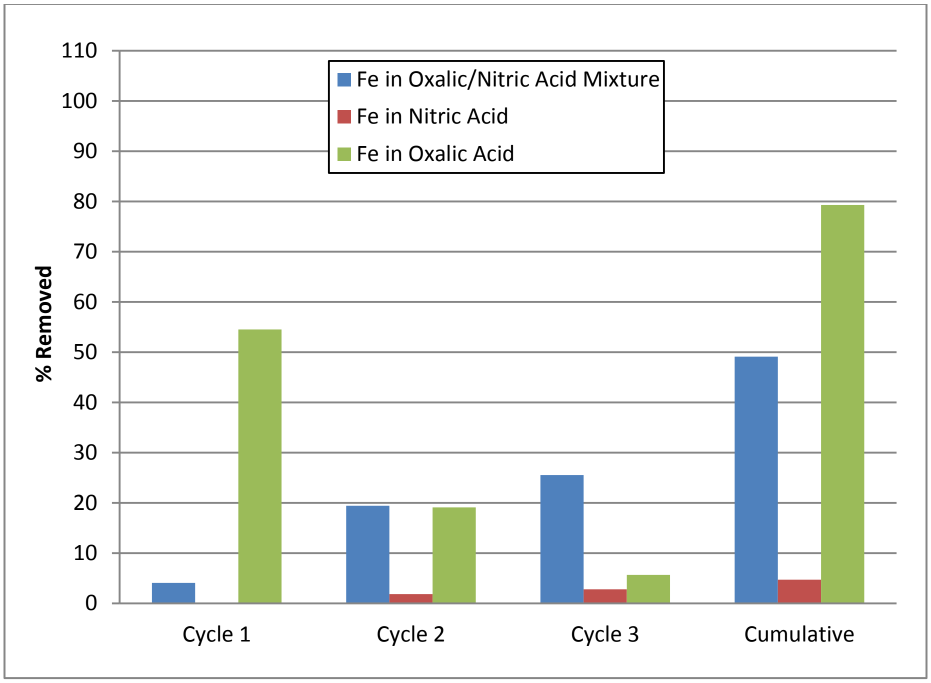


Figure 3-16. Iron Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant.

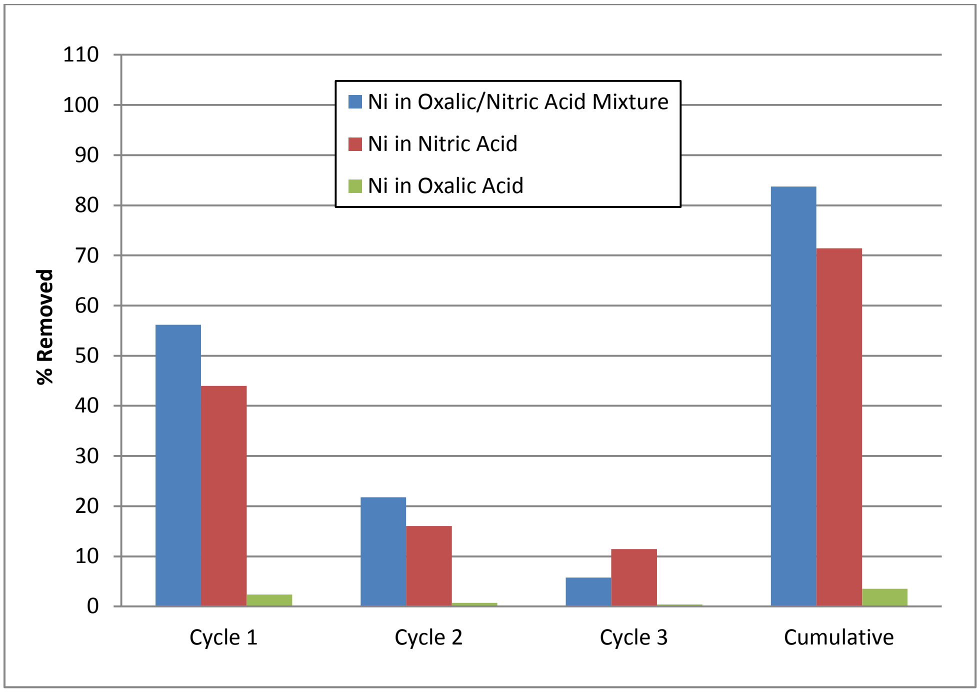


Figure 3-17. Nickel Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant.

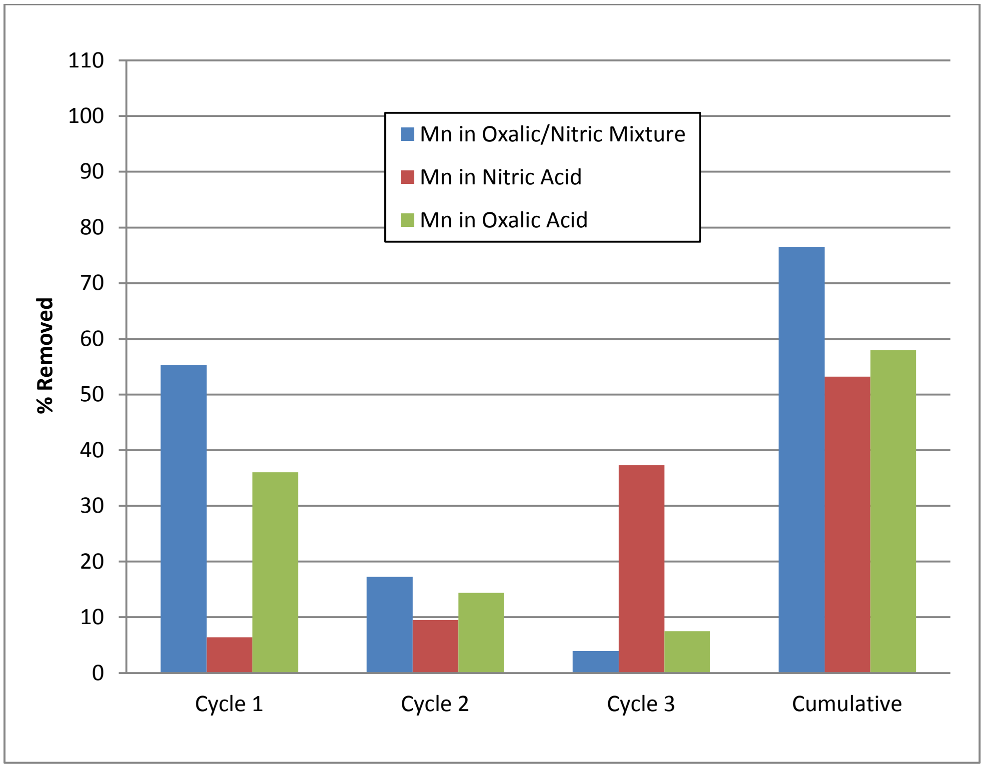


Figure 3-18. Manganese Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant.

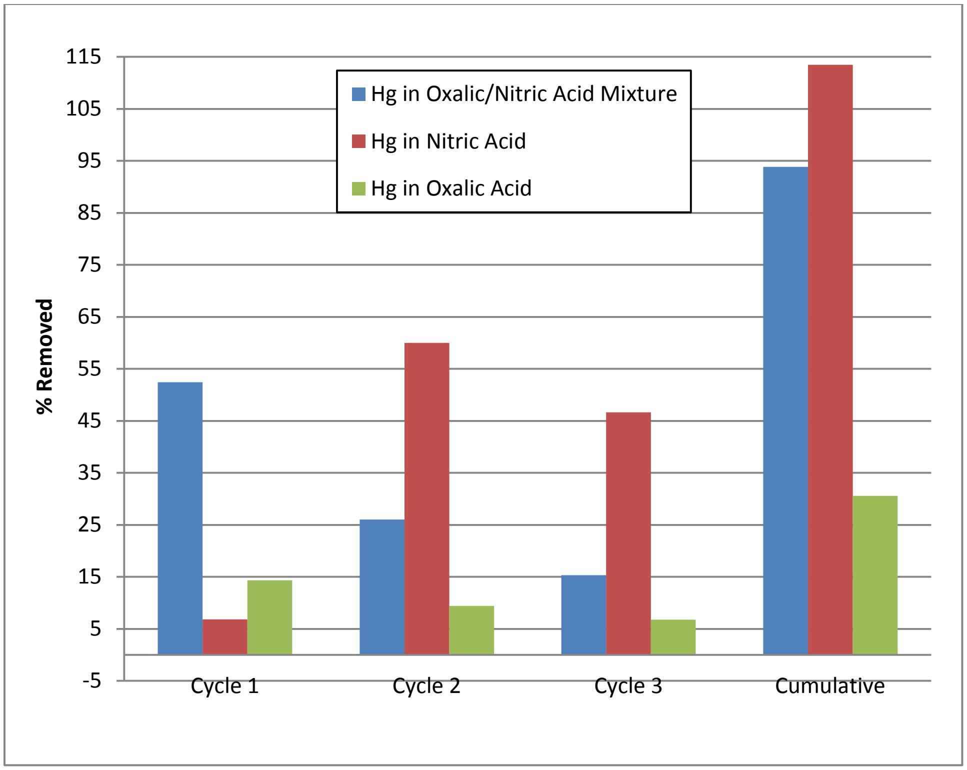


Figure 3-19. Mercury Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant (Note: Mercury analysis results are not considered to be highly quantitative. See text comments in Section 3.1).

The effectiveness of each cleaning solution at removing sludge by dissolution varies depending on the metal species involved. Tests conducted on pure metal reagents allows for direct evaluation of the effectiveness of the cleaning solutions toward dissolving specific metal phases without the complicating effects of competition for acid equivalents or complexants from other metals. In contrast, tests conducted with PUREX simulants allow for simultaneous evaluation of the relative solubilities of the various metals in a representative sludge matrix. Both the oxalic/nitric acid mixture and pure oxalic acid are effective at dissolving iron from simple hematite/gibbsite mixtures and from the complex PUREX simulant. In 8 wt. % oxalic acid, most of the iron (79 wt. %) was removed from the hematite/gibbsite mixtures during the first acid contact cycle and the remaining iron (99 wt. %) was removed in succeeding cycles (see Figure 3-11). For PUREX simulant in pure oxalic acid, where various other metals compete for the oxalate complexant, the iron removed in the first acid contact was lower (55 wt. %) than was observed in the hematite/gibbsite reagent test, and only 79 wt. % of the iron had been removed following the third contact cycle (Figure 3-16). In the oxalic/nitric acid mixture, only 13 and 4 wt. % of the iron was removed in the first contact cycle from the hematite/gibbsite mixture and the PUREX simulant, respectively (Figures 3-11 and 3-16). This low iron removal was presumably due to competition with aluminum (and other metal phases in the case of PUREX simulant) for oxalate complexant. For the PUREX simulant, the pH was also slightly elevated (pH 1.4) in the first contact cycle, which leads to lower iron solubility. Iron removal increased with each successive cycle in the oxalic/nitric acid mixture resulting in total iron removal over three acid contact cycles of 59 and 49 wt. % for the hematite/gibbsite mixture and PUREX simulant, respectively.

Cumulative aluminum removal over three contact cycles in 8 wt. % oxalic acid of 99 and 70 wt. % were observed for the gibbsite/hematite mixture and PUREX simulant, respectively (Figures 3-10 and 3-15; as was observed for Fe with the hematite/gibbsite mixture). Cumulative aluminum removal over three contact cycles in the oxalic/nitric acid mixture of 81 and 71 wt. % were observed for the gibbsite/hematite mixture and PUREX simulant, respectively. Pure nitric acid is also somewhat effective at removing aluminum. Percent removal values in nitric acid of 43 and 70 wt. % were observed over three contact cycles for the gibbsite/hematite mixture and PUREX simulant, respectively.

Use of nitric acid either as a pure reagent or as part of a mixture with oxalic acid results in significant improvements in nickel dissolution (Figures 3-12 and 3-17). Three contact cycles with pure nitric acid resulting in the dissolution of most of the nickel reagent (88 wt. % removed) based on analysis (which is consistent with visual observations, Figure 3-2). The formation of nickel oxalate precipitate appears to limit the effectiveness of oxalic/nitric acid reagent towards nickel dissolution (39 wt. % removed) while pure oxalic acid is very ineffective at removing nickel (<1 wt. % removed) for this same reason. As mentioned above, nickel oxalate is the dominant species present in simulant residues remaining after contact with 8 wt. % oxalic acid. Nitric acid and nitric/oxalic blends are effective at dissolving manganese (II) oxide (70 and 77 wt. % removal, respectively), while pure oxalic acid is not highly effective (21 wt. % removal; see Figure 3-13). The oxalic/nitric acid mixture is the superior cleaning solution for manganese (IV) oxide (62 wt. % removal), while pure nitric acid is ineffective (5 wt. % removal; Figure 3-14). The oxalic/nitric acid mixture was the superior reagent (77 wt. % removal) for the dissolution of mixed valence (presumably, based on the synthesis) manganese from PUREX simulant (Figure 3-18), though all three cleaning solutions were effective (>50 wt. % dissolution over three cycles).

Significantly different results were observed in repeated analysis for mercury and the results provided in Figure 3-19 are questionable with regard to the value of the data from a quantitative perspective. It is assumed, however, that relative comparisons between the cleaning reagents can be made and the general effectiveness of the reagents can be evaluated based on this data. Based on the results, nitric acid and the oxalic/nitric acid mixture were the most effective reagents (94 and 114 wt. % removal, respectively) for mercury dissolution from PUREX simulant (Figure 3-19). The lowest mercury removal was observed with oxalic acid, though the total removal (31%) was higher than was reported for SRS Tank 12 following three oxalic acid cleaning cycles (<6%).[18] In future work, mercury analysis methods and results should be carefully scrutinized and controls should be used in an attempt to obtain more quantitative results. Surprisingly, concentrated oxalic acid is the most effective reagent for the removal of Ca (Figure 3-20).

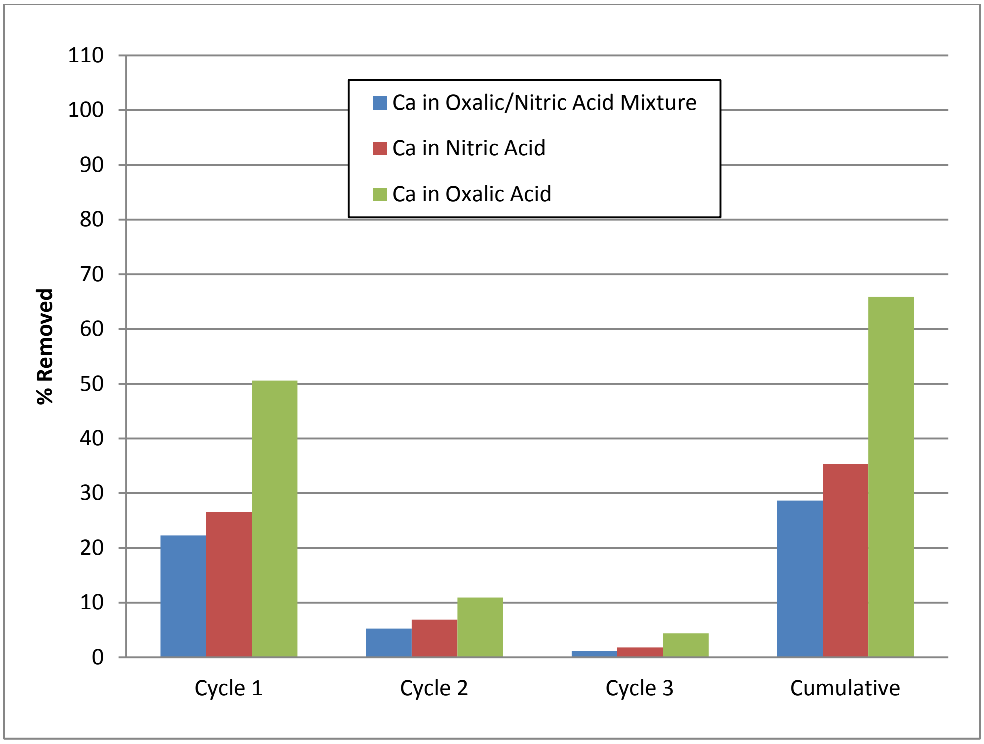


Figure 3-20. Calcium Removed per Contact Cycle and Cumulative in each Cleaning Reagent from the Non-Radioactive PUREX Simulant.

A primary purpose for the recommendation of using the dilute oxalic/nitric acid mixture containing 0.056 M oxalic acid and 0.18 M nitric acid for sludge heel dissolution is to minimize oxalate additions to the tank farm. This recommendation was based on observations during previous chemical cleaning campaigns that significantly more oxalic acid was being added to the tanks than was believed necessary to promote sludge dissolution. As described in previous reports, the optimum oxalate:iron molar ratio for iron dissolution is equal to 1, based on the formation of the bi-oxalate complex, $FeHC_2O_4^{2+}$.[19] Oxalate additions per cycle and cumulative for each test involving the optimized and baseline (BOAC) oxalic acid methods with PUREX simulant are provided in Table 3-4 along with measured pH values, iron dissolution amounts, and oxalate:iron molar ratios. As previously observed during chemical cleaning campaigns, the addition of 8 wt. % oxalic acid to PUREX sludge results in larger oxalate:iron molar ratios than the optimum (molar ratio range of 5 to >100) with an overall ratio for the three contact cycles of 7.6. The extremely high oxalate:Fe ratio observed in Cycle 3 is a consequence of the fact that most of the iron had dissolved in the first two contact cycles. In contrast, with the optimized mixture of oxalic and nitric acids the overall ratio over three contact cycles was 2.6, indicating an increase in the efficiency of oxalate usage for iron dissolution of 2.9. In addition, oxalate:iron molar ratios of 2.1 and 1.7 were observed with the oxalic/nitric acid mixture in contact Cycles 2 and 3, while the ratio exceeded 9 for the first cycle. As mentioned earlier, competition with Al and other species for oxalate complexation and the slightly elevated pH in Cycle 1 resulted in less efficient iron dissolution. It is estimated that 1.5 additional contact cycles with the oxalic/nitric acid mixture would have resulted in nearly complete iron dissolution from the test sample. Based on this result, pH adjustment and aluminum dissolution with nitric acid prior to the addition of oxalic/nitric acid mixtures would allow for further minimization of oxalate additions to allow for oxalate:iron molar ratios approaching the optimal value (≤1.5).

Table 3-4. Performance Comparisons of Baseline and Optimized Oxalic Acid Chemical Cleaning Reagents with PUREX Sludge Simulant – Non Radioactive Simulant Testing.

	Cycle 1	Cycle 2	Cycle 3	Total
	pH			
optimized	1.40	1.12	1.10	---
baseline	0.76	0.80	0.78	---
	oxalate mmoles added			
optimized	8.4	8.4	8.4	25.2
baseline	68.9	23.0	23.0	114.9
ratio baseline:optimized	8.2	2.7	2.7	4.6
	iron mmoles dissolved			
optimized	0.9	4.0	4.8	9.7
baseline	12.9	1.9	0.2	15.0
	ratio oxalate:dissolved Fe			
optimized	9.2	2.1	1.7	2.6
baseline	5.3	12.2	111.4	7.6

3.2 Radioactive Simulant Testing

The elemental masses in the simulated PUREX sludge used in the radioactive testing are summarized in Table 3-5. Concentrations using 100 mL of the acidic waste solution as the basis are also provided. Although, these concentrations changed as the components of the sludge were combined, the ratios of the elements remained constant through neutralization of the acidic solution. The composition of the waste solution is generally consistent with the target composition provided in Table 2-3 with the exception of insoluble iron which was inadvertently added at twice the target value. Therefore, the ratios of the elements in the neutralized sludge (with the exception of iron) are near the selected compositional bases (see section 2.2.1). The presence of the additional insoluble iron should have no effect on the precipitation of the transuranic elements during neutralization. The concentrations of the nonradioactive components and uranium in the simulated PUREX sludge (Table 3-5) are provided for information. No effort was made to analyze for these elements following the sludge treatment processes or the solubility experiments.

Table 3-5. Elemental Composition of Radioactive PUREX Sludge Simulant.

Element	Acid PUREX Waste Solution		
	Mass	Concentration(1)	Concentration(1)
	(g)	(g/L)	(dpm/mL)
U	6.5560	65.56	4.90E+07
Np	7.28E-02	7.28E-01	1.13E+06
Pu	1.06E-02	1.06E-01	1.02E+09
Am	5.40E-03	5.40E-02	4.12E+08
Fe (soluble)	5.5524	55.52	
Fe (insoluble)(2)	5.5690	111.4	
Al (soluble)	2.0508	20.51	
Al (insoluble)	2.0523	20.52	
Ni	1.3009	13.01	
Mn	1.2019	12.02	

(1) Concentration based on 100 mL total volume.

(2) Insoluble iron was inadvertently added as two times the mass of soluble iron.

The majority of the plutonium in the PUREX sludge is weapons grade ($^{239/240}$Pu); however, the total plutonium was based on the amount of plutonium-238 measured ($^{238}\mathrm{Pu}_{\mathrm{measured}}$) by the GPHA. The total plutonium ($^{\mathrm{total}}$Pu) in a sample was calculated using the ratio of the total plutonium ($^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}$) to the plutonium-238 ($^{238}\mathrm{Pu}_{\mathrm{initial}}$) initially added to the simulated PUREX waste solution (Equation 11).

$$^{\mathrm{total}}\mathrm{Pu} = {}^{238}\mathrm{Pu}_{\mathrm{measured}}\left(\frac{^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}}{^{238}\mathrm{Pu}_{\mathrm{initial}}}\right) \tag{11}$$

3.2.1 Evaluation of Radioactive Simulant Solubility Experiments

The activities of neptunium-237, plutonium-238, and americium-241 measured in the solubility samples and in the solutions collected during the sludge treatment processes are provided in Appendix B. The appendix summarizes the calculations used to convert the actinide activities to appropriate concentration units. The total volume of solution collected during each sludge treatment process is reported. The concentrations of neptunium, plutonium, and americium measured as a function of time during the solubility experiments are plotted in Figures 3-21 to 3-23, respectively.

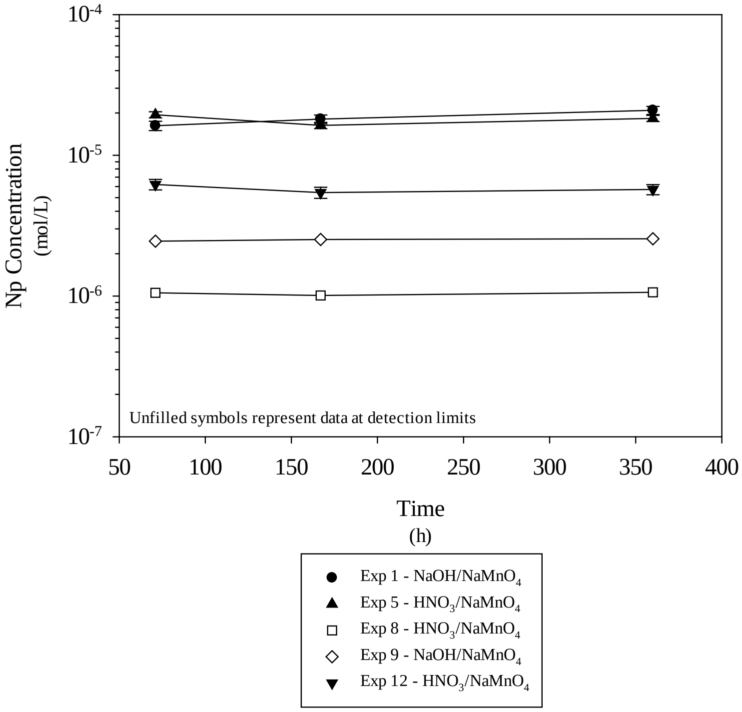


Figure 3-21. Solubility of Neptunium in Acidic and Basic Sodium Permanganate Solutions During Radioactive Simulant Testing.

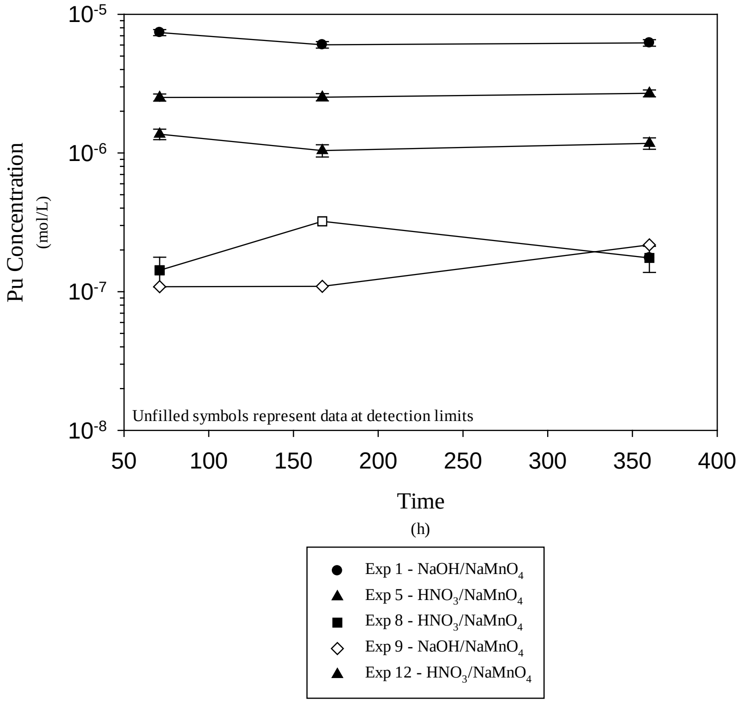


Figure 3-22.Solubility of Plutonium in Acidic and Basic Sodium Permanganate Solutions During Radioactive Simulant Testing.

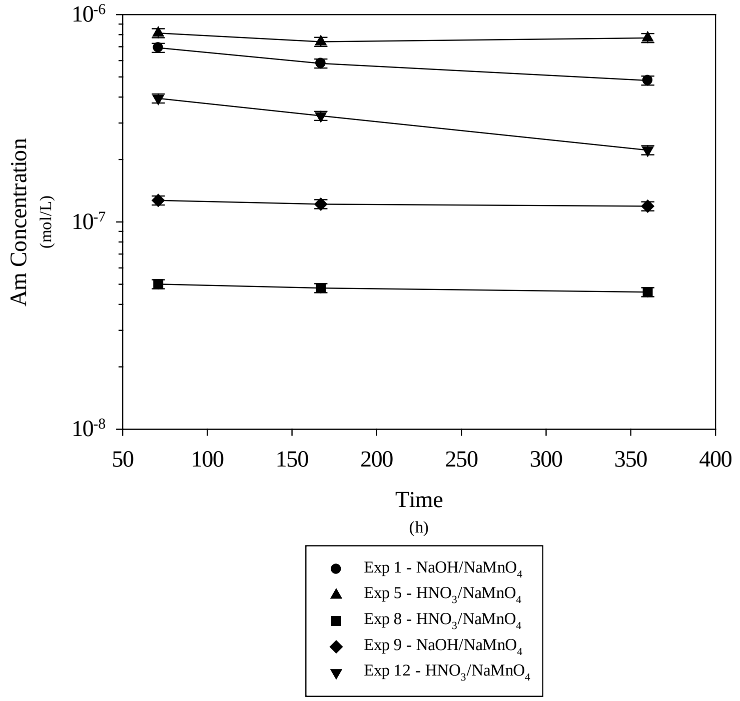


Figure 3-23. Solubility of Americium in Acidic and Basic Sodium Permanganate Solutions During Radioactive Simulant Testing.

3.2.1.1 Radioactive Simulant Solubility Experiment 1

The objective of solubility Experiment 1 was to evaluate the efficiency of a caustic solution containing sodium permanganate in solubilizing neptunium, plutonium, and americium in the simulated PUREX sludge without pretreatment. The fractions of the actinides solubilized during the experiment were estimated using the measured concentrations and the (estimated) mass of each actinide in the sludge sample. The masses of the actinides used in the experiment were calculated from their starting masses in the original PUREX waste solution, the estimated volume of the simulated sludge, and the volume of the sludge sample used in the experiment. The calculations including an estimate of the one sigma uncertainty are summarized in Appendix C and the results of the calculations are provided in Table 3-6.

Table 3-6. Fraction of Actinide Masses Solubilized during Radioactive Sludge Simulant Experiment 1.

Element	Sample	Fraction	1 Sigma	Relative
	Time	Solubilized	Uncertainty	Standard Dev.
	(day)	(%)	(%)	(%)
Neptunium	3	9.8	1.0	10
	7	11	1	9.7
	15	12	1	9.2
Plutonium	3	31	3	8.7
	7	26	2	8.7
	15	26	2	8.7
Americium	3	5.7	0.5	8.7
	7	4.9	0.4	8.4
	15	4.2	0.4	8.2

The fractions of the actinides solubilized during Experiment 1 were somewhat limited. Potential explanations for the low solubility are discussed in the following paragraphs. However, it should be noted that the fraction of each actinide solubilized during the experiment was relatively constant from one sample time to the next. The uncertainty in the fractions solubilized could account for any differences in the calculated values for the three sample times. The uncertainty analysis was based on the one sigma uncertainties in the measured actinide concentrations and the volumes of the neutralized PUREX waste simulant, 3 mL sludge sample (used for the solubility experiment), and the 2.5 mL solubility samples (removed periodically during the experiment). The uncertainties in other measurements (or analyses) were considered small compared to the uncertainties in these values. The removal of a homogeneous sample from the neutralized PUREX waste simulate for use in Experiment 1 was likely another major source of uncertainty which could not be quantified. We assumed the composition (i.e., the actinide concentrations) of the sludge sample was the same as the waste simulate in the analysis performed to calculate the fraction of the actinides solubilized in the experiment; however, this was likely not the case. Therefore the 1 sigma uncertainties shown in Table 3-6 should be considered a lower bound on the values.

The results from Experiment 1 are somewhat different from a previous study performed by Rudisill et al.[10] in which a 10 M sodium hydroxide solution containing 0.2 M sodium permanganate was very effective in solubilizing plutonium and neptunium in a simulated sludge containing only the actinide elements. The measured plutonium concentration in the previous test solution was approaching the maximum value possible based on the estimated amount of sludge added to the test solution; therefore, it was possible that the plutonium concentration may not have been at the solubility limit. In Rudisill's study, the increased solubility can be attributed to the oxidation of plutonium(IV) to plutonium(VI) (Equation 12) which is consistent with the plutonium solubility generally increasing with increasing oxidation state.[20]

$$3Pu^{4+} + 2MnO_4^- + 2H_2O \rightarrow 3PuO_2^{2+} + 2MnO_2 + 4H^+ \tag{12}$$

In the previous work by Rudisill, the neptunium concentration measured in the permanganate-containing solution was also approaching the maximum value based on the estimated amount of sludge added to the test solutions and may not have been at the solubility limit. In the permanganate-containing solutions, the oxidation of neptunium(IV) to neptunium(V) or neptunium(VI) (Equations 13 and 14) generates neptunium species with higher solubility.[10]

$$3Np^{4+} + MnO_4^- + 4H_2O \rightarrow 3NpO_2^+ + MnO_2 + 8H^+ \tag{13}$$

$$3Np^{4+} + 2MnO_4^- + 2H_2O \rightarrow 3NpO_2^{2+} + 2MnO_2 + 4H^+ \tag{14}$$

The lower concentrations measured for neptunium and plutonium in the current study compared to the previous work performed by Rudisill can likely be attributed to the coprecipitation of the actinides with other components in the sludge. In a summary of work by other investigators, Delegard et al. described studies performed for the Hanford site in which plutonium was coprecipitated with other metal ions. These studies showed there are strong interactions between plutonium(IV) and iron(III) under alkaline coprecipitation conditions. Investigators also observed strong interactions between plutonium(IV) and uranium(VI) and manganese (IV) under similar conditions; although, the interactions were not as strong as with iron(III). Little to no interactions between plutonium(IV) and aluminum(III) or nickel(II) were found.[21] Based on these results, it is likely that coprecipitation of plutonium with iron (and perhaps uranium and manganese) decreased the solubility due to a reduction in the degree of oxidation of plutonium(IV) to the more soluble plutonium(VI) valence. A similar mechanism could also reduce the solubility of neptunium(IV) assuming it coprecipitates with iron(III), uranium(VI), and manganese(IV) in a similar manner. In contrast to the behavior of neptunium and plutonium, the solubility data for americium measured in this study was similar to the previous data measured by Rudisill using actinide oxides which were not coprecipitated with bulk sludge solids.[10] In each study, the americium concentrations were reasonably constant at nominally 1E-06 mol/L in the caustic solutions. It appears that coprecipitation of the americium with Fe(III), U(VI), or Mn(IV) had little impact on the measured concentrations.

3.2.1.2 Radioactive Simulant Solubility Experiment 5

Solubility Experiment 5 was performed using a sample of the PUREX sludge following treatment by a dilute (0.01 M) sodium hydroxide washing process and a subsequent acidification process. The sludge caustic washing step reduced the free hydroxide concentration from 1.2 M to nominally 0.2 M. Very little of the neptunium, plutonium, and americium masses were solubilized during washing. The estimated fractions of each element retained in the sludge after washing is shown in Table 3-7. The calculations used to obtain these values are summarized in Appendix C.

Table 3-7. Estimated Percentage of Sludge Actinides Remaining in Caustic-Washed Sludge Conducted Prior to Experiments 5, 8, 9, and 12 -Radioactive Simulant Testing.

Element	Estimated Percentage
	in Washed Sludge
	(%)
Neptunium	> 99.8
Plutonium	> 99.7
Americium	100

The intent of the acidification process was to acidify an aliquot of the sludge to a pH of approximately 2 to prevent partial neutralization of the acidic permanganate solution when initiating the solubility experiment. However as discussed in Section 2.2.2.2, the plan could not be executed due to peptization of the solids in the low ionic strength acidic wash solution. The final pH of the solution was approximately 4 at the conclusion of the acidification treatment. As a result of the higher than desired pH, little neptunium, plutonium, or americium was solubilized during the acidification process based on the analysis of the composite solution removed during the treatment process. The estimated percentage of each element retained in the sludge after the acid treatment is shown in Table 3-8. The calculations used to obtain these values are summarized in Appendix C.

Table 3-8. Estimated Percentage of Sludge Actinides Remaining in the Sludge Following Acidification Conducted Prior to Experiments 5 and 8 - Radioactive Simulant Testing.

Element	Estimated Percentage
	in Acidified Sludge
	(%)
Neptunium	> 99.8
Plutonium	> 99.6
Americium	100

The fractions of the actinides solubilized during Experiment 5 in the 0.18 M nitric acid/0.05 M sodium permanganate solution were estimated using the measured concentrations in the cleaning solution and the (estimated) mass of each actinide in the sludge sample using the same general procedure as used for Experiment 1. The calculations are summarized in Appendix C and the results of the calculations are provided in Table 3-9. The uncertainties in the fractions of the actinides solubilized were not calculated for Experiment 5; although, the relative standard deviation would be expected to be in the 10-15% range based on the assumptions and results from Experiment 1. The uncertainty introduced by splitting the sludge stream between the acidification and the BOAC treatment processes would also contribute to the uncertainties in the fractions solubilized, but the data does not exist for its quantification.

The results from the Experiment 5 show that the acidic permanganate solution was very effective in solubilizing the neptunium and plutonium in the sludge used to perform Experiment 5. The estimated fraction of both elements solubilized during the 15 day contact period was approximately 90%. These results are consistent with experiments performed by Rudisill et al.[10] in which a 0.18 M nitric acid solution containing 0.2 M sodium permanganate solubilized essentially all of the neptunium and plutonium in a simulated sludge containing only actinide elements (no coprecipitated non-radioactive sludge components). It should also be noted that the estimated fractions of neptunium and plutonium solubilized at 3, 7, and 15 days were also reasonably constant which implies that equilibrium conditions were obtained quickly without kinetic limitations.

Table 3-9. Fraction of Actinide Masses Solubilized during Experiment 5 - Radioactive Simulant Testing.

Actinide	3 days	7 days	15 days
	(%)	(%)	(%)
Neptunium	96	82	90
Plutonium	86	87	92
Americium	55	50	52

The amount of americium solubilized by the acidic permanganate solution was not as high as the neptunium and plutonium. The estimated fraction for Experiment 5 was only about 50% of the americium in the treated sludge. The fraction of the americium solubilized at 3, 7, and 15 days was also reasonably constant. This behavior was significantly different than the behavior observed by Rudisill et al.[10] in the previous study. When the actinide sludge was contacted with a 0.18 M nitric acid solution containing 0.2 M sodium permanganate, the concentration of the americium measured following the first day of contact was near its maximum possible value; however, following 33 days of contact, the concentration declined by almost two orders of magnitude. The authors postulated that americium(III) could be oxidized by the permanganate to americium(V) which subsequently coprecipitated with manganese dioxide. This theory was based on the use of manganese dioxide to remove protactium(V) from uranium-233 solution during purification by a coprecipitation process. It is unclear why the americium solubility behavior was so different in the two studies unless the presence of other components had an effect on the amount solubilized during Experiment 5 in this study. Additional experimentation would be required to test this hypothesis.

3.2.1.3 Comparison of the Use of Acidic and Basic Permanganate for Waste Tank Cleaning Prior to Oxalic Acid Contact

A comparison of the results from Experiments 1 and 5 provide a measure of the relative efficiency of acidic and basic permanganate solutions in solubilizing neptunium, plutonium, and americium from the simulated sludge without the use of a treatment process containing oxalic acid. The sludge used in Experiment 5 was washed with a dilute sodium hydroxide solution and acidified to a pH of 4 to 5; however, very little of the actinide mass was solubilized during the treatment processes (Section 3.2.1.2). The net result of the two treatments was primarily a reduction in pH which averted the partial neutralization of nitric acid when the permanganate-containing solution and the simulated sludge were combined.

One interesting observation from the neptunium, plutonium, and americium concentrations plotted on Figures 3-21 to 3-23, respectively, is that the magnitude of the values for each actinide element are not substantially different for Experiments 1 and 5. For neptunium, the concentration measured in the acidic solution was initially higher, but the curves crossed between the 3 and 7 day sample times resulting in a higher concentration in the basic solution in the last two samples; although, the Experiment 1 and 5 concentrations at each sample time differed by less than approximately 20%. The plutonium concentrations measured in the basic permanganate solution were also higher (by a factor of approximately two) than measured in the acidic solutions. However, for americium, the concentration measured in the acidic permanganate was higher than in the basic solution increasing from about 20% to 50% over the course of the experiments.

We think that the closeness of the measured actinide concentrations in Experiments 1 and 5 was somewhat coincidental. The volume of the precipitate sludge slurry used in both experiments was the same (i.e., 3 mL); however, the mass of the actinides used in Experiment 1 was approximately a factor of 8 higher. Therefore, it appears that the concentrations measured in Experiment 1 were likely near the solubility limits since the estimated recoveries of the actinides in the permanganate test solution were all less than 25% (Table 3-6). In experiment 5, the estimated recoveries of neptunium and plutonium were at least 90% and the estimated recovery of americium was approximately 50% (Table 3-9); therefore, the solubility limits (at least for neptunium and plutonium) were probably not reached. The lower recovery of americium in Experiment 5 may be related to the partial coprecipitation of americium(V) with manganese dioxide or americium(III) with iron or another impurity (see Section 3.2.1.2). However, it is clear from the results of these experiments that treatment of the simulated sludge with the acidic permanganate solution had the potential to solubilize more of the actinides than the caustic permanganate solution.

Even though the actinide concentrations measured in Experiment 1 were likely near the solubility limits, there is still potential for solubilizing a significant amount of transuranic activity in actual tank waste. Characterization data for HLW supernates which were in contact with sludge show plutonium and neptunium concentrations several orders of magnitude below the concentrations measured in Experiment 1. Hay et al. characterized a 3 L sample of HLW slurry from Tank 51 to demonstrate a low temperature dissolution process to reduce the total mass of sludge solids being fed to the Defense Waste Processing Facility. In a filtered sample of the supernate, the measured plutonium concentration was 4E-08 mol/L. The neptunium concentration was below the MDA (3E-07 mol/L).[22] King et al. also measured the concentration of plutonium in supernate from SRS waste tanks. In this study, the concentration ranged from 2E-09 to 2E-08 mol/L.[23] The values from these previous studies can be compared to average neptunium and plutonium concentrations of 1.8E-05 and 6.6E-06 mol/L, respectively, measured in the caustic permangate solution in Experiment 1. Therefore, the much higher concentrations observed in caustic permanganate solution would likely result in the dissolution of significant neptunium and plutonium from waste tank sludge above that normally observed in caustic supernate, especially if the ratio of the treatment volume to the residual sludge is increased.

3.2.1.4 Radioactive Simulant Solubility Experiments 8, 9, and 12

The majority of the simulated sludge solids remaining from the earlier treatment processes were observed to dissolve during the optimized BOAC and BOAC treatments (see Figure 2-2). However, only the dissolution efficiency of the neptunium, plutonium, and americium were evaluated in the radioactive simulant experiments. Unfortunately, the material balance closure for the optimized BOAC and BOAC contacts were very poor. The poor material balance closure was attributed to working with trace level concentrations of the actinides (which are representative of actual HLW sludge), uncertainty in the volume measurements, and primarily the nonhomogeneous nature of the precipitate slurry. When the sludge streams were split for subsequent treatment scenarios and the solubility experiments (see Figure 2-2), the fractions of liquid and solids transferred were different from the parent material to a varying extent; therefore, assuming the fractions of the liquid and solids were equal to the fractions in the parent material likely introduced a significant error in the actinide material balances. When a transfer was made, the precipitate slurry was stirred to uniformly suspend the solids; however, as the amount of solids and volume diminished, this became more difficult to accomplish and resulted in larger differences in the fractions of the solids and liquids transferred. In future experiments, the mass balance closure can be significantly improved if sample streams are not split to accommodate multiple experiments with the same starting material.

The results from Experiments 8, 9, and 12 cannot be quantified in the same manner as Experiments 1 and 5 due to the poor material balance closure; however, qualitative conclusions concerning the efficiency of the treatment scenarios can be reached based on the concentrations of neptunium, plutonium, and americium measured in the solutions from the pretreatment processes and the solubility experiments. The neptunium and plutonium concentrations measured in Experiment 8 using 0.18 M nitric acid/0.05 M sodium permanganate solution were below the MDA. The concentration of americium was quantifiable; however, the concentration was greater than an order of magnitude less than the concentration measured in Experiment 5. Therefore, it appears that the optimized BOAC treatment process was very effective in removing the neptunium, plutonium, and americium activity. The presence of 0.18 M nitric acid in the optimized BOAC contact solution likely facilitated the dissolution of the actinide elements and suggests that this cleaning reagent may promote improved actinide removal during tank cleaning.

The neptunium and plutonium concentrations measured in Experiment 9 using 10 M sodium hydroxide/0.05 M sodium permanganate solution to solubilize the actinides were also below the MDA. The americium concentration was measurable, but was also greater than an order of magnitude less than the americium concentration measured in Experiment 5. However, prior to washing a portion of the precipitate slurry from the BOAC treatment process with a 0.25 M sodium nitrate solution (to remove a majority of the oxalic acid), the concentration of the actinides in the solution from the contact of a sample of the washed sludge with an acidic permanganate solution (Experiment 12) were all above the MDA. The masses of neptunium, plutonium, and americium measured in Experiment 12 were 30 to 50% of the masses of the actinides measured in Experiment 5. The calculations are summarized in Appendix C and the results are shown in Table 3-10.

Table 3-10. Comparison of the Actinide Masses Solubilized in Experiments 5 and 12 - Radioactive Simulant Testing

Element	Sample 1	Sample 2	Sample 3
	Mass Ratio	Mass Ratio	Mass Ratio
	(g/g)	(g/g)	(g/g)
$\text{Np}_{\text{Exp 12/Exp 5}}$	0.32	0.33	0.31
$\text{Pu}_{\text{Exp 12/Exp 5}}$	0.54	0.42	0.44
$\text{Am}_{\text{Exp 12/Exp 5}}$	0.48	0.44	0.31

The masses of neptunium, plutonium, and americium recovered in the wash solutions from the BOAC and the sodium nitrate contact (used to remove oxalic acid) were compared to see if significant amounts of the actinides were removed during the sodium nitrate wash prior to Experiment 9. The mass ratios for the neptunium, plutonium, and americium in the composite solutions are shown in Table 3-11. The mass ratios in the table show that very little actinide mass was solubilized during the contact of the sludge with the 0.25 M sodium nitrate solution. Therefore, it appears that the BOAC treatment was effective in solubilizing the neptunium, plutonium, and americium in the simulated sludge; although, the BOAC treatment was not as effective as the optimized BOAC treatment process. The presence of nitric acid in the treatment process is likely the key to maximizing the dissolution of the actinide elements. Qualitatively, the neptunium, plutonium, and americium solubilized during Experiment 12 was only a small amount of the material added to the BOAC treatment process, since most of the sludge dissolved during the treatment process (section 2.2.2.5). The solubilization of significant masses of neptunium, plutonium, and americium using the acidic permanganate solution in Experiment 12 (compared to the use of a basic permanganate solution in Experiment 9) implies that the acidic permanganate solution was more effective in dissolving the actinides in the simulated sludge following the BOAC treatment.

Table 3-11. Comparison of the Actinide Masses Solubilized During the BOAC and Oxalic Acid Removal Process - Radioactive Simulant Testing

Element	Mass Ratio
	(g/g)
$Np_{NaNO_3/BOAC}$	0.019
$Pu_{NaNO_3/BOAC}$	0.034
$Am_{NaNO_3/BOAC}$	0.013

3.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

4.0 Conclusions

The results of the solubility tests conducted with non-radioactive pure phase metal reagents, binary mixtures of reagents, and PUREX tank heel simulant lead to the following conclusions.

Significantly more oxalic acid than necessary has likely been used in previous waste tank chemical cleaning campaigns for the removal of sludge heels. Optimal use of oxalate ion for sludge dissolution can be accomplished through the use of both dilute nitric acid (≤0.2 M) and dilute oxalic (0.06 M)/nitric (0.2 M) acid mixtures. This cleaning method will require larger water addition volumes, which places greater demand on evaporator operations. Cleaning reagent volume increases of approximately 100% are anticipated, although decreased water additions are anticipated during sludge washing since minimal sodium oxalate salts should be present in the sludge heel. The baseline concentrated (8 wt. %) oxalic acid reagent is not effective for the removal of nickel and mercury sludge phases. Concentrated oxalic acid is somewhat effective at removing most sludge manganese species and is very effective at removing iron and aluminum (gibbsite) sludge phases. Dilute nitric/oxalic acid mixtures are effective for the removal of most primary (Fe and Al) and secondary (Mn, Ni, and Hg) sludge phases. Dilute nitric acid is effective at removing aluminum, nickel, divalent manganese, and mercury. Dilute nitric acid should be considered for heel pre-acidification and removal of selected sludge components (aluminum, nickel, and possibly actinides, see below) prior to oxalic acid addition. A processing sequence involving dilute nitric acid followed by the recommended dilute nitric/oxalic acid mixture appears to be the optimal cleaning approach resulting in minimal oxalate additions and dissolution of sludge primary and secondary metal phases.

The results of the solubility tests conducted with co-precipitated radioactive sludge containing actinide elements (radioactive PUREX simulant) lead to the following conclusions.

Co-precipitation of the major sludge components with the actinide elements had a significant effect on the solubility of neptunium and plutonium during radioactive simulant testing. In previous studies, the oxidation of neptunium and plutonium to higher oxidation states by a caustic permanganate solution resulted in concentrations approaching their maximum values for a sludge containing only the actinide elements.[10] In the current study, the coprecipitation of plutonium, and presumably neptunium, with iron(III), uranium(VI), and manganese(IV) substantially reduced the soluble fraction of the actinides when contacted with the caustic permanganate solution. This observation is consistent with experimental studies performed for the Department of Energy's Hanford site in which the coprecipitation of plutonium with other elements under alkaline conditions reduced the plutonium solubility.[17] The small amount of the transuranic elements which were solubilized by the caustic permanganate solution indicates that the actinide concentrations were likely near the solubility limits. Even though the fractions of the actinides solubilized in Experiment 1 were lower than obtained using an acidic permanganate solution in Experiment 5 and likely near the solubility limits, there is still potential for solubilizing a significant amount of transuranic activity in actual tank waste using a caustic permanganate solution. Characterization data for HLW supernates which were in contact with sludge, show that the plutonium and neptunium concentrations in the supernate were several orders of magnitude below the concentrations measured in Experiment 1.[22,23] Therefore, the contact of HLW sludge with a caustic permanganate solution could solubilize a significant amount of plutonium or neptunium before solubility limits are reached, especially if the ratio of the treatment volume to the residual sludge is increased.

Pretreatment of the radioactive sludge simulant with a dilute (0.01 M) sodium hydroxide solution and the subsequent acidification to a pH of ~4 resulted in minimal dissolution of the actinide elements. However, when the sludge was contacted with an acidic permanganate solution, approximately 90% of the neptunium and plutonium in the radioactive simulant was solubilized. The estimated fractions of neptunium and plutonium solubilized at each sample time were also reasonably constant which implies that equilibrium conditions were obtained quickly without kinetic limitations. Only about 50% of the americium was solubilized which likely indicates some interaction with a component in the simulated sludge or manganese dioxide precipitate formed from the added permanganate. The high fractions of neptunium and plutonium solubilized when contacted with the acidic permanganate solution indicate that solubility limits were probably not reached in these tests. Based on these observations, it is clear that the treatment of waste tank sludge with an acidic permanganate solution has the potential to solubilize a higher fraction of the actinides than a caustic permanganate solution for the same volume of solution.

The pretreatment processes in which the radioactive simulant was contacted with either a 0.18 M nitric acid solution containing 0.056 M oxalic acid (optimized BOAC) or 0.9 M oxalic acid (BOAC) dissolved a majority of the sludge including the neptunium, plutonium, and americium. Following contact of the sludge sample remaining from the optimized BOAC treatment with the acidic permanganate cleaning reagent, the neptunium and plutonium concentrations were below the MDAs. Similar results were obtained when a sample of sludge from the BOAC treatment was contacted with a basic permanganate solution. However, following contact of a small portion of the sludge from the BOAC treatment process with 0.25 M sodium nitrate to remove oxalic acid, the subsequent contact of the sludge with an acidic permanganate solution resulted in neptunium, plutonium, and americium concentrations above the MDAs. It appears that the BOAC treatment was effective in solubilizing the actinides in the simulated sludge; although, not as effective as the optimized BOAC treatment process. The presence of nitric acid in the optimized process and in the permanganate solution is likely the key to maximizing the dissolution of the actinide elements.

These combined results from non-radioactive and radioactive simulant testing indicate that the optimized BOAC method is effective not only for the dissolution of bulk and most secondary sludge components, but for the dissolution of the actinide species as well.

5.0 Recommendations, Path Forward or Future Work

Solubility testing of actual tank waste sludge heel samples is recommended following the methodologies developed in this and previous reports. The goal of the testing is to identify the optimal tank heel chemical cleaning flow sheet for potential use in future tank closure operations. Specifically, the testing would target development of a cleaning flow sheet that minimizes the amounts of oxalic acid used for bulk sludge component removal and maximizes removal of actinide elements.

6.0 References

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Appendix A. Analytical Data from Non-Radioactive Simulant Testing.

Table A.1 Soluble Metal Concentrations Measured During Non-Radioactive Simulant Testing With PUREX Simulant.

	0.18 M HNO_3/0.056 M $H_2C_2O_4$ Contact Cycle (mg/L)			0.18 M HNO_3 Contact Cycle (mg/L)		
Element	1	2	3	1	2	3
Al	1.29E+03	2.62E+02	5.38E+01	1.00E+03	4.60E+02	1.15E+02
Ba	4.57E+01	9.68E+00	1.92E+00	4.58E+01	1.08E+01	2.81E+00
Ca	1.58E+02	3.22E+01	7.22E+00	1.93E+02	4.56E+01	1.15E+01
Ce	5.06E+01	1.11E+01	2.32E+00	3.78E+01	1.81E+01	6.47E+00
Cu	2.87E+01	5.40E+00	6.77E-01	2.75E+01	6.63E+00	1.23E+00
Fe	3.11E+02	1.27E+03	1.70E+03	5.77E-01	1.32E+02	1.92E+02
Mn	5.52E+02	1.48E+02	3.48E+01	6.55E+01	8.81E+01	3.33E+02
Na	1.53E+01	4.48E+00	4.50E+00	1.32E+01	5.15E+00	2.97E+00
Ni	5.11E+02	1.71E+02	4.61E+01	4.09E+02	1.35E+02	9.30E+01
Pb	2.08E+01	4.72E+00	<2.02E+00	5.13E+00	1.02E+01	6.58E+00
Zn	6.13E+01	1.29E+01	2.71E+00	5.86E+01	1.45E+01	3.89E+00
Hg	1.12E+02	4.81E+01	2.89E+01	1.50E+01	1.19E+02	8.94E+01

	0.952 M $H_2C_2O_4$ Contact Cycle (mg/L)		
Element	1	2	3
Al	1.38E+03	3.71E+02	1.00E+02
Ba	5.72E+01	1.59E+01	4.33E+00
Ca	3.96E+02	1.03E+02	4.12E+01
Ce	2.49E+01	5.41E+00	2.34E+00
Cu	7.43E+00	4.86E+00	3.23E+00
Fe	4.54E+03	1.92E+03	5.65E+02
Mn	3.96E+02	1.91E+02	9.91E+01
Na	3.23E+02	8.38E+01	2.36E+01
Ni	2.41E+01	8.43E+00	5.06E+00
Pb	1.41E+01	6.15E+00	3.78E+00
Zn	1.07E+01	3.50E+00	1.67E+00
Hg	3.40E+01	2.68E+01	1.91E+01

Table A.2 Soluble Metal Concentrations Measured During Non-Radioactive Simulant Testing With Pure Reagents.

	Metal Concentrations (mg/L) Observed with Indicated Reagents					
Cycle	MnO	MnO_2	Fe_2O_3	$Al(OH)_3$	$Ni(OH)_2$	Cleaning Reagent
1	3.71E+03	2.38E+03	8.67E+02	1.21E+03	3.95E+03	0.056 M $H_2C_2O_4$/0.18 M HNO_3
2	4.46E+03	2.77E+03	1.55E+03	9.31E+02	7.91E+02	0.056 M $H_2C_2O_4$/0.18 M HNO_3
3	3.90E+03	2.88E+03	1.75E+03	5.98E+02	2.15E+01	0.056 M $H_2C_2O_4$/0.18 M HNO_3
1	3.52E+03	1.31E+02	6.05E+01	6.18E+02	3.84E+03	0.18 M HNO_3
2	4.25E+03	2.47E+02	1.04E+02	5.03E+02	4.96E+03	0.18 M HNO_3
3	3.26E+03	2.73E+02	1.21E+02	3.89E+02	2.01E+03	0.18 M HNO_3
1	8.22E+02	9.52E+02	3.41E+03	1.58E+03	4.80E+00	0.92 M $H_2C_2O_4$
2	7.15E+02	8.97E+02	8.42E+02	4.95E+02	3.99E+00	0.92 M $H_2C_2O_4$
3	7.00E+02	8.93E+02	1.98E+02	1.28E+02	4.11E+00	0.92 M $H_2C_2O_4$

Appendix B Analytical Data from Radioactive Simulant Experimental Studies.

Measured Actinide Concentrations

The activities of neptunium-237, plutonium-238, and americium-241 measured in the samples from each solubility experiment are provided in Tables B.1-B.3.

Table B.1. Actinide Activities in Three Day Samples.

Experiment	Neptunium-237		Plutonium-238		Americium-241	
Number	Activity	1 sigma	Activity	1 sigma	Activity	1 sigma
	(dpm/mL)	(%)	(dpm/mL)	(%)	(dpm/mL)	(%)
1	1.50E+03	7.61	4.18E+06	5.00%	3.18E+05	5.00
5	4.79E+03	5.00	3.79E+06	5.92%	9.98E+05	5.00
8	< 2.60E+02	MDA	2.15E+05	24.3%	6.14E+04	5.00
9	< 2.27E+02	MDA	< 6.14E+04	MDA	5.84E+04	5.00
12	1.53E+03	8.49	2.06E+06	8.58%	4.83E+05	5.00

MDA – minimum detection of analysis

Table B.2. Actinide Activities in Seven Day Samples.

Experiment	Neptunium-237		Plutonium-238		Americium-241	
Number	Activity	1 sigma	Activity	1 sigma	Activity	1 sigma
	(dpm/mL)	(%)	(dpm/mL)	(%)	(dpm/mL)	(%)
1	1.67E+03	7.10%	3.41E+06	5.43%	2.67E+05	5.00%
5	4.02E+03	5.12%	3.81E+06	6.04%	9.06E+05	5.00%
8	< 2.49E+02	MDA	< 4.85E+05	MDA	5.88E+04	5.00%
9	2.33E+02	MDA	< 6.18E+04	MDA	5.60E+04	5.00%
12	1.34E+03	9.09%	1.57E+06	10.2%	3.98E+05	5.00%

MDA – minimum detection of analysis

Table B.3. Actinide Activities in Fifteen Day Samples.

Experiment	Neptunium-237		Plutonium-238		Americium-241	
Number	Activity	1 sigma	Activity	1 sigma	Activity	1 sigma
	(dpm/mL)	(%)	(dpm/mL)	(%)	(dpm/mL)	(%)
1	1.93E+03	6.65%	3.52E+06	5.50%	2.21E+05	5.00%
5	4.51E+03	5.00%	4.06E+06	5.70%	9.45E+05	5.00%
8	< 2.62E+02	MDA	2.64E+05	21.4%	5.62E+04	5.00%
9	< 2.36E+02	MDA	< 1.23E+05	MDA	5.47E+04	5.00%
12	1.41E+03	8.22%	1.77E+06	9.45%	2.72E+05	5.00%

MDA – minimum detection of analysis

The activities of neptunium-237, plutonium-238, and americium-241 measured in the solutions collected during the sludge treatment processes are provided in Tables B.4.

Table B.4. Actinide Activities in Solutions Collected during Sludge Treatment Processes.

Name	Activity	1 sigma	Activity	1 sigma	Activity	1 sigma
	(dpm/mL)	(%)	(dpm/mL)	(%)	(dpm/mL)	(%)
Sludge Washing	< 2.18E+02	MDA	< 3.16E+05	MDA	< 1.02E+02	MDA
Acidification	< 2.15E+02	MDA	< 3.21E+05	MDA	3.96E+02	8.95
Optimized BOAC	8.32E+03	5.00	1.07E+07	10.80	4.18E+06	5.00
BOAC	1.15E+04	5.00	1.69E+07	5.00	4.81E+06	5.00
Oxalic Acid Removal	4.69E+02	17.8	1.22E+06	7.93	1.29E+05	5.00

MDA – minimum detection of analysis

To calculate the concentrations of neptunium-237, plutonium-238, and americium-241 in the solutions from the solubility experiments and the solutions from the sludge treatment processes, the activities from the GPHA were converted to appropriate concentration units using the specific activities given in Table B.5.

Table B.5. Specific Activities of Selected Actinide Isotopes.

Isotope	Specific Activity
	(dpm/g)
Neptunium-237	1.56E+09
Plutonium-238	3.81E+13
Americium-241	7.63E+12

For the solubility experiments, the molar concentrations of neptunium, total plutonium, and americium were calculated using Equations B.1-B.3, respectively. The equations take into account the sample dilution which resulted from the addition of 5 M nitric acid during sample preparation (Table 2-10).

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

$$\mathrm{Pu}\left(\frac{\mathrm{mol}}{\mathrm{L}}\right)=\left(\frac{{}^{238}\mathrm{Pu}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{238}\mathrm{Pu}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{{}^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}\ (\mathrm{g})}{{}^{238}\mathrm{Pu}_{\mathrm{initial}}\ (\mathrm{g})}\right)\left(\frac{1\ \mathrm{mole\ Pu}}{238.80\ \mathrm{g\ Pu}}\right)\left(\frac{1\ \mathrm{mL} + \mathrm{vol}\ 5\ \mathrm{M\ HNO_3(mL)}}{1\ \mathrm{mL}}\right) \tag{B.2}$$

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

The atomic mass of the total plutonium was calculated from the masses of weapons grade plutonium and plutonium-238 added to the acidic PUREX waste solution (Table 2-10) and by assuming the isotopic concentrations of weapons grade plutonium are nominally 94 wt % plutonium-239 and 6 wt %

plutonium-240. The molar concentrations of neptunium, total plutonium, and americium in the solubility solution samples are provided in Tables B.6-B.8. Less than reportable values were calculated for the analyses which were reported as below the minimum detection of the GPHA and are provided in the tables.

Table B.6. Actinide Concentrations in Three Day Samples.

Experiment	Neptunium		Total Plutonium		Americium	
Number	Conc.	1 sigma	Conc.	1 sigma	Conc.	1 sigma
	(mol/L)	(%)	(mol/L)	(%)	(mol/L)	(%)
1	1.62E-05	7.61	7.39E-06	5.00%	6.92E-07	5.00
5	1.94E-05	5.00	2.51E-06	5.92%	8.14E-07	5.00
8	< 1.05E-06	MDA	1.43E-07	24.30%	5.01E-08	5.00
9	< 2.46E-06	MDA	< 1.09E-07	MDA	1.27E-07	5.00
12	6.21E-06	8.49	1.37E-06	8.58%	3.94E-07	5.00

MDA – minimum detection of analysis

Table B.7 Actinide Concentrations in Seven Day Samples.

Experiment	Neptunium		Total Plutonium		Americium	
Number	Conc.	1 sigma	Conc.	1 sigma	Conc.	1 sigma
	(mol/L)	(%)	(mol/L)	(%)	(mol/L)	(%)
1	1.81E-05	7.10	6.03E-06	5.43%	5.81E-07	5.00
5	1.63E-05	5.12	2.53E-06	6.04%	7.39E-07	5.00
8	< 1.01E-06	MDA	< 3.22E-07	MDA	4.80E-08	5.00
9	< 2.52E-06	MDA	< 1.09E-07	MDA	1.22E-07	5.00
12	5.44E-06	9.09	1.04E-06	10.20%	3.25E-07	5.00

MDA – minimum detection of analysis

Table B.8. Actinide Concentrations in Fifteen Day Samples.

Experiment	Neptunium		Total Plutonium		Americium	
Number	Conc.	1 sigma	Conc.	1 sigma	Conc.	1 sigma
	(mol/L)	(%)	(mol/L)	(%)	(mol/L)	(%)
1	2.09E-05	6.65	6.22E-06	5.50%	4.81E-07	5.00
5	1.83E-05	5.00	2.69E-06	5.70%	7.71E-07	5.00
8	< 1.06E-06	MDA	1.75E-07	21.4%	4.58E-08	5.00
9	< 2.55E-06	MDA	2.17E-07	MDA	1.19E-07	5.00
12	5.72E-06	8.22	1.17E-06	9.45%	2.22E-07	5.00

MDA – minimum detection of analysis

For the solutions removed during the sludge treatment processes, the actinide concentrations (in g/L) were calculated using Equations B.4-B.6, respectively. The equations take into account the sample dilution which resulted from the addition of 5 M nitric acid during sample preparation (Table 2-9).

$$\mathrm{Np}\left(\frac{\mathrm{g}}{\mathrm{L}}\right)=\left(\frac{{}^{237}\mathrm{Np}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{237}\mathrm{Np}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mL} + \mathrm{vol}\ 5\ \mathrm{M}\ \mathrm{HNO_3(mL)}}{1\ \mathrm{mL}}\right) \tag{B.4}$$

$$\mathrm{Pu}\left(\frac{\mathrm{g}}{\mathrm{L}}\right)=\left(\frac{{}^{238}\mathrm{Pu}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{238}\mathrm{Pu}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{{}^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}(\mathrm{g})}{{}^{238}\mathrm{Pu}_{\mathrm{initial}}(\mathrm{g})}\right)\left(\frac{1\ \mathrm{mL} + \mathrm{vol}\ 5\ \mathrm{M}\ \mathrm{HNO_3(mL)}}{1\ \mathrm{mL}}\right) \tag{B.5}$$

$$\mathrm{Am}\left(\frac{\mathrm{g}}{\mathrm{L}}\right)=\left(\frac{{}^{241}\mathrm{Am}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{241}\mathrm{Am}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{1\ \mathrm{mL} + \mathrm{vol}\ 5\ \mathrm{M}\ \mathrm{HNO_3(mL)}}{1\ \mathrm{mL}}\right) \tag{B.6}$$

The concentrations of neptunium, total plutonium, and americium in the solutions removed during the sludge treatment processes are provided in Table B.9. Less than reportable values were calculated for the analyses which were reported as below the minimum detection of the GPHA and are provided in the table.

Table B.9. Actinide Concentrations in Solutions Collected during Sludge Treatment Processes.

Solution	Neptunium		Plutonium		Americium	
Name	Conc.	1 sigma	Conc.	1 sigma	Conc.	1 sigma
	(g/L)	(%)	(g/L)	(%)	(g/L)	(%)
Sludge Washing	< 2.10E-04	MDA	< 5.00E-05	MDA	< 2.01E-08	MDA
Acidification	< 2.07E-04	MDA	< 5.08E-05	MDA	7.79E-08	8.95
Optimized BOAC	8.00E-03	5.00	1.69E-03	10.80	8.22E-04	5.00
BOAC	1.11E-02	5.00	2.68E-03	5.00	9.46E-04	5.00
Oxalic Acid Removal	4.51E-04	17.8	1.93E-04	7.93	2.54E-05	5.00

MDA – minimum detection of analysis

The total volume of solution collected during each sludge treatment process is provided in Table B.10.

Table B.10. Volume of Solution Collected during Sludge Treatment Processes.

Solution Name	Volume (mL)
Sludge Washing	500
Acidification	340
Optimized BOAC	1713
BOAC	2162
Oxalic Acid Removal	815

Appendix C. Analysis of Data from Radioactive Sludge Simulant Treatment Processes and Solubility Experiments.

Estimated Actinide Solubility in Experiment 1

The total volume of the neutralized PUREX waste solution was 168 mL. The volume was calculated based on the sum of the initial volume (including the solution of the primary sludge components and the volume of actinide materials) (115 mL), the volume of 19.4 M sodium hydroxide added during neutralization (51 mL), and the water produced during neutralization (2 mL). A 3 mL aliquot of the neutralized waste solution was used in solubility Experiment 1; therefore the fraction of the neptunium, plutonium, and americium used in the experiment was 0.018. The mass of the actinides added to the sludge (from Table 3-5) and the amount used in Experiment 1 (based on the mass fraction) are provided in Table C.1.

Table C.1. Mass of Actinides Used in Experiment 1.

Element	Mass in Sludge	Mass Used in Exp. 1
	(g)	(g)
Neptunium	7.28E-02	1.30E-03
Plutonium	1.06E-02	1.89E-04
Americium	5.40E-03	9.64E-05

To estimate the fraction of the mass of each actinide element solubilized in Experiment 1, the concentrations were initially calculated using the measured activities from Tables B.1-B.3 and the specific activities from Table B.5 (Equations C.1-C.3). The equations take into account the sample dilution which resulted from the addition of 5 M nitric acid during sample preparation (Table 2-9). The calculations are summarized in Table C.2.

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

$$\mathrm{Pu}\left(\frac{\mathrm{g}}{\mathrm{L}}\right)=\left(\frac{{}^{238}\mathrm{Pu}\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}{{}^{238}\mathrm{Pu}_{\mathrm{Sp\ Act}}\left(\frac{\mathrm{dpm}}{\mathrm{g}}\right)}\right)\left(1000\frac{\mathrm{mL}}{\mathrm{L}}\right)\left(\frac{{}^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}(\mathrm{g})}{{}^{238}\mathrm{Pu}_{\mathrm{initial}}(\mathrm{g})}\right)\left(\frac{1\ \mathrm{mL} + \mathrm{vol}\ 5\ \mathrm{M}\ \mathrm{HNO_3(mL)}}{1\ \mathrm{mL}}\right) \tag{C.2}$$

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

Table C.2. Actinide Concentrations Measured During Experiment 1.

Element	Sample 1	Sample 2	Sample 3
	(g/L)	(g/L)	(g/L)
Neptunium	3.85E-03	4.28E-03	4.95E-03
Plutonium	1.77E-03	1.44E-03	1.49E-03
Americium	1.67E-04	1.40E-04	1.16E-04

The masses of neptunium, plutonium, and americium solubilized in Experiment 1 were estimated using the concentrations from Table C.2, the volume of sludge (3 mL) and the volume of 10 M sodium hydroxide/0.05 M sodium permanganate (30 mL) used in the experiment, and the volume of each sample removed (2.5 mL). Equations C.4-C.6 summarize the calculations for neptunium. The estimated mass of each actinide in solution for each sample time is provided in Table C.3.

$$\text{Mass}_{\text{Np}_1}(\text{g}) = \left(\text{C}_{\text{Np}_1}\frac{\text{g}}{\text{L}}\right)(33\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) \tag{C.4}$$

$$\text{Mass}_{\text{Np}_2}(\text{g}) = \left(\text{C}_{\text{Np}_2}\frac{\text{g}}{\text{L}}\right)(33\text{ mL} - 2.5\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) + \left(\text{C}_{\text{Np}_1}\frac{\text{g}}{\text{L}}\right)(2.5\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) \tag{C.5}$$

$$\text{Mass}_{\text{Np}_3}(\text{g}) = \left(\text{C}_{\text{Np3}}\frac{\text{g}}{\text{L}}\right)(33\text{ mL} - 2.5\text{ mL - }2.5\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) + \left(\text{C}_{\text{Np}_1}\frac{\text{g}}{\text{L}}\right)(2.5\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) + \left(\text{C}_{\text{Np}_2}\frac{\text{g}}{\text{L}}\right)(2.5\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right) \tag{C.6}$$

Table C.3. Actinide Mass Measured During Experiment 1.

Element	Sample 1	Sample 2	Sample 3
	(g)	(g)	(g)
Neptunium	1.27E-04	1.40E-04	1.59E-04
Plutonium	5.82E-05	4.83E-05	4.96E-05
Americium	5.50E-06	4.69E-06	4.01E-06

The fraction of the mass solubilized at each sample time is calculated as a percentage of the total mass of the actinide used in the experiment (equation C.7) using the data in Tables C.1 and C.3. The calculated percentages are presented in Table 3-6.

$$\text{F}_{\text{An}_\text{i}} = \left(\frac{\text{M}_{\text{An}_\text{i}}}{\text{M}_{\text{An}_{\text{Exp}}}}\right)100 \tag{C.7}$$

Uncertainty Analysis for the Fraction of the Actinides Solubilized in Experiment 1

The one sigma uncertainties in the fraction of the actinides (i.e., neptunium, plutonium, and americium) solubilized in Experiment 1 (using a 10 M sodium hydroxide solution containing 0.05 M sodium permanganate) were estimated using propagation of errors techniques. To perform the analysis, the uncertainties in the actinide concentration measurements and the volumes of the neutralized PUREX waste simulant, 3 mL sludge sample (used for the solubility experiments), and the 2.5 mL solubility samples (removed periodically during the experiment) were assumed to dominate the uncertainty analysis. The uncertainties in other measurements (or analyses) were considered small compared to the uncertainties in these values. The 1 sigma uncertainty in the actinide concentration (i.e., activity) measurements from the solubility experiments are given in Tables B.1-B.3. The 1 sigma uncertainties assumed for the volume measurements and calculated variances are provided in Table C.4.

Table C.4. Volume Uncertainties in Radioactive Solubility Experiments.

Description	Volume	1 Sigma Uncertainty	Variance
	(mL)	(%)	(mL^2)
Neutralized PUREX Waste Simulant	168	5	70.6
Sludge Samples	3.0	5	0.023
Solubility Samples	2.5	20	0.25

The fraction of the actinides solubilized at each sample time ($\mathrm{F}_{\mathrm{An}_i}$) was calculated from equation C.7 where $\mathrm{M}_{\mathrm{An}_i}$ is the mass of the actinide solubilized and $\mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}}$ is the total mass of the actinide which was used in Experiment 1. To calculate the uncertainty in the fractions solubilized, an expression for the variance ($V_{F_{An_i}}$) in the fraction of the actinide solubilized can be derived using equation C.8,

$$V_{F_{An_i}} = \left(\frac{\partial \mathrm{F}_{\mathrm{An}_i}}{\partial \mathrm{M}_{\mathrm{An}_i}}\right)^2 V_{M_{An_i}} + \left(\frac{\partial \mathrm{F}_{\mathrm{An}_i}}{\partial \mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}}}\right)^2 V_{M_{An\,Exp}} \tag{C.8}$$

where $V_{M_{An_i}}$ and $V_{M_{An\,Exp}}$ are the variances in the mass of the actinide solubilized and the total mass of the actinide used in the solubility experiment, respectively. The masses of the actinides used in Experiment 1 were calculated from the mass of each actinide added to the sludge (M_{An}) using the ratio of the volume of the sludge sample ($\mathrm{V}_{\mathrm{sample}}$) to the total volume of the sludge ($\mathrm{V}_{\mathrm{sludge}}$) (equation C.9).

$$\mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}} = \mathrm{M}_{\mathrm{An}} \frac{\mathrm{V}_{\mathrm{sample}}}{\mathrm{V}_{\mathrm{sludge}}} \tag{C.9}$$

The equation for the variances in the masses of the actinides used in Experiment 1 are derived using equation C.10 and subsequently calculated using equation C.11 with data from Tables 3-5 and C.4. The calculated variances are provided in Table C.5.

$$V_{M_{AnExp}} = \left(\frac{\partial \mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}}}{\partial \mathrm{V}_{\mathrm{sample}}}\right)^2 V_{V_{sample}} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}}}{\partial \mathrm{V}_{\mathrm{sludge}}}\right)^2 V_{V_{sludge}} \tag{C.10}$$

$$V_{M_{An\,Exp}} = \left(\frac{\mathrm{M}_{\mathrm{An}}}{\mathrm{V}_{\mathrm{sludge}}}\right)^2 V_{V_{sample}} + \left(-\frac{\mathrm{M}_{\mathrm{An}}\mathrm{V}_{\mathrm{sample}}}{\mathrm{V}_{\mathrm{sludge}}^2}\right)^2 V_{V_{sludge}} \tag{C.11}$$

Table C.5. Variances in the Total Masses of the Actinides Used in Experiment 1.

Element	$V_{M_{An\,Exp}}$
	(g^2)
Np	8.45E-09
Pu	1.79E-10
Am	4.65E-11

To calculate the variances in the masses of the actinides solubilized in Experiment 1, the variance in the concentrations of the actinides solubilized are initially calculated. The concentrations of neptunium, plutonium, and americium solubilized in Experiment 1 were calculated using equations C.1-C.3. The variances in the actinide concentrations ($V_{An_{\left(\frac{g}{L}\right)}}$) are given by equation C.12,

$$V_{An_{\left(\frac{g}{L}\right)}} = \left(\frac{\mathrm{dAn}_{\left(\frac{\mathrm{g}}{\mathrm{L}}\right)}}{\mathrm{dAn}_{\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}} \right)^2 V_{An_{\left(\frac{dpm}{mL}\right)}} \tag{C.12}$$

where $\mathrm{An}_{\left(\frac{\mathrm{dpm}}{\mathrm{mL}}\right)}$ is the measured actinide activity (Tables B.1-B.3) and $V_{An_{\left(\frac{dpm}{mL}\right)}}$ is the variance in the measured activity. The variance in the measured activity is calculated from the 1 sigma uncertainties given in Tables B.1-B.3 using the relationship between the variance and the standard deviation ($s_{An_{\left(\frac{dpm}{mL}\right)}}$) of the measured activities (equation C.13).

$$V_{An_{\left(\frac{dpm}{mL}\right)}} = s_{An_{\left(\frac{dpm}{mL}\right)}}{}^2 \tag{C.13}$$

The equations derived to calculate the variances in the masses of the actinides solubilized in Experiment 1 are shown as equations C.14-C.16.

$$V_{Np_{\left(\frac{g}{L}\right)}} = \left[\left(\frac{1}{{}^{237}\mathrm{Np}_{\mathrm{Sp\ Act}}} \right) (1000) \left(\frac{1+\mathrm{vol\ 5\ M\ HNO_3}}{1} \right) \right]^2 V_{Np_{\left(\frac{dpm}{mL}\right)}} \tag{C.14}$$

$$V_{Pu_{\left(\frac{g}{L}\right)}} = \left[\left(\frac{1}{{}^{238}\mathrm{Pu}_{\mathrm{Sp\ Act}}} \right) (1000) \left(\frac{{}^{\mathrm{total}}\mathrm{Pu}_{\mathrm{initial}}}{{}^{238}\mathrm{Pu}_{\mathrm{initial}}} \right) \left(\frac{1+\mathrm{vol\ 5\ M\ HNO_3}}{1} \right) \right]^2 V_{Pu_{\left(\frac{dpm}{mL}\right)}} \tag{C.15}$$

$$V_{Am_{\left(\frac{g}{L}\right)}} = \left[\left(\frac{1}{{}^{241}\mathrm{Am}_{\mathrm{Sp\ Act}}} \right) (1000) \left(\frac{1+\mathrm{vol\ 5\ M\ HNO_3}}{1} \right) \right]^2 V_{Am_{\left(\frac{dpm}{mL}\right)}} \tag{C.16}$$

The calculated variances for each sample time are given in Table C.6.

Table C.6. Variances in the Concentrations of the Actinides Solubilized in Experiment 1.

Element	Sample	$V_{An_{\left(\frac{g}{L}\right)}}$
	(day)	(g^2/L^2)
Np	3	8.57E-08
Np	7	9.24E-08
Np	15	1.08E-07
Pu	3	7.79E-09
Pu	7	6.11E-09
Pu	15	6.68E-09
Am	3	6.95E-11
Am	7	4.90E-11
Am	15	3.36E-11

The equations used to calculate the mass of the actinides solubilized in Experiment 1 are illustrated for neptunium by equations C.4-C.6. More general expressions for the calculation of the mass of neptunium, plutonium, or americium at the 3, 7, and 15 day sample times are shown as equations C.17-C.19, respectively.

$$\mathrm{M}_{\mathrm{An}_1}=\left(\mathrm{C}_{\mathrm{An}_1}\right)\left(\mathrm{V}_{\mathrm{sample}}+\mathrm{V}_{\mathrm{MnO}_4^-}\right)\left(\frac{1}{1000}\right) \tag{C.17}$$

$$\mathrm{M}_{\mathrm{An}_2}=\left(\mathrm{C}_{\mathrm{An}_2}\right)\left(\mathrm{V}_{\mathrm{sample}}+\mathrm{V}_{\mathrm{MnO}_4^-}-\mathrm{V}_{\mathrm{sol\ sample}_1}\right)\left(\frac{1}{1000}\right)+\left(\mathrm{C}_{\mathrm{An}_1}\right)(\mathrm{V}_{\mathrm{sol\ sample}_1})\left(\frac{1}{1000}\right) \tag{C.18}$$

$$\mathrm{M}_{\mathrm{An}_3}=\left(\mathrm{C}_{\mathrm{An}_3}\right)\left(\mathrm{V}_{\mathrm{sample}}+\mathrm{V}_{\mathrm{MnO}_4^-}-\mathrm{V}_{\mathrm{sol\ sample}_1}-\mathrm{V}_{\mathrm{sol\ sample}_2}\right)\left(\frac{1}{1000}\right)+\left(\mathrm{C}_{\mathrm{An}_1}\right)(\mathrm{V}_{\mathrm{sol\ sample}_1})\left(\frac{1}{1000}\right) \tag{C.19}$$
$$+\left(\mathrm{C}_{\mathrm{An}_2}\right)\left(\mathrm{V}_{\mathrm{sol\ sample}_2}\right)\left(\frac{1}{1000}\right)$$

Equations used to derive expression for the variances in the mass of the actinides solubilized at each sample time are shown as equations C.20-C-22.

$$V_{M_{An_1}}=\left(\frac{\partial \mathrm{M}_{\mathrm{An}_1}}{\partial \mathrm{C}_{\mathrm{An}_1}}\right)^2 V_{C_{An_1}}+\left(\frac{\partial \mathrm{M}_{\mathrm{An}_1}}{\partial \mathrm{V}_{\mathrm{sample}}}\right)^2 V_{sample} \tag{C.20}$$

$$V_{M_{An_2}}=\left(\frac{\partial \mathrm{M}_{\mathrm{An}_2}}{\partial \mathrm{C}_{\mathrm{An}_2}}\right)^2 V_{C_{An_2}}+\left(\frac{\partial \mathrm{M}_{\mathrm{An}_2}}{\partial \mathrm{V}_{\mathrm{sample}}}\right)^2 V_{sample}+\left(\frac{\partial \mathrm{M}_{\mathrm{An}_2}}{\partial \mathrm{V}_{\mathrm{sol\ sample}_1}}\right)^2 V_{sol\ sample_1}+\left(\frac{\partial \mathrm{M}_{\mathrm{An}_2}}{\partial \mathrm{C}_{\mathrm{An}_1}}\right)^2 V_{C_{An_1}} \tag{C.21}$$

$$V_{M_{An_3}} = \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{C}_{\mathrm{An}_3}}\right)^2 V_{C_{An_3}} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{V}_{\mathrm{sample}}}\right)^2 V_{sample} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{V}_{\mathrm{sol\ sample}_1}}\right)^2 V_{sol\ sample_1} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{V}_{\mathrm{sol\ sample}_2}}\right)^2 V_{sol\ sample_2} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{C}_{\mathrm{An}_1}}\right)^2 V_{C_{An_1}} + \left(\frac{\partial \mathrm{M}_{\mathrm{An}_3}}{\partial \mathrm{C}_{\mathrm{An}_2}}\right)^2 V_{C_{An_2}} \tag{C.22}$$

The expressions for the variances in the mass of the actinides solubilized at each sample time derived using equations C.20-C.22 are shown as equations C.23-C.25.

$$V_{M_{An_1}} = \left(\frac{\left(\mathrm{V}_{\mathrm{sample}} + \mathrm{V}_{\mathrm{MnO}_4^-}\right)}{1000}\right)^2 V_{C_{An_1}} + \left(\frac{\mathrm{C}_{\mathrm{An}_1}}{1000}\right)^2 V_{sample} \tag{C.23}$$

$$V_{M_{An_2}} = \left(\frac{\mathrm{V}_{\mathrm{sample}} + \mathrm{V}_{\mathrm{MnO}_4^-} - \mathrm{V}_{\mathrm{sol\ sample}_1}}{1000}\right)^2 V_{C_{An_2}} + \left(\frac{\mathrm{C}_{\mathrm{An}_2}}{1000}\right)^2 V_{sample} + \left(\frac{-\mathrm{C}_{\mathrm{An}_2} + \mathrm{C}_{\mathrm{An}_1}}{1000}\right)^2 V_{sol\ sample_1} + \left(\frac{\mathrm{V}_{\mathrm{sol\ sample}_1}}{1000}\right)^2 V_{C_{An_1}} \tag{C.24}$$

$$V_{M_{An_3}} = \left(\frac{\mathrm{V}_{\mathrm{sample}} + \mathrm{V}_{\mathrm{MnO}_4^-} - \mathrm{V}_{\mathrm{sol\ sample}_1} - \mathrm{V}_{\mathrm{sol\ sample}_2}}{1000}\right)^2 V_{C_{An_3}} + \left(\frac{\mathrm{C}_{\mathrm{An}_3}}{1000}\right)^2 V_{sample} + \left(\frac{-\mathrm{C}_{\mathrm{An}_3} + \mathrm{C}_{\mathrm{An}_1}}{1000}\right)^2 V_{sol\ sample_1} + \left(-\frac{\mathrm{C}_{\mathrm{An}_s} + \mathrm{C}_{\mathrm{An}_2}}{1000}\right)^2 V_{sol\ sample_2} + \left(\frac{\mathrm{V}_{\mathrm{sol\ sample}_1}}{1000}\right)^2 V_{C_{An_1}} + \left(\frac{\mathrm{V}_{\mathrm{sol\ sample2}}}{1000}\right)^2 V_{C_{An_2}} \tag{C.25}$$

The calculated variances for each sample time are given in Table C.7.

Table C.7. Variances in the Masses of the Actinides Solubilized in Experiment 1.

Element	Sample	$V_{M_{An_i}}$
	(day)	(g^2)
Np	3	9.36E-11
Np	7	8.70E-11
Np	15	8.70E-11
Pu	3	8.55E-12
Pu	7	5.81E-12
Pu	15	5.40E-12
Am	3	7.63E-14
Am	7	4.66E-14
Am	15	2.81E-14

Now that variances in the masses of the actinides solubilized at each sample time and the total masses of the actinides used in Experiment 1 have been calculated, equation C.8 was used to derive the expression for the variance in the fraction of the actinides solubilized in the experiment at each sample time (equation C.26).

$$V_{F_{An_i}} = \left(\frac{100}{\mathrm{M}_{\mathrm{An}_{\mathrm{Exp}}}}\right)^2 V_{M_{An_i}} + \left(\frac{-100\mathrm{M}_{\mathrm{An}_\mathrm{i}}}{\mathrm{M}^2_{\mathrm{An}_{\mathrm{Exp}}}}\right)^2 V_{M_{Exp}} \tag{C.26}$$

The fraction of the actinides solubilized and the calculated variances, one sigma uncertainties ($s_{F_{An_i}}$) (based on the relationship between the variance and the standard deviation), and the relative standard deviations ($100\left(\frac{s_{F_{An_i}}}{\mathrm{F}_{\mathrm{F}_{\mathrm{An}_\mathrm{i}}}}\right)$) are provided in Table C.8 for each sample time.

Table C.8. Uncertainty in the Fraction of the Actinides Solubilized in Experiment 1.

Element	Sample Time	$\mathrm{F}_{\mathrm{An}_\mathrm{i}}$	$V_{F_{An_i}}$	$s_{F_{An_i}}$	$100\left(\frac{s_{F_{An_i}}}{\mathrm{F}_{\mathrm{F}_{\mathrm{An}_\mathrm{i}}}}\right)$
	(day)	(%)	(%^{2})	(%)	
Np	3	9.8	1.0	1.0	10
Np	7	11	1	1	9.7
Np	15	11	1	1	9.7
Pu	3	31	7	3	8.7
Pu	7	26	5	2	8.7
Pu	15	26	5	2	8.7
Am	3	5.7	0.2	0.5	8.7
Am	7	4.9	0.2	0.4	8.4
Am	15	4.9	0.2	0.4	8.4

Estimated Actinide Solubility in Experiment 5

The total volume of the neutralized PUREX waste solution was 168 mL; however, a 20 mL aliquot of the slurry was removed for use in Experiment 1 leaving a volume 148 mL. The fraction of the neptunium, plutonium, and americium remaining and subsequently washed with the 0.1 M sodium hydroxide solution was 0.88. The mass of the actinides added to the sludge (from Table 3-5) and the amount transferred to the washing process (based on the mass fraction) are provided in Table C.9.

Table C.9. Mass of Actinides to Sludge Washing.

Element	Mass in Sludge	Mass to Sludge Washing
	(g)	(g)
Neptunium	7.28E-02	6.41E-02
Plutonium	1.06E-02	9.32E-03
Americium	5.40E-03	4.76E-03

The concentrations of the actinides in the sludge wash solution (Table B.9) were below the MDA; however the MDA values were used to calculate a lower limit for the masses of neptunium, plutonium, and americium which remained in the washed sludge. The percentage of each actinide in the washed sludge was estimated using the upper limit on the actinide concentrations, the volume of sludge wash solution (Table B.10), and the total mass of each actinide transferred to the sludge washing process (Table C.9). The calculations are summarized in Table C.10.

Table C.10. Percentage of Actinides in Washed Sludge.

Element	Mass in Wash Solution	Percentage in Washed Sludge
	(g)	(%)
Neptunium	< 1.05E-04	> 99.8
Plutonium	< 2.50E-05	> 99.7
Americium	< 1.00E-08	100

The estimated volume of sludge after washing with 0.01 M sodium hydroxide was 268 mL (Table 2-6). A 125 mL aliquot of the slurry was subsequently used in the acidification pretreatment process. Therefore, the estimated fraction of the neptunium, plutonium, and americium transferred to the acidification process was 0.47. The mass of the actinides transferred to the acidification pretreatment process was estimated as the difference in the mass of the actinides used in the sludge washing processes (Table C.9) and the mass of the actinides solubilized in the wash solution (Table C.10) multiplied by this fraction. The concentrations of neptunium and plutonium in the supernate removed during the acidification pretreatment were below the MDA (Table B.9); however the MDA values were used to calculate a lower limit for the masses which remained in the acidified sludge. The percentage of each actinide in the acidified sludge was estimated using the upper limit on the neptunium and plutonium concentrations, the measured americium concentration (Table B.9), the volume of acidified supernate removed (Table B.10), and the total mass of each actinide transferred to the pretreatment process. The calculations are summarized in Table C.11.

Table C.11. Mass of Actinides Transferred to the Acidification Process.

Element	Mass to Acidification	Mass in Supernate	Percentage in Acidified Sludge
	(g)	(g)	(%)
Neptunium	2.98E-02	<7.03E-05	> 99.8
Plutonium	4.34E-03	<1.73E-05	> 99.6
Americium	2.22E-03	2.65E-08	100

To estimate the fraction of the mass of each actinide element solubilized in Experiment 5, the concentrations were initially calculated using the measured activities from Tables B.1-B.3 and the specific activities from Table B.5 using Equations C.1-C.3. The calculations are summarized in Table C.12.

Table C.12. Actinide Concentrations Measured During Experiment 5.

Element	Sample 1	Sample 2	Sample 3
	(g/L)	(g/L)	(g/L)
Neptunium	4.61E-03	3.87E-03	4.34E-03
Plutonium	6.00E-04	6.03E-04	6.43E-04
Americium	1.96E-04	1.78E-04	1.86E-04

The masses of neptunium, plutonium, and americium solubilized in Experiment 5 were estimated using the concentrations from Table C.12, the volume of sludge (3 mL) and the volume of 0.18 M nitric acid/0.05 M sodium permanganate (30 mL) used in the experiment, and the volume of each sample removed (2.5 mL). Equations C.4-C.6 illustrate the same calculations for neptunium for Experiment 1. The estimated mass of each actinide in solution for each sample time is provided in Table C.13.

Table C.13. Actinide Mass Measured During Experiment 13.

Element	Sample 1	Sample 2	Sample 3
	(g)	(g)	(g)
Neptunium	1.52E-04	1.29E-04	1.43E-04
Plutonium	1.98E-05	1.99E-05	2.10E-05
Americium	6.47E-06	5.92E-06	6.14E-06

The fraction of the mass of each actinide solubilized at each sample time is calculated as a percentage of the total mass of the actinide used in the experiment. The estimated volume of the sludge (i.e., slurry) following the acidification pretreatment process was 565 mL. A 3 mL aliquot of the slurry was used in Experiment 5; therefore, the fraction of the neptunium, plutonium, and americium used in the experiment was 0.0053. The mass of each actinide used in the experiment is calculated from the difference in the mass of the actinides transferred to the acidification process and the mass of the actinides in the supernate (Table C.11) multiplied by this fraction. The masses of the actinides are provided in Table C.14.

Table C.14. Mass of Actinides Used in Experiment 5.

Element	Mass Used in Experiment 5 (g)
Neptunium	1.58E-04
Plutonium	2.29E-05
Americium	1.18E-05

The fraction of the neptunium, plutonium, and americium masses solubilized at each sample time are presented in Table 3-9.

Comparison of the Actinide Masses Solubilized in Experiments 12 and 5

To estimate the masses of neptunium, plutonium, and americium solubilized in Experiment 12, the concentrations were initially calculated using the measured activities from Tables B.1-B.3 and the specific activities from Table B.5 using Equations C.1-C.3. The calculations are summarized in Table C.15.

Table C.15. Actinide Concentrations Measured During Experiment 12.

Element	Sample 1	Sample 2	Sample 3
	(g/L)	(g/L)	(g/L)
Neptunium	1.47E-03	1.29E-03	1.36E-03
Plutonium	3.26E-04	2.49E-04	2.80E-04
Americium	9.50E-05	7.82E-05	5.35E-05

The masses of the actinides solubilized in Experiment 12 were estimated using the concentrations from Table C.15, the volume of sludge (3 mL) and the volume of 0.18 M nitric acid/0.05 M sodium permanganate (30 mL) used in the experiment, and the volume of each sample removed (2.5 mL). Equations C.4-C.6 illustrate the same calculations for neptunium in Experiment 1. The estimated mass of each actinide in solution for each sample time is provided in Table C.16.

Table C.16. Actinide Mass Measured During Experiment 12.

Element	Sample 1	Sample 2	Sample 3
	(g)	(g)	(g)
Neptunium	4.85E-05	4.30E-05	4.49E-05
Plutonium	1.08E-05	8.40E-06	9.28E-06
Americium	3.13E-06	2.62E-06	1.93E-06

The masses of neptunium, plutonium, and americium solubilized during Experiment 5 for each sample time are given in Table C.13. The ratio of the mass of each actinide element at each sample time for the two experiments was calculated from the values provided in Tables C.16 and Table C.13. The results of the calculations are provided in Table 3-10.

Comparison of the Actinide Masses Solubilized During the BOAC and Oxalic Acid Removal Process

The masses of neptunium, plutonium, and americium solubilized during the BOAC and oxalic acid removal processes were calculated using the concentrations measured in the solutions (Table B.9) and the volume of the solutions (Table B.10). The calculations are summarized in Table C.17.

Table C.17. Actinide Masses Solubilized During the BOAC and Oxalic Acid Removal Processes.

Element	BOAC	Oxalic Acid
	Process	Removal Process
	(g)	(g)
Neptunium	1.89E-02	3.68E-04
Plutonium	4.58E-03	1.57E-04
Americium	1.62E-03	2.07E-05

The ratio of the mass of each actinide element solubilized in the sodium nitrate wash solution compared to the BOAC solution was calculated from the values provided in Tables C.17. The results of the calculations are provided in Table 3.11.

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