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# Alternative Chemical Cleaning Methods for High Level Waste Tanks: Actual Waste Testing with SRS Tank 5F Sludge

William D. King

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August 2016

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## **PREFACE OR ACKNOWLEDGEMENTS**

The completion of all sample manipulations in the SRNL shielded cells facility by Rita Sullivan and Jeff Mixon is greatly appreciated. Rita and Jeff worked tirelessly to accomplish the test objectives. Their positive attitudes and work ethic resulted in an enjoyable and productive work environment. In addition, support from numerous other personnel in the shielded cells was periodically needed. We also acknowledge support from the SRNL Analytical Development (AD) section. Specifically, David Diprete and Mark Jones provided the metal concentrations for sub-samples collected during the Chemical Cleaning tests.

## EXECUTIVE SUMMARY

Solubility testing with actual High Level Waste tank sludge has been conducted in order to evaluate several alternative chemical cleaning technologies for the dissolution of sludge residuals remaining in the tanks after the exhaustion of mechanical cleaning and sludge sluicing efforts. Tests were conducted with archived Savannah River Site (SRS) radioactive sludge solids that had been retrieved from Tank 5F in order to determine the effectiveness of an optimized, dilute oxalic/nitric acid cleaning reagent toward dissolving the bulk non-radioactive waste components. Solubility tests were performed by direct sludge contact with the oxalic/nitric acid reagent and with sludge that had been pretreated and acidified with dilute nitric acid. For comparison purposes, separate samples were also contacted with pure, concentrated oxalic acid following current baseline tank chemical cleaning methods. One goal of testing with the optimized reagent was to compare the total amounts of oxalic acid and water required for sludge dissolution using the baseline and optimized cleaning methods. A second objective was to compare the two methods with regard to the dissolution of actinide species known to be drivers for SRS tank closure Performance Assessments (PA). Additionally, solubility tests were conducted with Tank 5 sludge using acidic and caustic permanganate-based methods focused on the “targeted” dissolution of actinide species.

Based on the results, significantly more oxalic acid than necessary has been used in previous tank chemical cleaning campaigns. The baseline oxalic acid cleaning method (BOAC) involving 0.92 M oxalic acid is ineffective for the removal of the nickel sludge component, but is effective at removing other sludge components such as manganese, uranium, iron, and aluminum. The proposed optimized oxalic acid cleaning method (OOAC) involving a dilute nitric/oxalic acid mixture (0.18 M nitric acid and 0.056 M oxalic acid) is effective for the removal of all sludge components analyzed. Preliminary pretreatment of the sludge with dilute nitric acid prior to contact with the OOAC reagent increases the efficiency of oxalate usage for sludge dissolution. As shown in the table below, the total mass of oxalic acid required to completely dissolve each gram of sludge is approximately 0.82 g when using the OOAC method versus 1.7 g using the baseline method. This indicates that approximately half as much oxalic acid is required for sludge dissolution using the OOAC method versus the BOAC method. However, approximately 3.7 times as much water is required when utilizing the OOAC method due to the lower reagent oxalic acid concentration. The dissolution of 1,000 gallons of sludge heel (approximate residual volume following recent mechanical cleaning campaigns) would require 260,000 gallons of the OOAC reagents (both dilute nitric acid and the dilute oxalic/nitric acid mixture) versus 71,000 gallons of BOAC reagent (see table below). These volume comparisons, however, do not account for pre- and post-chemical cleaning washing operations that are typically required with the BOAC method and may not be needed with the optimized method.

Analyses of composited decant solutions from the baseline and optimized oxalic acid cleaning methods were conducted to determine the amounts of actinide elements removed by each method. Decant concentrations and total percent removal for plutonium, neptunium, and americium are provided for the two methods in the table below. Direct comparison of the results is complicated by the fact that the sludge:reagent volume ratios used in these tests were different, with approximately twice as much reagent volume (per original sludge volume) being utilized for the OOAC method versus the BOAC method. Percent removal values for neptunium are listed as “greater than” values because neptunium was below detectable limits in the original Tank 5F sample (based on current results, extractable Np was present at a level below analytical detection). The BOAC cleaning method was not very effective at removing the actinides (0.2 to ~20% removal) while the OOAC method removed 47-90% of the actinides. Removal of americium was significantly improved for the OOAC method, where 90% removal was observed versus <1% removal for the BOAC method. Based on the results, the OOAC method is believed to be superior to the baseline BOAC method for actinide removal and utilization of the OOAC cleaning method should result in significantly enhanced removal of actinide elements from tank residual solids.

Actinide concentrations and percent removal for the caustic and acidic permanganate cleaning reagents are provided in the table below. Plutonium concentrations observed with the caustic permanganate method ( $3\text{E-}06\text{ M}$ ) approached but were lower than the concentrations observed during similar testing with radioactive simulants ( $7\text{E-}06\text{ M}$ ). In contrast, plutonium concentrations observed for the acidic permanganate method ( $\leq 5\text{E-}06\text{ M}$ ) were higher than those observed with radioactive simulants ( $\sim 3\text{E-}06\text{ M}$ ). However, due to the amount of plutonium present in the sample, less than 10% plutonium removal was observed by each method. Actual washed heel samples (as opposed to unwashed sludge) would likely contain less total plutonium, and a greater percentage of the metal would be removed. Although the original Tank 5F sample contained neptunium below the detectable limit, neptunium was observed in the caustic and acidic permanganate contact solutions, with higher concentrations being observed in the caustic permanganate reagent. Much higher neptunium concentrations were observed during radioactive simulant testing ( $\sim 2\text{E-}05\text{ M}$ ) using these methods where a known and detectable amount of neptunium had been added. No detectable americium was observed during caustic permanganate testing, while an americium concentration of  $7\text{E-}07\text{ M}$  was observed with simulated waste. In the acidic permanganate reagent, an americium concentrations of  $5\text{E-}07\text{ M}$  was observed versus the concentration observed during simulant testing of  $8\text{E-}07\text{ M}$ .

In general, during contact of the first portion (Cycle 1) of the permanganate solution with Tank 5F sludge solids, the observed concentrations were comparable to simulant testing (excluding neptunium which was present at below detectable amounts). However, due to observations during testing of a loss of color from the deeply-colored permanganate cleaning solutions (both caustic and acidic), additional permanganate reagent volume was added to the samples. Surprisingly, lower actinide concentrations were observed in successive contacts using both the caustic and acidic permanganate methods, even though significant amounts of actinides remained in the samples. These observations may indicate that the amounts of the actinide elements that can be removed from the sludge using permanganate cleaning methods are limited. However, degradation of the permanganate reagents may be associated with the fact that the Tank 5F sludge sample had not been extensively washed to remove soluble oxalate salts. Additional evaluations to understand the impacts of these observations are necessary prior to implementation of this cleaning method. Nonetheless, the concentrations observed during contact Cycle 1 using these reagents are in the range where utilization of this method for the treatment of washed tank heels for the removal of trace actinides may be useful.

For comparison, the plutonium concentrations observed when utilizing both the caustic and acidic permanganate methods exceeded the concentrations observed with the OOAC method. However, due to the larger volume of cleaning reagent used with the OOAC method, a much greater percentage of the actinides were removed. Neptunium concentrations observed with the caustic permanganate method exceeded the values observed with the oxalic acid cleaning methods, while the concentrations observed with the acidic permanganate reagent were lower than those observed with the oxalic acid based methods. Americium concentrations observed with the acidic permanganate cleaning method were comparable to those observed with the OOAC method, but the percentage of americium removed with the OOAC method was much larger due to the reagent volume used. No detectable americium was observed with the caustic permanganate method.



**Total Oxalate Molar and Reagent Volume Estimates for Complete Tank 5F Sludge Dissolution.**

Cleaning Method	total oxalate g per sludge g	total reagent gallons per 1000 sludge gallons
BOAC	1.7	71k
OOAC*	0.82	260k

\* method includes preliminary sludge pretreatment with dilute nitric acid

**Actinide Concentrations and Percent Removal From Tank 5F Sludge Based on Cleaning Reagent Composite Decant Analysis.**

Cleaning Method	Molarity			% Removed		
	Pu	Np	Am	Pu	Np**	Am
BOAC	6.4E-07	1.2E-06	2.8E-09	4.4	≥19	0.19
OOAC*	2.9E-06	2.1E-06	5.5E-07	47	≥82	90

\* method includes preliminary sludge pretreatment with dilute nitric acid

\*\* original Tank 5F neptunium-237 concentration below detectable limits

**Actinide Concentrations and Percent Removal Observed for Caustic and Acidic Permanganate Solutions Following Contact with Tank 5F Sludge (Cycle 1 Data).**

Reagent	Day	Molarity			% Removal		
		Pu	Np	Am	Pu	Np	Am
10 M NaOH/ 0.05 M NaMnO <sub>4</sub> (Caustic)	4	3E-06	3E-06	<2E-07	3.6	≥7.3	<1.8
	12	3E-06	1E-06	<1E-07	3.1	≥3.5	<1.5
	15	3E-06	2E-06	<7E-08	3.2	≥6.1	<0.8
0.18 M HNO <sub>3</sub> / 0.05 M NaMnO <sub>4</sub> (Acidic)	4	4E-06	2E-07	4E-07	6.2	≥0.6	5.8
	12	4E-06	2E-07	4E-07	6.0	≥0.6	5.8
	14	5E-06	2E-07	5E-07	7.4	≥0.7	8.9

## TABLE OF CONTENTS

LIST OF TABLES .....	x
LIST OF FIGURES .....	x
LIST OF ABBREVIATIONS .....	xii
1.0 Introduction .....	1
2.0 Experimental Procedure .....	2
3.0 Results and Discussion .....	6
3.1 Quality Assurance .....	11
4.0 Conclusions .....	22
5.0 Recommendations, Path Forward and Future Work .....	23
6.0 References .....	24

## LIST OF TABLES

Table 2-1. Samples, Reagents, Methods, and Contact Times Used for Tank 5F Sludge Dissolution Studies. ....	3
Table 2-2. Summarized SRS Tank 5F Sludge Sample Bulk Elemental Composition Based on Data Reported by Hay. ....	3
Table 2-3. Summarized SRS Tank 5F Sludge Sample Trace Radionuclide Composition Based on Data Reported by Hay. ....	4
Table 2-4. Sludge and Reagent Masses and Volumes Used During Tank 5F Sludge Dissolution Studies. ....	5
Table 2-5. Acid Decant Volumes Isolated During Tank 5F Sludge Dissolution Studies. ....	6
Table 3-1. Measured Slurry pH Data for Each Contact Cycle and Weight Percent Solids Removed at Test Conclusion. ....	12
Table 3-2. Concentrations of Selected Metals in Acid Decant Solutions Isolated During Tank 5F Sludge Dissolution Studies. ....	12
Table 3-3. Percent Removal of Selected Metals in Acid Decant Solutions Isolated During Tank 5F Sludge Dissolution Studies. ....	13
Table 3-4. Weight Percentage Removal Based on Assumed Compounds for Tank 5F Sludge Using each Cleaning Method. ....	13
Table 3-5. Performance Comparisons of Chemical Cleaning Methods with Tank 5F Sludge. ....	14
Table 3-6. Total Oxalate Molar and Reagent Volume Estimates for Complete Tank 5F Sludge Dissolution. ....	14
Table 3-7. Actinide Concentrations Observed for Caustic and Acidic Permanganate Solutions Following Contact with Tank 5F Sludge. ....	15
Table 3-8. Actinide Concentrations and Percent Removal From Tank 5F Sludge Based on Decant Composite Analysis. ....	14

## LIST OF FIGURES

Figure 3-1. XRD Pattern Observed for Residual Solids Isolated Following Tank 5F Sludge Contact with Concentrated Oxalic Acid. ....	16
Figure 3-2. XRD Pattern Observed for Residual Solids Isolated Following Tank 5F Sludge Contact with the Oxalic/Nitric Acid Mixture. ....	16
Figure 3-3. XRD Pattern Observed for Residual Solids Isolated Following Tank 5F Sludge Contact with Dilute Nitric Acid followed by the Dilute Oxalic/Nitric Acid Mixture. ....	17
Figure 3-4. Metal Concentrations Observed in Each Contact Cycle During BOAC Testing with Concentrated Oxalic Acid. ....	17

Figure 3-5. Cumulative Metal Percent Removal Observed in Each Contact Cycle During BOAC Testing with Concentrated Oxalic Acid. ....	18
Figure 3-6. Metal Concentrations Observed in Each Contact Cycle During D-OOAC Testing with the Dilute Oxalic/Nitric Acid Mixture.....	18
Figure 3-7. Cumulative Metal Percent Removal Observed in Each Contact Cycle During D-OOAC Testing with the Dilute Oxalic/Nitric Acid Mixture.....	19
Figure 3-8. Metal Concentrations Observed in Each Contact Cycle During P-OOAC Testing with Dilute Nitric Acid Followed by the Dilute Oxalic/Nitric Acid Mixture.....	19
Figure 3-9. Cumulative Metal Percent Removal Observed in Each Contact Cycle During P-OOAC Testing with Dilute Nitric Acid Followed by the Dilute Oxalic/Nitric Acid Mixture.....	20
Figure 3-10. Metal Concentrations Observed for First and Second Contact Cycles Using the Caustic Permanganate Mixture.....	20
Figure 3-11. Metal Concentrations Observed Using the Caustic Dilute Permanganate Mixture .....	21
Figure 3-12. Metal Concentrations Observed for First, Second, and Third Contact Cycles Using the Acidic Permanganate Mixture .....	21

## LIST OF ABBREVIATIONS

AD	Analytical Development
APHA	Alpha Pulse Height Analysis
BOAC	Bulk Oxalic Acid Cleaning
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
D-OOAC	Direct Optimized Oxalic Acid Cleaning
EM	Environmental Management
GPHA	Gamma Pulse Height Analysis
HLW	High Level Waste
HM	H-Modified
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
LTAD	Low Temperature Aluminum Dissolution
OA	Oxalic Acid
OOAC	Optimized Oxalic Acid Cleaning
P-OOAC	Pretreated Optimized Oxalic Acid Cleaning
PMP	Polymethylpentene
PUREX	Plutonium Uranium Reduction Extraction
PSAL	Process Science Analytical Laboratory
RPM	Revolutions per Minute
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTA	ThenoylTrifluoroAcetone
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 and assist in heel removal. Chemical cleaning operations are conducted following the removal of 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.<sup>1</sup> 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 in 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.<sup>2</sup> 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 processes, and insoluble oxalate salts are accumulating within the SRS tank farm and waste processing facilities (evaporators, etc.).<sup>3</sup> 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 should be minimized.

The use of supplementary acids has been shown to assist bulk sludge dissolution in oxalic acid (OA). Previous SRNL testing<sup>4,5</sup> revealed the importance of pH control, recommended the use of a supplementary acid (dilute  $\text{HNO}_3$ ) with dilute OA to minimize oxalate additions,<sup>6</sup> and indicated that manageable corrosion rates would be observed with these oxalic/nitric acid mixtures.<sup>7</sup> Methods to decompose the oxalate solids have also been identified<sup>8</sup> 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 during the Tank 12 cleaning campaign.

Primary drivers in SRS Tank Closure Performance Assessments,<sup>9</sup> which evaluate the fate of tank sludge residuals on a geological timescale, are alpha-emitting radionuclides such as plutonium, neptunium, and americium. The amounts of these radionuclides remaining in tank residuals following chemical cleaning operations 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 HLW tank residual solids.<sup>10</sup> Oxidation of the actinides with permanganate in either strong caustic (10 M NaOH) or dilute acid (0.18 M  $\text{HNO}_3$ ) solutions resulted in the dissolution of simple surrogate oxy/hydroxide phases of these metals. Either of these two permanganate-based methods for alpha removal may be suitable for incorporation into a chemical cleaning flow sheet, though they would likely be utilized at different times in the waste processing sequence. The utilization of permanganate-

based methods results in the addition of manganese dioxide solids to the waste, so minimization of permanganate additions is needed.

Testing of an actual SRS waste tank residual sludge sample from Tank 5F has been conducted using the alternative chemical cleaning methods described above. In a separate study, corrosion evaluations of the alternative cleaning reagents were conducted using carbon steel coupons representative of SRS waste tanks. Results from the corrosion evaluations are reported separately.<sup>11</sup>

## 2.0 Experimental Procedure

Commercially-purchased, concentrated nitric acid ( $\text{HNO}_3$ ) solution, 50 wt. % sodium hydroxide ( $\text{NaOH}$ ) solution, oxalic acid dihydrate ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) solids, and sodium permanganate ( $\text{NaMnO}_4$ ) solids were utilized for the preparation of chemical cleaning solutions for testing. All solutions were prepared using the above reagents and appropriate amounts of ultrapure, deionized water (Milli-Q) to achieve the target concentrations provided in Table 2-1. Sludge solubility tests were conducted in order to evaluate the six different tank cleaning/sludge dissolution reagents indicated in the table.

Bulk Oxalic Acid Cleaning (BOAC) is the current baseline tank cleaning method involving concentrated oxalic acid reagent. Direct Optimized Oxalic Acid Cleaning (D-OOAC) involved the use of the previously developed optimized cleaning reagent containing a dilute mixture of oxalic and nitric acids, but did not include a preliminary acidification step with dilute nitric acid. Pretreated Optimized Oxalic Acid Cleaning (P-OOAC) involved the use of the optimized cleaning reagent with a preliminary acidification step with dilute nitric acid. Caustic and acidic permanganate testing focused on the “targeted” dissolution of only actinide elements (excluding bulk sludge components) from tank waste through the use of concentrated sodium hydroxide and dilute nitric acid solutions containing sodium permanganate. Two permanganate concentrations were evaluated for the caustic permanganate cleaning reagent. Target contact times for each sample with the cleaning reagents are also provided in Table 2-1.

An archived Tank 5F sample was retrieved prior to tank chemical cleaning. The sample was a dry powder that had been stored in the SRNL shielded cells for nearly 10 years and was used for previous Tank 5F characterization and baseline oxalic acid cleaning tests as reported by Hay.<sup>12</sup> The bulk elemental and radionuclide contents of the Tank 5F sludge are provided in Tables 2-2 and 2-3, respectively. Iron was the dominant metal present in the sludge (approaching 40 wt. %) while secondary metals present included uranium, manganese, nickel, and sodium. The sample did not contain detectable amounts of technetium or neptunium.

Separate sludge samples were weighed and transferred to graduated glass centrifuge tubes along with inhibited water (0.01 M  $\text{NaOH}$ ) for the purpose of rewetting and washing the dry solids and determining the hydrated volume and density for each solid sample. The tubes were capped and the samples were agitated for several minutes before allowing the solids to settle. Settling of the solids in the tubes occurred within a few minutes and the solution above the solids was clear with few visible suspended solid particles. Evaluation of the wet slurry bulk density values for the samples revealed that smaller sample sizes resulted in lower densities, presumably due to bridging of the solids in the tapered bottom portion of the centrifuge tubes. As a result, the volume of each solid sample was calculated based on the measured densities for the ~10 g sludge samples only (average density: 1.38 g/mL). Test sample masses and volumes and chemical cleaning reagent volumes are provided in Table 2-4. The sludge slurry samples in the centrifuge tubes were transferred to 125 or 250 mL polymethylpentene (PMP) or Teflon bottles for dissolution testing.

**Table 2-1. Samples, Reagents, Methods, and Target Contact Times Used for Tank 5F Sludge Dissolution Studies.**

Test Sample	Reagent	Target Contact Time Per Cycle
BOAC	0.92 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> diluted after 1 day to 0.46 M for Cycles 1 and 2 and to 0.23 M for Cycles 3-5	1 week
Direct OOAC-A	0.18 M HNO <sub>3</sub> /0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture	4 days for Cycles 1-2; 2 weeks for Cycles 3-5
Direct OOAC-B	0.18 M HNO <sub>3</sub> /0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture (A replicate)	4 days for Cycles 1-2; 2 weeks for Cycles 3-5
Pretreated OOAC-A	0.18 M HNO <sub>3</sub> for Cycles 1 and 2; 0.18 M HNO <sub>3</sub> /0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture for Cycles 3-5	4 days for Cycles 1-2; 2 weeks for Cycles 3-5
Pretreated OOAC-B	0.18 M HNO <sub>3</sub> for Cycles 1 and 2; 0.18 M HNO <sub>3</sub> /0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture for Cycles 3-5 (A replicate)	2 weeks
Caustic Permanganate-A	10 M NaOH/0.05 M NaMnO <sub>4</sub>	2 weeks
Caustic Permanganate-B	10 M NaOH/0.017 M NaMnO <sub>4</sub>	2 weeks
Acidic Permanganate	0.18 M HNO <sub>3</sub> /0.05 M NaMnO <sub>4</sub>	2 weeks

All samples were washed to remove residual soluble salts by transferring inhibited water into the bottle, agitating the slurry, allowing the solids to settle, and decanting the free liquid. To be more representative of the baseline chemical cleaning process, less inhibited water was used to wash the BOAC sample. The BOAC sample was contacted with inhibited water at a liquid:sludge volume ratio of 9.4 while the volume ratio used for the other test samples was 41±3.

**Table 2-2. Summarized SRS Tank 5F Sludge Sample Bulk Elemental Composition Based on Data Reported by Hay.<sup>12</sup>**

Element	Wt. %
Al	1.4
Ca	0.3
Fe	38.3
Mn	6.9
Na	4.3
Ni	4.6
U (total)	9.6



**Table 2-3. Summarized SRS Tank 5F Sludge Sample Trace Radionuclide Composition Based on Data Reported by Hay.<sup>12</sup>**

Element	mCi/kg
Tc-99	<1.2E-02
Np-237	<4.4E-02
Pu-239	8.4
Pu-241	7.7
Am-241	50.7
Cm-244	3.9

Chemical cleaning tests were conducted by transferring the sample bottles into a remotely-operated and temperature-controlled Innova incubator shaker oven (Model 4230). The samples were maintained at a temperature of 55 °C throughout testing and continuously agitated by orbital rotation at 225-250 RPM. The test temperature was selected because it is considered to be the nominal tank temperature during mixing operations.

Analysis sub-samples were periodically collected by removing the sample bottles from the oven. The solids were allowed to settle in the bottle for several minutes prior to the removal of liquid sub-samples with a slurry pipet. The sub-samples were collected while the samples were still at elevated temperature. The liquid sub-samples were transferred directly into 10 mL polyethylene syringes (Becton-Dickerson Luer-Lok tip) fitted with either 0.45 µm Nalgene Nylon or 0.02 µm Whatman Anotop 25 inorganic membrane filters. The smaller pore size filters were used for samples analyzed for actinide elements in order to be consistent with previous testing protocols.<sup>13</sup> The sub-samples were filtered directly into 15 mL shielded polyethylene bottles containing 5 M nitric acid for sample dilution and stabilization. The volume-based target acid dilution factor was 4.

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. Slurry pH data were collected during sludge dissolution testing using sealed, double-junction Oakton pH Electrodes with Epoxy bodies (Models WD-35805-01 and WD-35805-06). The pH meters were calibrated prior to each use with pH 4, 7, and 10 standard buffer solutions. The pH was typically measured at elevated temperature (~50 °C).

Sludge solubility testing was conducted with concentrated oxalic acid reagent to emulate the baseline BOAC process used at SRS. The most recent SRS chemical cleaning campaign was conducted on Tank 12H. 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.<sup>2</sup> Water was subsequently added to the HLW tank to provide sufficient volume for mixing. For the initial contact cycles, the oxalic acid was diluted to 4 wt. %. For later contact cycles the oxalic acid was diluted to 2 wt. %. In the current testing, five contact cycles were used following this approach. The volume-based BOAC test phase ratio utilized for the first and second contact cycles with Tank 5F sludge was 10:1 (concentrated acid:original sludge) and the solution was diluted after one day to an oxalic acid concentration of 4 wt. %. The volume-based test phase ratio used for the third through fifth contact cycles with Tank 5F sludge was 3.1:1 (concentrated acid:original sludge), and the solution was diluted after one day to an oxalic acid concentration of 2 wt. %. The target total acid contact time per cycle was 1 week (experimental range: 7-10 days). Reagent volumes added during BOAC testing are provided in Table 2-4.

Direct OOAC cleaning testing was conducted using the 0.18 M HNO<sub>3</sub>/0.056 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> mixture with no sample pre-acidification. Two duplicate samples (indicated as –A and –B) were prepared for D-OOAC testing (Table 2-4). Acid contact durations during testing ranged 3-5 days for Cycles 1 and 2 and 13-14 days for contact Cycles 3-5. Pretreated OOAC cleaning testing was conducted by contacting the sludge with 0.18 M HNO<sub>3</sub> to pre-acidify and partially dissolve the sludge prior to oxalic acid contact. Cycles 1 and 2 involved 0.18 M HNO<sub>3</sub> acid contact, while Cycles 3-5 involved contact with the 0.18 M HNO<sub>3</sub>/0.056 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> acid mixture. Two duplicate samples (indicated as –A and –B) were prepared for P-OOAC testing. Acid contact durations during testing ranged from 4-6 days for Cycles 1 and 2 and 14-15 days for Cycles 3-5. A reagent:sludge volume phase ratio of 20 was used for all OOAC testing (Direct and Pretreated) cycles based on both the approximate minimum amount of reagent that could be mixed within a HLW tank and an assumed nominal sludge residual volume. Reagent volumes added during D-OOAC and P-OOAC testing are provided in Table 2-4.

Decant volumes isolated for the sludge solubility tests with oxalic acid cleaning solutions (BOAC and OOAC) are provided in Table 2-5. For samples involving replicates, the decant solutions from each sample were combined. The isolated decant volumes are generally in good agreement with the reagent volumes added, as shown in the table.

Caustic and acidic permanganate cleaning tests were conducted similarly to the oxalic acid tests but with a smaller reagent:sludge volume ratio (10-15 per cycle) that was based on tests conducted with radioactive simulants.<sup>13</sup> The acidic permanganate sludge sample was pre-acidified with two cycles of dilute nitric acid at a phase ratio of 20:1 prior to contact with the permanganate solution. Due to the small volumes involved in these tests, the settling characteristics of the material, and the challenges of seeing the settled solids in the shielded cells environment, decantation of the permanganate cleaning reagents at the conclusion of each test cycle was not possible with these samples. Fewer test cycles were conducted with the permanganate solutions (1-2 cycles for Caustic Permanganate and 3 cycles for Acidic Permanganate). Three filtered sub-samples were collected for analysis over a period of approximately 2 weeks in each test cycle.

**Table 2-4. Sludge and Reagent Masses and Volumes Used During Tank 5F Sludge Dissolution Studies.**

Test Sample	Tank 5F (g)	Tank 5F (mL)	Total Reagent Volume Added (mL)*					Total Reagent (mL)	Reagent: Sludge Volume Ratio
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5		
BOAC	10.005	7.3	130	130	60	60	60	440	62
D-OOAC-A	10.114	7.4	138	138	138	138	138	690	94
D-OOAC-B	10.020	7.3	138	138	138	138	138	690	95
P-OOAC-A	1.991	1.4	28	28	28	28	84	196	137
P-OOAC-B	1.947	1.4	28	28	28	28	84	196	140
Caustic Permanganate-A**	2.676	1.9	20	20	---	---	---	40	22
Caustic Permanganate-B**	2.572	1.9	20	20	---	---	---	40	22
Acidic Permanganate**	1.993	1.4	20	20	20	---	---	60	42

\* total reagent including the added water during BOAC testing

\*\* due to the small sample volumes involved with these tests, reagent was not decanted from the bottles between cycles

**Table 2-5. Acid Decant Volumes Isolated During Tank 5F Sludge Dissolution Studies.**

Test Sample	Decant Volume Isolated (mL)					Total Decant Volume (mL)	Total Volume Added (mL)
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5		
BOAC*	120	125	62	55	63	425	440
D-OOAC (-A and -B composite)	231	257	250	255	262	1255	1380
P-OOAC** (-A and -B composite)	53***	53***	60	55	175	397	384

\* 8 wt. % oxalic acid diluted with water after one day to either 4 (Cycles 1-2) or 2 wt. % (Cycles 3-5); volumes correspond to diluted acid

\*\* 0.18 M HNO<sub>3</sub> acid used for Cycles 1 and 2; 0.18 M HNO<sub>3</sub>/0.056 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> used for Cycles 3-5

\*\*\* corrected for contribution from acidic permanganate pre-acidification solution

Reagent and sample analyses were conducted by the SRNL Analytical Development (AD) section. Primary analysis methods for the filtered sub-samples included Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Selected samples were also analyzed for plutonium by alpha spectroscopy following separation using thenoyltrifluoroacetone (TTA) and for americium and curium by alpha and gamma pulse height analysis (APHA/GPHA). Good agreement was observed between sample plutonium concentrations determined by ICP-MS and the Pu TTA method. As a result, mass 239 and 240 data obtained by mass spectroscopy were used exclusively to determine the plutonium concentrations of many samples. Pu-238 concentrations were negligibly small (two orders of magnitude smaller on a molar concentration basis) relative to Pu-239 for all samples. Neptunium concentrations were based on ICP-MS data. Most americium concentrations were based on mass 241 ICP-MS data with corrections for the contribution from mass Pu-241. The Pu-241 concentration corrections were based on the previously determined ratio of Pu-239 to Pu-241 in the original sample characterization report authored by Hay.<sup>12</sup> X-ray Diffraction (XRD) analysis was also conducted for the residual solids isolated from each of the three oxalic acid cleaning tests (BOAC, D-OOAC, and P-OOAC) after contact Cycle 5.

At the conclusion of the last chemical cleaning cycle, the residual solids were transferred from the test bottles to Nylon Nalgene filter cups and washed with inhibited water, at which point the damp solid masses were determined. Sub-samples of the residual solids were collected to determine the weight percent solids for the damp solids. These data were then utilized to calculate the dry solid masses of the residual solids. Due to the fact that a smaller sample size was used for the P-OOAC testing and the fact that the residual solids for these samples were not easily transferred from the bottle, the residual solids mass was not determined for this test method.

### 3.0 Results and Discussion

Five acid contact cycles were utilized for each oxalic acid based cleaning method tested with Tank 5F sludge solids. Solution pH data measured at the conclusion of each acid contact cycle and the weight percentages of solids removed after Cycle 5 are provided in Table 3-1. For Cycle 1, the slurry pH values ranged from 2 to 5, with the highest pH being observed for the BOAC sample and the lowest being observed for the P-OOAC sample. For Cycle 2, the slurry pH values were all near 1. For Cycles 3-5, the

slurry pH values for all samples were  $\leq 0.8$ . Residual sample weights for the BOAC and D-OOAC samples at test conclusion indicated that 61-71% of the solids had been removed by liquid decantation.

XRD analysis of the residual solids at the conclusion of each oxalic acid-based cleaning test are provided in Figures 3-1 through 3-3. The only crystalline phases observed for the BOAC residual sample were nickel oxalate and the frequently observed sludge iron phase, hematite,  $\text{Fe}_2\text{O}_3$ . The observation of nickel oxalate is consistent with simulant testing which indicated the formation of the same phase during contact of nickel hydroxide reagent with oxalic acid.<sup>13</sup> XRD results for the OOAC tests (both direct and pretreated) revealed the presence of the same crystalline phases in each sample (though a large amorphous peak was also observed for the P-OOAC sample). Both samples contained hematite and the previously unobserved trimetallic sludge phase trevorite,  $\text{NiFe}_2\text{O}_4$ . Presumably, trevorite is a minor sludge phase that is typically difficult to observe in samples dominated by other phases. Though this phase has not been observed in tank waste sludge, it has been observed in cold crucible vitrification tests with SRS sludge simulants.<sup>14</sup>

The concentrations of selected metals observed in the decant solutions from each acid contact cycle are provided in Table 3-2. The metal concentrations in each contact cycle for the BOAC test are plotted in Figure 3-4. The trends in the concentrations indicate effective dissolution and removal of most metals from the sludge sample except for nickel (concentration never exceeded  $1.1\text{E-}03\text{ M}$ ). The average iron concentration was  $9.7\text{E-}02\text{ M}$  and the maximum iron concentration was  $2.2\text{E-}01\text{ M}$  (Cycle 2) versus the oxalic acid concentration in this solution of  $0.452\text{ M}$ . Trends in the data indicated that the iron, manganese, and nickel concentrations in Cycle 3 were lower than would be expected based on Cycles 2 and 4. It is possible that post-decant precipitation of these metals occurred in this sample during storage in the shielded cells due to exposure of the samples to light in the cells facility. The decant samples were not rigorously isolated from light exposure during testing, but were typically stored away from the light source. Light exposure was observed to promote precipitation from similar sample types in previous studies.<sup>4</sup>

Calculated weight percentages of the metals removed in each BOAC contact cycle are provided in Table 3-3. The cumulative weight percentages of the metals removed during in each BOAC cycle are provided in Figure 3-5. The data trends in the figure indicate that  $>100\%$  of the aluminum and nearly all of the calcium were removed from the sample. Approximately 80-85% of the uranium, manganese, and sodium were removed. In contrast, less than 5% of the nickel was removed from the sludge sample. Trends in the iron concentrations during BOAC testing indicated that a small percentage of the iron was removed in Cycle 1, but a large percentage of the iron ( $\sim 40\%$ ) was removed in Cycle 2. This is a typical observation for BOAC tests where little iron is removed during initial contact when the pH is higher and many other metals compete for oxalate complexation. The total iron removed from the sample during testing was 67%. Calculated weight percentages of assumed metal species removed (as a fraction of the total sludge) in each BOAC contact cycle are provided in Table 3-4. Based on the metal concentrations observed and the assumed speciation, the fraction of total sludge removed was  $\sim 71\%$ . This result compares well with the amount of total sludge removed of 71% based on the residual mass measured at test conclusion (Table 3-1). These results are very similar to previous oxalic acid testing with Tank 5F sludge, although previous testing only involved one acid contact.<sup>12</sup>

The concentrations of various metals observed in the decant solutions for the D-OOAC test from each acid contact cycle are provided in Table 3-2. The metal concentrations in each contact cycle are plotted in Figure 3-6. The trends in the concentrations indicate effective dissolution and removal of most metals from the sludge sample including nickel (maximum concentration  $8\text{E-}03\text{ M}$ ). The maximum iron concentration was  $0.046\text{ M}$  (Cycle 4) versus the oxalic acid concentration in this solution of  $0.056\text{ M}$ . Trends in the concentrations of the other metals (excluding Fe and Ni) indicate significant initial dissolution and depletion of the metals from the sample during successive contacts. The cumulative

weight percentages of the metals removed during each contact cycle are provided in Figure 3-7. The data trends in the figure indicate ~85% removal of calcium and manganese and 65-80% removal of sodium, uranium, and aluminum. In contrast to the BOAC cleaning method, nickel is gradually removed from the solution and the final weight percent removed is nearly 50%. Trends in the iron concentrations indicate gradual iron dissolution starting at Cycle 3, but only ~20% total iron removal was achieved during the course of testing. The initial low iron removal is presumably associated with the higher pH in early contact solutions and the fact that other metals compete with iron for oxalate complexation. Calculated weight percentages of the metals removed in each D-OOAC contact cycle are provided in Table 3-3, while calculated weight percentages of assumed metal species removed (as a fraction of the total sludge) are provided in Table 3-4. Based on the calculations, 45% of the sludge was removed, which is lower than the percent removal calculated based on the final measured solid mass (61%; Table 3-1).

The concentrations of various metals observed in the decant solutions for the P-OOAC test from each acid contact cycle are provided in Table 3-2. The metal concentrations in each contact cycle are plotted in Figure 3-8. The trends in the concentrations indicate effective dissolution and removal of many of the metals in dilute nitric acid without oxalic acid during contact Cycles 1 and 2. Surprisingly, significant iron dissolution was observed in contact Cycle 2 even though this solution was not believed to contain any oxalic acid. The maximum iron concentration was 0.043 M (Cycle 4) versus the reagent oxalic acid concentration of 0.056 M. Trends in the concentrations of metals other than iron and nickel indicated significant initial dissolution and depletion of the metals from the sample during successive contacts. The cumulative weight percentages of the metals removed in each cycle are provided in Figure 3-9. The data trends in the figure indicate nearly 100% removal of manganese, 75-90% removal of calcium, uranium, and aluminum, and ~60% removal of Na. Nickel was gradually removed from the solution and the final weight percent removal approached 60%. Trends in the iron concentrations indicate gradual iron dissolution starting at Cycle 2, and 33% total iron removal was achieved during the course of testing. Calculated weight percentages of the metals removed in each P-OOAC contact cycle are provided in Table 3-3. Calculated weight percentages of assumed metal species removed versus total sludge mass in each P-OOAC contact cycle are provided in Table 3-4. Based on the calculations, 56% of the sludge mass was removed using the P-OOAC method.

Performance comparisons of the oxalic acid-based cleaning methods are provided in Table 3-5, where the mmol of oxalate added and iron dissolved are calculated for each acid contact cycle. As discussed in earlier reports, the optimal oxalate:Fe mole ratio is 1:1 based on the formation of the iron oxalate complex,  $\text{FeHC}_2\text{O}_4^{2+}$ , which is the dominant species present below pH 1.<sup>4</sup> Earlier cycles for each oxalic acid based cleaning method involved elevated oxalate to iron molar ratios and non-ideal usage of oxalate for sludge dissolution. Very high oxalate:iron molar ratios were observed for the D-OOAC testing in Cycles 1 and 2, where very little iron dissolved. Due to the high ratios observed for the first two cycles, the D-OOAC testing exhibited the least efficient oxalate usage with a composite oxalate to iron molar ratio of approximately 7. However, in Cycles 4 and 5 the oxalate:iron molar ratios ranged from 1.3-1.4, which approaches the ideal value of 1. In comparison, the most efficient oxalate usage was observed in the P-OOAC test where the composite oxalate to iron molar ratio was 1.8 and the lowest oxalate to iron molar ratio was 1.3 (Cycle 4). For the BOAC test, the lowest oxalate:iron ratio observed was 2.2 and the composite ratio was 3.5. Based on these results, it appears that the efficiency of oxalate usage can be improved by a factor of approximately two relative to the baseline method (BOAC) by using the optimized cleaning reagent (oxalic/nitric acid mixture) and pretreating the sample with dilute nitric acid.

Based on the results, the total amount of oxalate required to dissolve the entire sludge sample was calculated for each method. As shown in Table 3-6, approximately 0.82 g of oxalate per gram of sludge are predicted for complete sludge dissolution using the P-OOAC method versus approximately 1.7 g of oxalate per gram of sludge for the BOAC method. The volume of cleaning reagent per gallon of sludge was also calculated for each method. Based on these calculations, 260 gallons of OOAC reagent are

required to dissolve each sludge gallon, versus 74 gallons of BOAC reagent. Assuming a residual sludge heel volume of 1000 gallons, 260,000 gallons of OOAC reagent would be required for complete sludge dissolution versus 74,000 gallons using BOAC reagents. In summary, approximately half as much oxalate is required for complete sludge heel dissolution using the optimized P-OOAC method, but approximately 3.7 times as much water would be added to the tank. The reagent volume estimate for the BOAC method does not account for additional water that is typically required for sludge washing to remove sodium prior to chemical cleaning and additional water that is typically added after chemical cleaning to remove oxalate salts when preparing the waste for processing in the Defense Waste Processing Facility (DWPF). These washing steps are not expected when utilizing the optimized cleaning method because the nitric acid pretreatment step should remove sodium salts from the tank residual solids and oxalate additions and sodium oxalate precipitation are minimized using this method. Sludge washing is expected to decrease the reagent volume difference between the methods further.

Analysis of the composited decant solutions from the oxalic acid cleaning methods was conducted to evaluate the amounts of actinide elements removed by each method. Composite decant molar concentrations and total percent removal for uranium, plutonium, neptunium, and americium are provided for each method in Table 3-7. Percent removal values for neptunium are listed as greater than values because neptunium was below detectable limits in the original Tank 5F sample. All three cleaning methods removed most uranium from the sample (wt. % removal range: 79-97%). For the dissolution and removal of plutonium, neptunium, and americium the P-OOAC cleaning method was observed to be superior to the BOAC method. The BOAC cleaning method was not very effective at removing these metals (0.2 to ~20% removal), while the P-OOAC method removed 47-90% of these metals. Removal of americium was significantly improved with the P-OOAC method where 90% removal was observed versus <1% removal for the BOAC method. It should be emphasized that the sludge:oxalate volume ratios used in these tests were different, with approximately twice as much reagent volume (per original sludge volume) being utilized for the P-OOAC method versus the BOAC method (see reagent:sludge volume ratios in Table 2-4). Despite this difference, the P-OOAC method is superior to the baseline BOAC method for actinide removal. Based on these results, utilization of the P-OOAC cleaning method should result in significantly enhanced removal of actinide elements from the residual solids and thus have a positive impact on tank closure efforts.

Sludge solubility tests were also conducted using caustic and acidic permanganate reagents. Actinide concentrations (uranium, plutonium, neptunium, and americium) for filtered sub-samples from these tests are plotted in Figures 3-10 through 3-12. The actinide concentration data for these tests are provided in Table 3-8 while the weight the percent actinide removal calculation results are provided in Table 3-9.

Caustic permanganate tests were conducted with two permanganate concentrations (0.05 and 0.017 M) because it was believed that the more concentrated reagent used in radioactive simulant testing contained excess permanganate. However, within four days after contact of the reagents with Tank 5F sludge samples, the purple color of the permanganate in the more dilute reagent was observed to disappear, indicating a reaction between permanganate and reductants in the waste (such as oxalate anions). Subsequent analysis of the filtered solutions from these tests at approximately 4, 12, and 14 days (Table 3-8) revealed that the plutonium concentrations observed for the dilute permanganate solution ranged from 3E-07 to 8E-07 M while the concentrations observed for the more concentrated permanganate reagent (0.05 M) ranged from 2E-06 to 3E-06 M. For comparison, plutonium concentrations observed by this method using radioactive simulants were near 7E-06 M.<sup>13</sup> As shown in Table 3-9, the plutonium concentrations observed for the more concentrated permanganate reagent correspond to only 3-4% removal of plutonium from the sample.

While characterization results for the original Tank 5F sample indicated that neptunium was not present above detectable limits, measurable neptunium was removed from the Tank 5F sample using the caustic

permanganate method. Neptunium concentrations observed for the more concentrated permanganate method (0.05 M) ranged from  $1\text{E-}06$  to  $3\text{E-}06$  M, while concentrations observed for the dilute permanganate method were  $\leq 5\text{E-}07$  M (Table 3-8). Significantly higher neptunium concentrations were observed in simulant studies ( $\sim 2\text{E-}05$  M), but since the actual neptunium concentration in the original sample is unknown, quantitative comparisons between the two tests are not possible. As shown in Table 3-9, 4-8% removal of neptunium from the sludge was observed for the more concentrated permanganate reagent (assuming that the neptunium detection limit reported by Hay for this sample represents a real number). No detectable americium (detection limits  $\leq 1.5\text{E-}07$  M) was observed in the filtered solution from the caustic permanganate test involving 0.05 M permanganate in Cycle 1. For comparison, americium concentrations near  $7\text{E-}07$  M were observed in the simulant studies.

Due to concerns regarding the consumption of the permanganate by reductants in the waste during contact with the caustic permanganate reagent, an additional portion of reagent was added to the sample containing the more concentrated permanganate (0.05 M) following the initial two-week contact period (no decantation of Cycle 1 liquid). After two additional weeks, a sub-sample was collected, filtered, and sub-sampled for analysis. Analysis results are provided in Table 3-8 for this sample (Cycle 2). As shown in the table, the concentration of plutonium and neptunium decreased relative to the Cycle 1 data while the concentration of americium increased slightly to above detectable limits. These results indicate that for this tank waste sample, the concentrations observed in Cycle 1 may represent the highest achievable concentrations for this tank cleaning method, which may limit the amount of the actinides that can be removed by this method. Percent removal values for plutonium and americium in Cycle 2 were estimated to be 1.3 and 2.0%, respectively (Table 3-9), both of which are lower than were observed in Cycle 1.

Tank 5F sludge solubility tests were also conducted using an acidic permanganate reagent (0.18 M  $\text{HNO}_3$ /0.05 M  $\text{NaMnO}_4$ ). As was observed with the dilute caustic permanganate reagent, the purple solution color was observed to disappear from the acidic permanganate sample within a few days. Analysis of filtered sub-samples after approximately 4, 12, and 14 days indicated that the plutonium concentration ranged from  $3\text{E-}06$  to  $5\text{E-}06$  M (Cycle 1; Table 3-8). For comparison, the plutonium concentrations observed during radioactive simulant testing were near  $2.5\text{E-}06$  M.<sup>13</sup> As shown in Table 3-9, these plutonium concentrations correspond to the removal of 6 to 7.5% of the plutonium from the sample.

Although no detectable neptunium was observed in the original Tank 5F sample, detectable neptunium was observed in the acidic permanganate solutions during Cycle 1 at concentrations ranging from  $1.5\text{E-}07$  to  $2.0\text{E-}07$  M. For comparison, neptunium concentrations observed during radioactive simulant testing were near  $2\text{E-}05$  M. These neptunium concentrations correspond to  $<1\%$  Np removal assuming that the detection limit reported for the original sample represents the actual concentration (Table 3-9). Since the actual neptunium concentration in the original sample is unknown, quantitative comparisons between the radioactive simulant and actual waste tests are not possible. Americium concentrations observed for the acidic permanganate reagent ranged from  $3.5\text{E-}07$  to  $5.5\text{E-}07$  M (Table 3-8), which corresponds to americium percent removal values ranging from approximately 5 to 9% (Table 3-9). For comparison, americium concentrations observed during radioactive simulant testing were near  $8\text{E-}07$  M.<sup>13</sup>

Due to concerns regarding the consumption of the permanganate by reductants in the waste during contact with the acidic permanganate reagent, two additional portions of reagent (Cycles 2 and 3 in Table 3-8) were added to the sample following the initial two week contact (no liquid decantation in any cycle). The actinide concentrations of filtered sub-samples isolated after approximately 4, 12, and 14 days during Cycles 2 and 3 are provided in Table 3-8. As was observed for the caustic permanganate reagent, the actinide concentrations in the samples decreased with each successive contact cycle. These results indicate that, for this tank waste sample, the concentrations observed in Cycle 1 may represent the highest

achievable concentrations when employing this tank cleaning method, which may limit the amount of the actinides that can be removed by this method.

Comparison of the actinide concentrations observed for the permanganate (both caustic and acidic; Cycle 1) and P-OOAC cleaning methods reveals that similar plutonium concentrations ( $2.5\text{E-}06$  to  $5\text{E-}06$  M) were observed for all three methods. Neptunium concentrations observed for the caustic permanganate method and the P-OOAC method were similar ( $1\text{E-}06$  to  $3\text{E-}06$  M), but significantly lower neptunium was observed with the acidic permanganate method. Americium concentrations observed for the acidic permanganate method and the P-OOAC method were similar ( $3.5\text{E-}07$  to  $8\text{E-}07$  M), but significantly lower americium was observed with the caustic permanganate method. However, due to the significantly higher cleaning reagent volume used for the P-OOAC method, much larger percentages of the actinides were removed (47% Pu removal,  $\geq 82\%$  Np removal, 90% Am removal) versus the permanganate based methods. In addition, it should be possible to remove more of the actinides with additional reagent using the P-OOAC method, which was not the case with the permanganate-based methods using the current approach (additional reagent does not dissolve significant quantities of additional actinides). It is unknown whether a single contact of Tank 5F sludge with a larger volume ratio of the permanganate reagents would result in greater actinide removal by these methods.

### 3.1 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. Datasheets, analytical results, and calculations associated with this testing are maintained in SRNL Electronic Laboratory Notebook experiment number A2341-00117-02.



**Table 3-1. Measured Slurry pH Data for Each Contact Cycle and Weight Percent Solids Removed at Test Conclusion.**

Chemical Cleaning Method	Slurry pH					Cleaning Reagent	Weight % Removed After Cycle 5
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5		
BOAC	5.0	≤0.8	≤0.8	≤0.8	≤0.8	0.92 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (diluted to 0.22-0.45 M after 1 day)	71
Direct OOAC	3.5	≤0.8	≤0.8	≤0.8	≤0.8	0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture	61
Pretreated OOAC	2.6	1.1	≤0.8	≤0.8	≤0.8	0.18 M HNO <sub>3</sub> followed by 0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mixture	---**

\* pH values ≤0.75 are assumed equivalent due to challenges in measuring pH below this value

\*\* residual solids could not be quantitatively recovered for mass determination

**Table 3-2. Concentrations of Selected Metals in Acid Decant Solutions Isolated During Tank 5F Sludge Dissolution Studies.**

Contact Cycle	Molarity							Cleaning Method
	Na	Al	Fe	Mn	Ni	Ca	U	
1	1.0E-01	4.2E-02	6.6E-02	5.6E-02	3.6E-04	3.3E-03	3.0E-02	BOAC (0.46 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> *)
2	1.5E-02	1.1E-02	2.1E-01	2.6E-02	1.1E-03	3.0E-03	4.1E-04	
3	2.7E-03	2.0E-03	1.2E-02	5.4E-04	5.6E-05	5.8E-04	3.9E-04	
4	1.6E-03	9.7E-04	9.8E-02	4.2E-03	4.1E-04	3.6E-04	4.9E-05	BOAC (0.23 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> *)
5	1.3E-03	8.1E-04	8.6E-02	3.6E-03	2.7E-04	3.1E-04	6.6E-05	
1	8.5E-02	1.1E-02	1.6E-05	2.7E-02	4.7E-03	4.8E-03	2.8E-03	D-OOAC (0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> )
2	1.3E-02	1.0E-02	1.1E-04	4.6E-02	4.4E-03	1.1E-03	1.9E-02	
3	2.4E-03	4.4E-03	2.7E-02	9.9E-03	5.9E-03	2.4E-04	3.0E-03	
4	7.8E-04	1.5E-03	4.6E-02	2.1E-03	7.2E-03	7.0E-05	2.2E-04	
5	6.0E-04	9.0E-04	4.1E-02	8.6E-04	7.6E-03	4.6E-05	7.0E-05	
1	7.1E-02	1.3E-02	2.3E-05	4.8E-03	1.9E-03	3.8E-03	2.2E-02	P-OOAC (0.18 M HNO <sub>3</sub> )
2	9.5E-03	1.4E-02	1.0E-02	1.2E-02	4.9E-03	5.7E-04	4.9E-03	
3	1.6E-03	3.6E-03	9.4E-03	5.4E-02	4.5E-03	3.3E-04	5.2E-04	P-OOAC (0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> )
4	6.2E-04	7.7E-04	4.3E-02	9.6E-03	4.6E-03	8.5E-05	6.9E-05	
5	4.2E-04	3.9E-04	3.0E-02	1.4E-03	5.3E-03	3.9E-05	7.1E-05	

\* initial reagent concentration of 0.92 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> diluted to concentrations indicated after 1 day

**Table 3-3. Percent Removal of Selected Metals in Acid Decant Solutions Isolated During Tank 5F Sludge Dissolution Studies.**

Contact Cycle	% Metal Removed							Cleaning Solution
	Na	Al	Fe	Mn	Ni	Ca	U	
1	67.9	94.1	11.5	53.5	0.5	46.1	87.8	0.46 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> *
2	10.4	26.3	38.9	25.5	1.8	43.3	1.3	
3	0.9	2.3	1.1	0.3	0.0	4.2	0.6	0.23 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> *
4	0.5	1.0	7.9	1.8	0.3	2.3	0.1	
5	0.4	1.0	7.9	1.8	0.2	2.3	0.1	
Cumulative	80.2	124.7	67.3	83.0	2.9	98.1	89.8	
1	52.7	24.8	0.0	24.5	6.8	64.0	7.9	0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
2	9.1	24.2	0.0	47.0	7.2	16.7	61.2	
3	1.6	10.3	4.9	9.8	9.2	3.5	9.3	
4	0.5	3.5	8.5	2.1	11.6	1.0	0.7	
5	0.4	2.2	7.8	0.9	12.6	0.7	0.2	
Cumulative	64.4	64.9	21.3	84.2	47.5	85.9	79.3	
1	52.0	33.6	0.0	5.2	3.2	59.2	73.6	0.18 M HNO <sub>3</sub>
2	7.0	35.3	2.0	13.1	8.4	8.9	16.4	
3	1.3	10.4	2.1	65.4	8.7	5.8	2.0	0.18 M HNO <sub>3</sub> / 0.056 M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
4	0.5	2.0	8.7	10.6	8.2	1.4	0.2	
5	1.0	3.3	19.7	4.8	29.8	2.0	0.8	
Cumulative	61.7	84.6	32.5	99.2	58.3	77.2	93.0	

\* originally added as 0.92 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and then diluted after 1 day to 0.46 M for Cycles 1 and 2 and to 0.23 M for Cycles 3-5

**Table 3-4. Weight Percentage Total Sludge Removal Based on Assumed Compounds for Tank 5F Sludge Using each Cleaning Method.**

Cleaning Method	Wt. % Total Sludge Removed							Total
	Na <sub>2</sub> CO <sub>3</sub>	Al(OH) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	Ni(OH) <sub>2</sub>	Ca(OH) <sub>2</sub>	Na((UO <sub>2</sub> )O)(OH)·H <sub>2</sub> O	
BOAC	7.9	4.1	37	9.1	0.2	0.6	12	71
D-OOAC	6.3	2.7	12	9.2	3.5	0.6	11	45
P-OOAC	6.1	3.5	18	11	4.3	0.5	13	56

**Table 3-5. Performance Comparisons of Chemical Cleaning Methods with Tank 5F Sludge.**

Cycle	mmol H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	mmol Fe	oxalate:Fe (molar ratio)
BOAC			
1	59.8	7.9	7.6
2	59.8	26.7	2.2
3	13.8	0.7	19.0
4	13.8	5.4	2.6
5	13.8	5.4	2.5
Composite	161.0	46.2	3.5
D-OOAC			
1	15.5	0.004	4308
2	15.5	0.03	550
3	15.5	6.8	2.3
4	15.5	11.8	1.3
5	15.5	10.8	1.4
Composite	77.3	10.8	7.2
P-OOAC			
1	---	---	---
2	---	0.5	---
3	3.1	0.6	5.6
4	3.1	2.4	1.3
5	9.4	5.3	1.8
Composite	15.7	8.8	1.8

**Table 3-6. Total Oxalate Molar and Reagent Volume Estimates for Complete Tank 5F Sludge Dissolution.**

Cleaning Method	total oxalic acid g per sludge g	total reagent gallons per sludge gallon	total reagent gallons per 1000 sludge gallon
BOAC	1.7	71	71240*
D-OOAC	1.0	265	265374
P-OOAC	0.82	260**	260339**

\* assumes 3 wt. % oxalic acid; does not account for additional water required for washing prior to DWPF processing

\*\* includes nitric acid pretreatment solution

**Table 3-7. Actinide Concentrations and Percent Removal From Tank 5F Sludge Based on Decant Composite Analysis.**

Cleaning Method	Molarity				% Removed			
	U	Pu	Np	Am	U	Pu	Np	Am
BOAC	9.3E-03	6.4E-07	1.2E-06	2.8E-09	97	4.4	≥19*	0.19
D-OOAC	5.1E-03	5.9E-07	3.2E-06	8.0E-07	79	6.0	≥75*	82
P-OOAC	3.9E-03	2.9E-06	2.1E-06	5.5E-07	97	47	≥82*	90

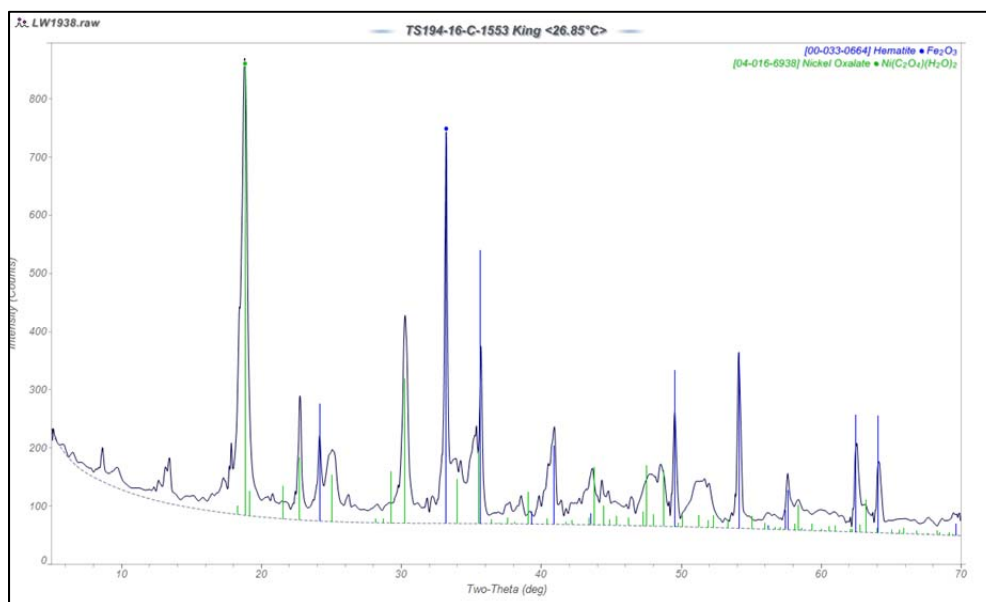
\* reported Tank 5F Neptunium-237 concentration was <5.5E-02 mg Np/kg sludge

**Table 3-8. Actinide Concentrations Observed for Caustic and Acidic Permanganate Solutions Following Contact with Tank 5F Sludge.**

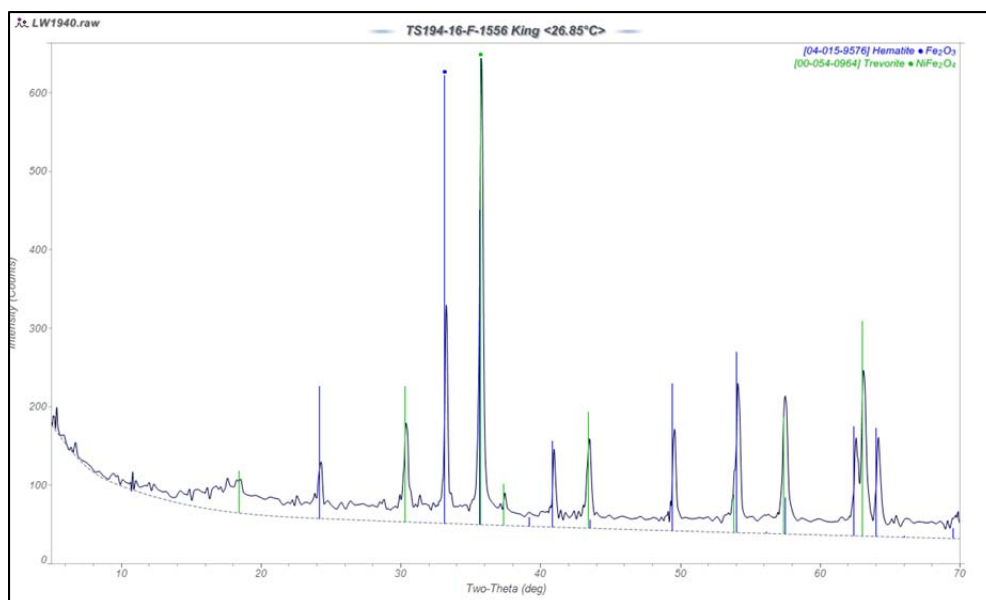
Cycle	Day	Pu (M)	Np (M)	Am (M)	U (M)	Reagent
1	4	3.0E-06	2.6E-06	<1.5E-07	6.5E-05	10 M NaOH/0.05 M NaMnO <sub>4</sub>
1	12	2.5E-06	1.2E-06	<1.2E-07	6.5E-05	
1	15	2.6E-06	2.2E-06	<6.9E-08	1.6E-04	
2	14	5.3E-07	1.5E-07	8.3E-08	1.03E-04	
1	4	8.1E-07	4.8E-07	---	7.0E-05	10 M NaOH/0.017 M NaMnO <sub>4</sub>
1	12	2.9E-07	<9.9E-8	---	5.1E-05	
1	15	3.1E-07	<7.6E-8	---	4.3E-05	
1	4	3.8E-06	1.6E-07	3.6E-07	2.9E-04	0.18 M HNO <sub>3</sub> /0.05 M NaMnO <sub>4</sub>
1	12	3.7E-06	1.5E-07	3.6E-07	2.6E-04	
1	14	4.6E-06	1.9E-07	5.4E-07	2.8E-04	
2	4	1.5E-06	3.8E-08	2.1E-07	4.4E-05	
2	12	1.7E-06	4.9E-08	2.5E-07	6.2E-05	
3	4	2.1E-07	<1.4E-7	---	8.8E-06	
3	12	2.5E-07	<1.5E-7	---	1.0E-05	
3	14	2.8E-07	<1.5E-7	---	9.4E-06	

**Table 3-9. Actinide Percent Observed for Caustic and Acidic Permanganate Solutions Following Contact with Tank 5F Sludge.**

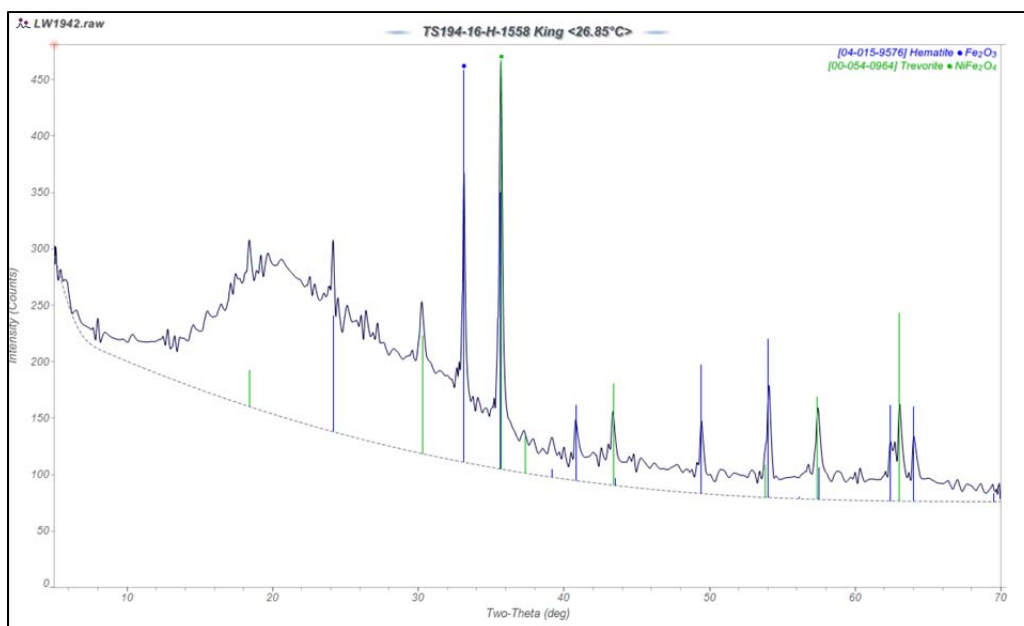
Cycle	Day	% Removal			Reagent
		Pu	Np	Am	
1	4	3.6	≥7.3	<1.8	10 M NaOH/0.05 M NaMnO <sub>4</sub>
1	12	3.1	≥3.5	<1.5	
1	15	3.2	≥6.1	<0.8	
2	14	1.3	≥0.9	2.0	
1	3	6.2	≥0.6	5.8	0.18 M HNO <sub>3</sub> /0.05 M NaMnO <sub>4</sub>
1	12	6.0	≥0.6	5.8	
1	14	7.4	≥0.7	8.9	
2	3	4.9	≥0.3	6.7	
2	12	5.6	≥0.4	8.1	
3	3	1.0	---	---	
3	12	1.2	---	---	
3	14	1.3	---	---	



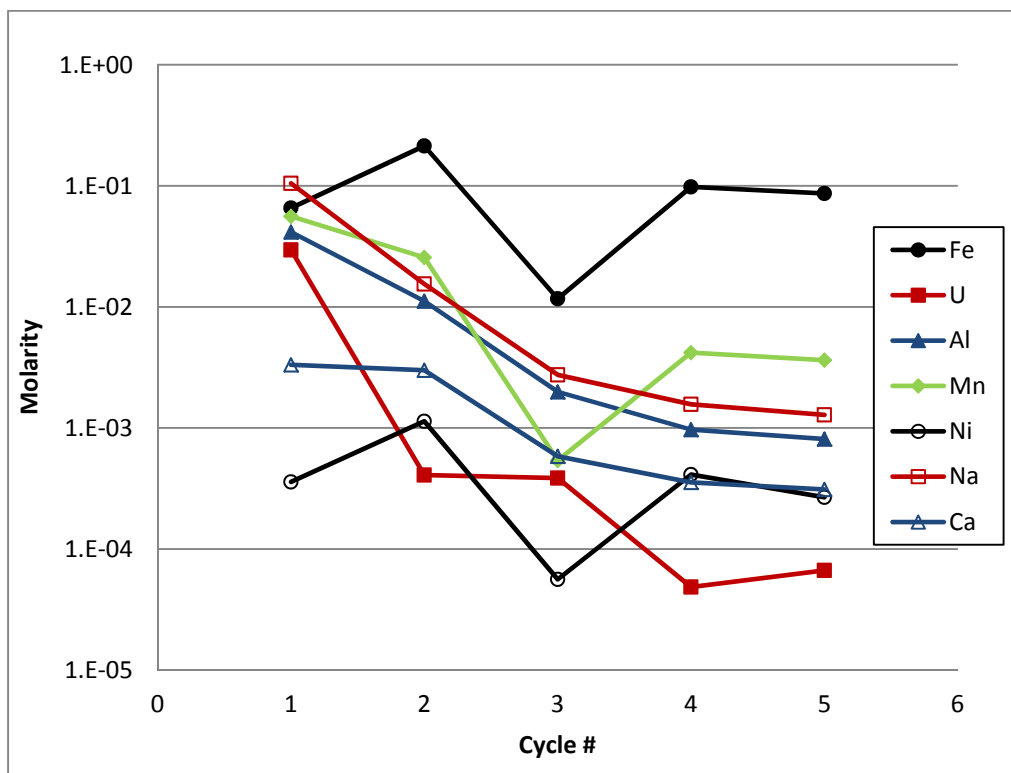
**Figure 3-1. XRD Pattern Observed for Residual Solids Isolated After Tank 5F Sludge Contact with Concentrated Oxalic Acid (5 Cycles, BOAC Testing).**



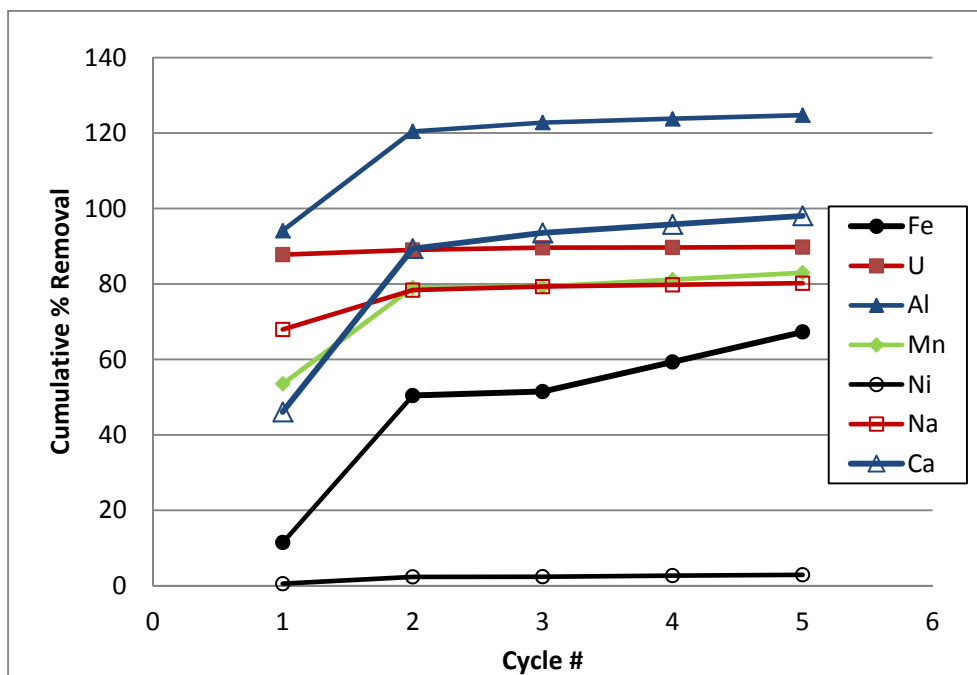
**Figure 3-2. XRD Pattern Observed for Residual Solids Isolated After Tank 5F Sludge Contact with the Oxalic/Nitric Acid Mixture (5 Cycles; D-OOAC Testing).**



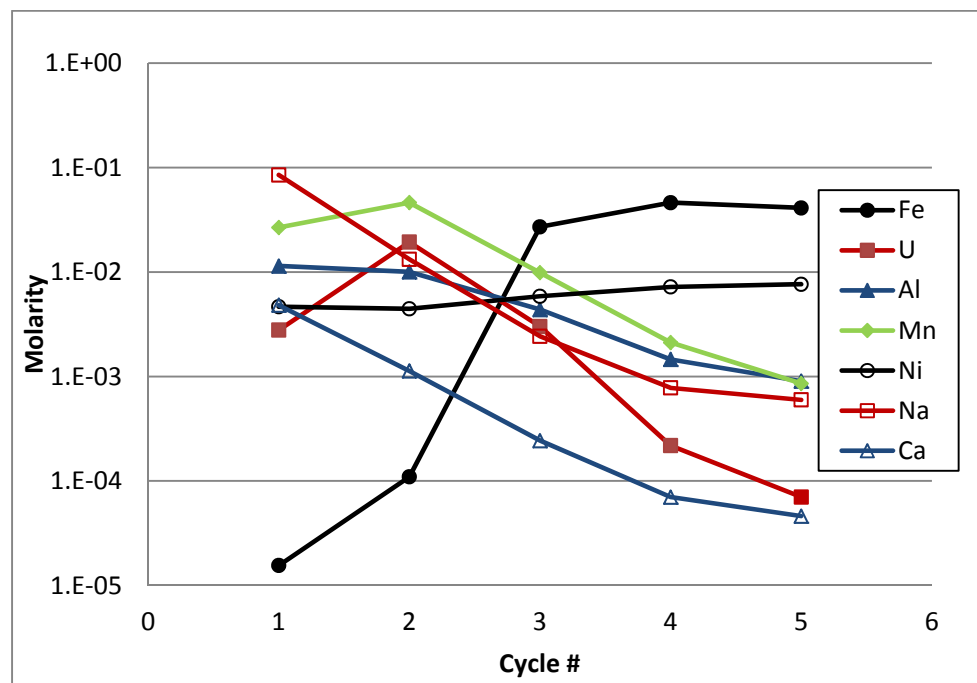
**Figure 3-3. XRD Pattern Observed for Residual Solids Isolated After Tank 5F Sludge Contact with Dilute Nitric Acid followed by the Dilute Oxalic/Nitric Acid Mixture (5 Cycles; P-OOAC).**



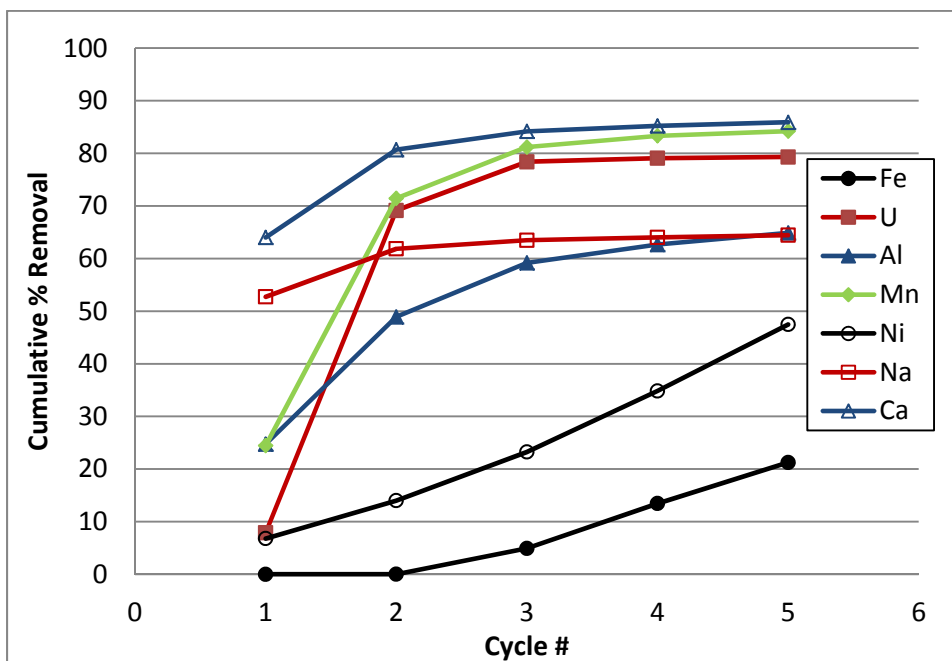
**Figure 3-4. Metal Concentrations Observed in Each Contact Cycle During BOAC Testing with Concentrated Oxalic Acid.**



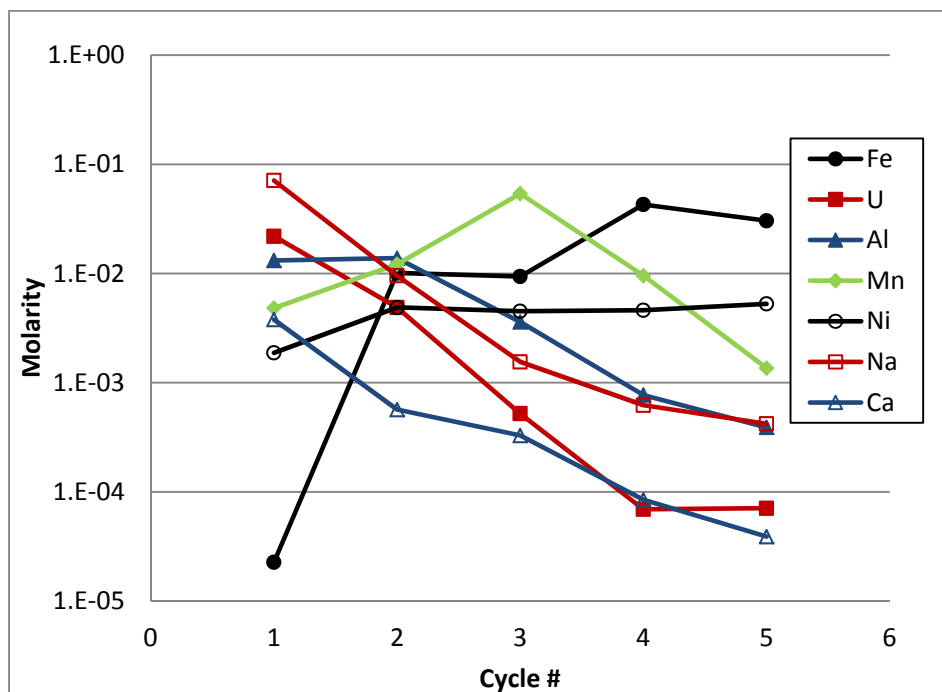
**Figure 3-5. Cumulative Metal Percent Removal Observed in Each Contact Cycle During BOAC Testing with Concentrated Oxalic Acid.**



**Figure 3-6. Metal Concentrations Observed in Each Contact Cycle During D-OOAC Testing with the Dilute Oxalic/Nitric Acid Mixture.**

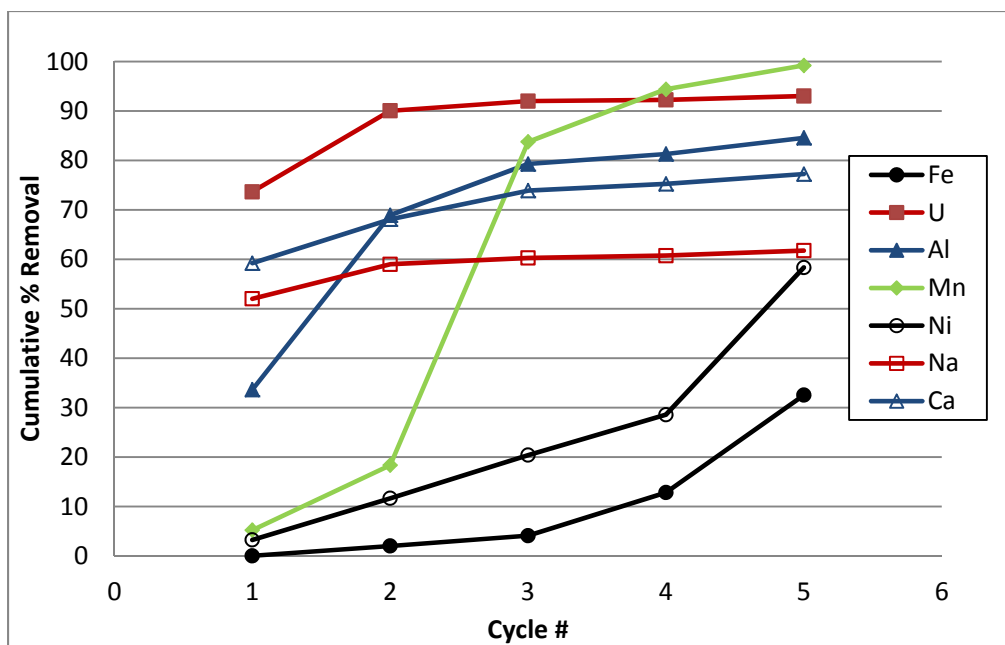


**Figure 3-7. Cumulative Metal Percent Removal Observed in Each Contact Cycle During D-OOAC Testing with the Dilute Oxalic/Nitric Acid Mixture.**

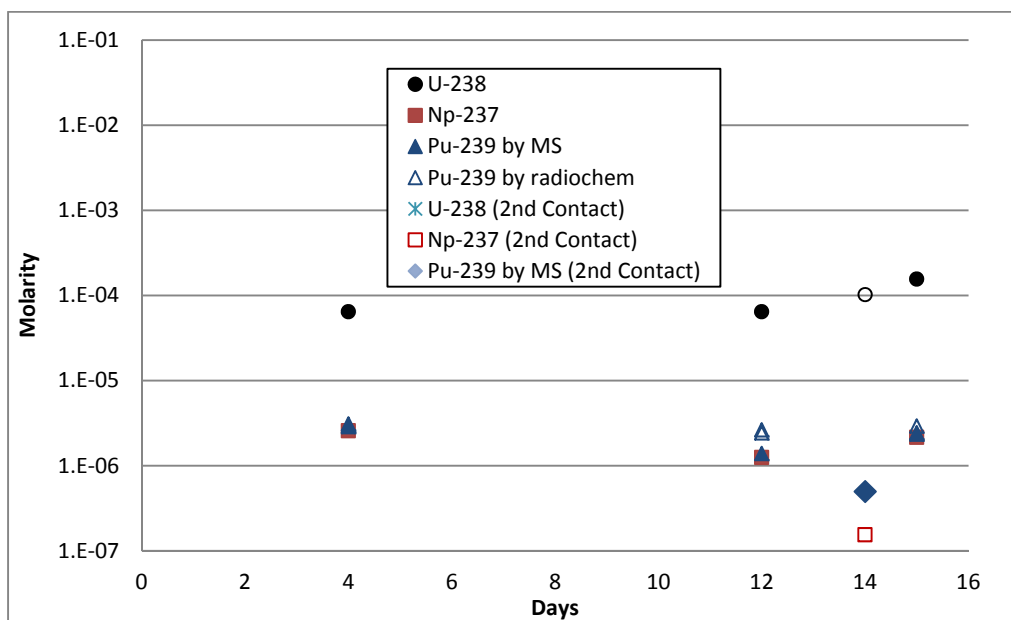


**Figure 3-8. Metal Concentrations Observed in Each Contact Cycle During P-OOAC Testing with Dilute Nitric Acid Followed by the Dilute Oxalic/Nitric Acid Mixture.**

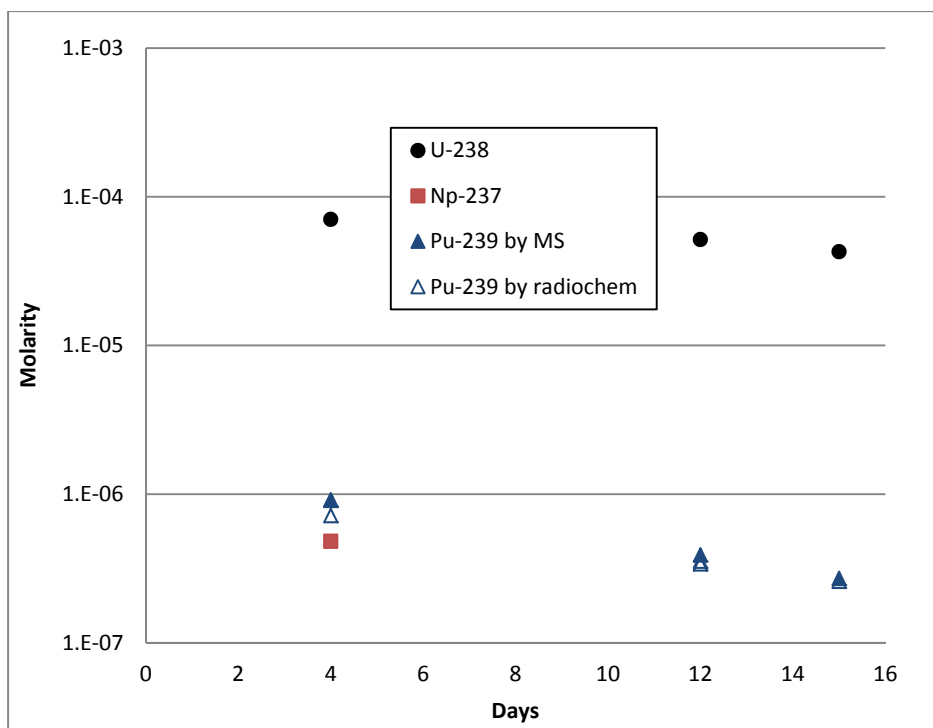




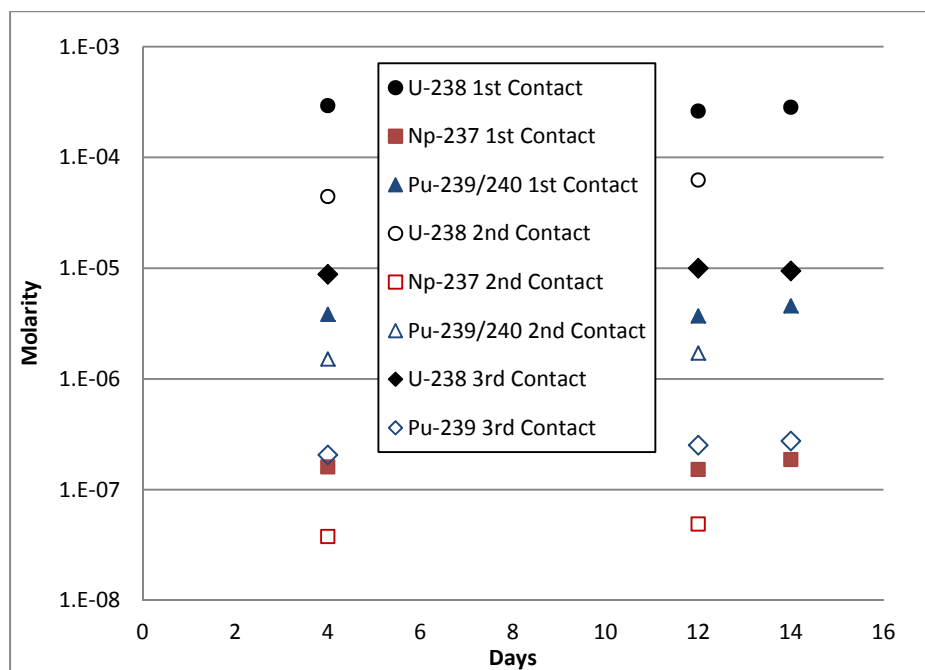
**Figure 3-9. Cumulative Metal Percent Removal Observed in Each Contact Cycle During P-OOAC Testing with Dilute Nitric Acid Followed by the Dilute Oxalic/Nitric Acid Mixture.**



**Figure 3-10. Metal Concentrations Observed for First and Second Contact Cycles Using the Caustic Permanganate Mixture (10 M NaOH/0.05 M NaMnO<sub>4</sub>).**



**Figure 3-11. Metal Concentrations Observed Using the Caustic Dilute Permanganate Mixture (10 M NaOH/0.017 M NaMnO<sub>4</sub>).**



**Figure 3-12. Metal Concentrations Observed for First, Second, and Third Contact Cycles Using the Acidic Permanganate Mixture (0.18 M HNO<sub>3</sub>/0.05 M NaMnO<sub>4</sub>).**

## 4.0 Conclusions

Solubility testing with a High Level Waste sludge sample from Tank 5F has been conducted in order to evaluate several alternative chemical cleaning technologies for the dissolution of sludge residuals remaining in the tanks after the exhaustion of mechanical cleaning and sludge washing efforts. Solubility tests were performed by direct sludge contact with the oxalic/nitric acid reagent and with sludge pretreated and acidified with dilute nitric acid. For comparison purposes, separate samples were also contacted with pure, concentrated oxalic acid following current baseline tank chemical cleaning methods. Solubility tests were also conducted with Tank 5F sludge using acidic and caustic permanganate-based methods focused on the “targeted” dissolution of actinide species.

Based on the results, significantly more oxalic acid than necessary has been used in previous tank chemical cleaning campaigns. The baseline oxalic acid cleaning method (BOAC) is ineffective for the removal of the nickel sludge component, but is effective at removing other sludge components including manganese, uranium, iron, and aluminum. The proposed optimized oxalic acid cleaning method (OOAC) involving a dilute nitric/oxalic acid mixture is effective for the removal of all sludge components. Preliminary pretreatment of the sludge with dilute nitric acid prior to contact with the OOAC reagent increases the efficiency of oxalate usage for sludge dissolution. The total mass of oxalic acid required to completely dissolve each gram of sludge is approximately 0.82 g when utilizing the OOAC method versus 1.7 g when using the baseline method. Although approximately half as much oxalic acid is required for sludge dissolution using the OOAC method versus the BOAC method, approximately 3.7 times as much water is required in the OOAC method due to the lower reagent oxalic acid concentration. This volume comparison, however, does not account for pre- and post-chemical cleaning washing operations that are typically required with the BOAC method and may not be needed with the optimized method. The dissolution of 1,000 gallons of sludge heel (approximate residual volume following recent mechanical cleaning campaigns) would require 260,000 gallons of the OOAC reagents (both dilute nitric acid and the dilute oxalic/nitric acid mixture) versus 74,000 gallons of BOAC reagent.

Analysis of composited decant solutions from the baseline and optimized oxalic acid cleaning methods was conducted to evaluate the amounts of actinide elements removed by each method. The BOAC cleaning method was not very effective at removing the plutonium, neptunium, and americium (0.2 to ~20% removal) while the OOAC method removed 47-90% of these metals. Removal of americium was significantly improved for the OOAC method where 90% removal was observed versus <1% removal for the BOAC method. Based on the results, the OOAC method is believed to be superior to the baseline BOAC method for actinide removal and utilization of the OOAC cleaning method should result in significantly enhanced removal of actinide elements from tank residual solids.

Plutonium concentrations observed with the caustic permanganate cleaning method approached, but were lower than, the concentrations observed during similar testing with radioactive simulants. Plutonium concentrations observed for the acidic permanganate method were higher than were observed with radioactive simulants. However, due to the amount of plutonium present in the sample, less than 10% plutonium removal was observed by either method. Actual washed heel samples (as opposed to unwashed sludge) would likely contain less total plutonium, and a greater percentage of the metal would be removed. Although the original Tank 5F sample contained no detectable neptunium, neptunium was observed in the caustic and acidic permanganate contact solutions, with higher concentrations being observed in the caustic permanganate reagent. Much higher neptunium concentrations were observed during radioactive simulant testing using these methods where a known and detectable amount of neptunium had been added. No detectable americium was observed during caustic permanganate testing, while americium removal was observed with simulated waste. In the acidic permanganate reagent, an americium concentration approaching the concentration observed during simulant testing was observed.

In general, during contact with the first portion (Cycle 1) of the permanganate solutions with Tank 5F sludge solids, the observed plutonium and americium concentrations were comparable to simulant testing. However, due to observations during testing of a loss of color from the deeply-colored permanganate cleaning solutions (both caustic and acidic), additional permanganate reagent volume was added. Surprisingly, lower actinide concentrations were observed in successive contacts using both the caustic and acidic permanganate methods, even though a significant fraction of the actinide mass remained in the samples. These observations may indicate that the amounts of actinide elements that can be removed from the sludge using these cleaning methods are limited. Degradation of the permanganate reagents may be associated with the fact that the Tank 5F sludge sample had not been extensively washed to remove soluble oxalate salts. Additional evaluations to understand the impacts of these observations are necessary prior to implementation of this cleaning method. Nonetheless, the concentrations observed during contact Cycle 1 using these reagents are in the range where utilization of this method for the treatment of washed tank heels for the removal of trace actinides may be useful.

Comparison of the actinide concentrations observed for the permanganate (both caustic and acidic) and P-OOAC cleaning methods reveals that similar plutonium concentrations ( $2.5\text{E-}06$  to  $5\text{E-}06$  M) were observed for all three methods. Neptunium concentrations observed for the caustic permanganate method and the P-OOAC method were similar ( $1\text{E-}06$  to  $3\text{E-}06$  M), but significantly lower neptunium was observed with the acidic permanganate method. Americium concentrations observed for the acidic permanganate method and the P-OOAC method were similar ( $3.5\text{E-}07$  to  $8\text{E-}07$  M), but significantly lower americium was observed with the caustic permanganate method. However, due to the significantly higher cleaning reagent volume used for the P-OOAC method, much larger percentages of the actinides were removed (47% Pu removal,  $\geq 82\%$  Np removal, 90% Am removal) versus the permanganate based methods ( $\leq 10\%$  actinide removal). In addition, it should be possible to remove more of the actinides with additional reagent using the P-OOAC method, which was not the case with the permanganate-based methods using the current approach (additional reagent does not dissolve significant quantities of additional actinides).

## 5.0 Recommendations, Path Forward, and Future Work

Mechanical removal of High Level Waste tank heels and sludge sluicing/washing operations should be exhausted prior to the implementation of any chemical cleaning method in order to minimize cleaning reagent additions to the tank farm inventory. Based on previous cleaning campaigns, a sludge heel volume near 1000 gallons is a reasonable residual volume goal prior to chemical cleaning. Dilute nitric acid should be considered for the pretreatment and acidification of sludge heels prior to the addition of any oxalic acid reagent in order to minimize oxalate additions to the inventory. The optimized cleaning method should be considered for any future chemical cleaning operations to minimize oxalate additions and remove residual actinides. Actinide concentrations similar to those obtained in simulant studies were observed for plutonium and americium using the permanganate-based cleaning methods. However, the fraction of actinides removed was low due to the amounts of actinides present in the sludge sample. Additional contacts with the permanganate-based reagents did not result in further actinide removal. Additional studies are recommended to understand these observations prior to method implementation. Analogous testing of other SRS sludge types would be useful to evaluate the performance of the various cleaning reagents and methods with these materials.

## 6.0 References

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