WSRC-TR-2003-00120
revision 0

Impacts of Sodium Oxalate on High-Level Waste Processing at the Savannah River Site

D. T. Hobbs

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC09-96SR18500

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

THIS PAGE INTENTIONALLY LEFT BLANK

WSRC-TR-2003-00120
Revision 0

Key Words: Sludge Leaching
Actinides
Evaporation
Mercury
Solids Formation
Salt Processing

Impacts of Sodium Oxalate on High-Level Waste Processing at the Savannah River Site

D. T. Hobbs

Publication Date: March 6, 2003

1.0 Summary and Conclusions

This report documents results from tests conducted to evaluate the impacts of elevated levels of oxalate on operations within the SRS High-Level Waste System. These operations include sludge washing, evaporation, mixing of supernates and wash waters and pretreatment of supernates to remove strontium and actinides by monosodium titanate. Key findings of this testing include the following:

- the addition of oxalate solids to a suspension of Tank 8F sludge did not enhance the leaching of metals from the sludge,
- analytical data proved inconclusive regarding increased leaching of uranium and plutonium from the Tank 8F sludge,
- the presence of dissolved oxalate did not exhibit an adverse impact upon the evaporation of wash water solutions initially containing 0.05 M oxalate,
- the presence of dissolved oxalate did not increase the deposition of uranium in saltcake produced from the evaporation of wash water solutions initially containing 0.05 M oxalate,
- the presence of dissolved oxalate did enhance the precipitation of solids upon mixing wash water solutions with a concentrated salt solution similar to that in evaporator feed tanks,
- the presence of dissolved oxalate did not increase the release of elemental mercury during evaporation of wash water solutions containing 0.01 M to 0.04 M oxalate,
- the presence of 0.008 M oxalate and other minor solution components did not affect the performance of monosodium titanate to remove strontium and actinides from an alkaline, 5.6 M sodium salt solution and
- scoping tests confirmed that uranyl oxalate is not stable upon contact with strongly alkaline salt solutions such as those found throughout the SRS HLW System.

Based on these findings I conclude that the presence of sodium oxalate does not significantly impact uranium and plutonium chemistry within normal operations of the HLW system at the SRS. I recommend that the archived wash water samples be prepared with a lower dilution factor as a means to better quantify plutonium and uranium dissolution across the entire series of wash water contacts with the Tank 8F-sludge material. Alternatively, I recommend that SRTC conduct washing experiments with Tank 7F sludge materials to determine evidence for increased leaching of uranium and plutonium. Of particular interest are the final stages of washing when the supernatant liquids contain similar concentrations of free hydroxide and oxalate. I also recommend that SRTC conduct additional tests investigating the mixing of wash waters with evaporator feed solutions to better understand the extent of solids formation over the range of conditions spanned by the three HLW evaporator systems at the SRS.

2.0 Introduction

Sludge from Tank 7F will be processed as part of Sludge Batch 3 in the DWPF. Based on process records, Tank 7F received large quantities of oxalate estimated at approximately 300,000 kilograms. Recent samples from Tank 7F, after slurrying a significant portion of the sludge, showed much less oxalate than expected (ca. 10,000 kilograms).[1] Prior to processing in DWPF, the slurry must be washed to adjust the sodium content and weight percent total solids. In typical sludge slurries, sodium is primarily soluble and easily adjusted by contacting with dilute sodium hydroxide solution and decanting the supernate (i.e., washing). For Tank 7F, sodium adjustment may be complicated by the presence of large quantities of solid sodium oxalate, which exhibits limited solubility in aqueous solutions. The presence of oxalate may also complicate glass processing (melter offgas, glass redox, etc.) and, therefore, should be reduced.

Upon washing of the Tank 7F sludge, solid sodium oxalate will dissolve resulting in supernate liquids near or at saturation with respect to sodium oxalate. Oxalate forms complexes with a wide variety of metallic ions including transition metals (e.g., Fe^{3+} and Al^{3+}) and actinides (e.g., UO_2^{2+} and PuO_2^{2+}). Complex formation can increase solubility resulting in increased actinide release to downstream processes involving supernates including evaporation and radionuclide separations. Oxalate can also serve as a reductant to mercuric species producing elemental mercury. Elevated oxalate in the waste solutions could result in increased release of elemental mercury to the overheads upon evaporation. The effects of oxalate on sludge processing and downstream operations are largely unknown. Thus, HLW Engineering requested SRTC to identify if the presence of sodium oxalate in Tank 7F sludge will affect the chemistry associated with actinides and mercury during sludge washing and downstream processing of the wash waters through the SRS HLW System.[2]

Technical Task Request HLE-PRE-TTR-0027 specifies SRTC to determine the following six tasks:

1. Determine if increased sodium oxalate levels will increase leaching of actinides from sludge in Sludge Batch 3,
2. Determine if actinides will precipitate upon evaporation of wash water from sludge washing,
3. Determine if increased sodium oxalate levels will increase aluminum and silicon solubilities resulting in increased solids deposition during waste evaporation,
4. Determine if sodium oxalate will reduce mercury to the elemental form,
5. Determine if increased sodium oxalate will decrease performance characteristics of monosodium titanate (MST) for the removal of strontium and actinides,
6. Determine if increased sodium oxalate levels will adversely impact Saltstone wasteform performance.

This document reports experimental details for the first four tasks. Previous testing documented the effect of oxalate and other minor solution components on the performance of MST for the removal of strontium and actinides. I detail these results in Section 4.4 of this report. Task 6 (Saltstone impact) was addressed separately by a letter report.[3]

Experimental work conducted under this task plan compared the affects of sodium oxalate on actinide and mercury chemistry through sludge processing, evaporation and supernate processing with simulated and tank waste materials. Testing compared chemical behavior of the actinides and mercury with simulated and tank waste materials in the presence and absence of sodium oxalate. The information obtained in this testing phase identified if impacts exist with some idea of magnitude, but did not provide detailed information over all waste compositions and processing conditions.

3.0 Experimental

3.1 Task 1

Ann unwashed sludge slurry sample from Tank 8F (identified as samples FTF-015 and FTF-016) was contacted with inhibited water (0.015 M NaOH and 0.015 M $NaNO_2$) for 2 weeks at ambient temperature to simulate dilution through the entire sludge processing operation. One test set treated the unwashed sludge slurry as received. The second test first added a quantity of solid reagent-grade sodium oxalate to the sludge at a level consistent to that estimated for Tank 7F sludge. The sludge slurries were contacted with four different volume ratios of inhibited water to sludge (1:1, 4:1, 10:1 and 25:1) to cover the dilution range spanned by Extended Sludge Processing planned for Sludge Batch 3.

For these tests between 1.3 to 6.9 grams of the Tank 8F-sample material were transferred into a preweighed 50-mL glass centrifuge tube marked with volume graduations. Based on the quantity of sludge, appropriate quantities of inhibited water followed by solid sodium oxalate were added to the centrifuge tubes. The centrifuge tubes were capped and placed each into a plastic sample holder mounted on an orbital shaker (Cole-Parmer Series 51704). Table 3.1.1 provides the quantities of sludge, inhibited water and sodium oxalate for each test.

Table 3.1.1 Experimental Quantities for Sludge Washing Tests

Test #	Water:Sludge Ratio[a]	Sludge (g)	Inhibited Water (g)	Sodium Oxalate (g)
1	25	1.266	26.183	1.088
2	10	2.625	21.601	0
3	1	6.698	5.401	0
4	10	2.520	21.820	0.787
5	4	6.514	21.629	0
6	10	2.579	21.396	0.803
7	10	2.624	21.703	0.823
8	1	6.740	5.411	1.966
9	10	2.576	21.213	0
10	blank	0	19.968	0
11	4	6.906	22.895	2.187
12	25	1.340	27.704	0
13	10	2.712	22.152	0

[a] targeted volume of wash water to volume of sludge slurry

Initially we set the orbital shaker at a rate of 100 rpm. After 1 week, visual inspection indicated that the sludge solids had settled to the bottom of each tube. Each tube was inverted manually to resuspend the solids. The tubes were placed back on the orbital shaker and the shaking rate was increased to 150 rpm. After an additional 3 days, visual inspection indicted that the solids had settled as before. Again each tube was inverted, returned to the shaker and shaken at an increased rate of 200 rpm. After another 24-hours, the solids had settled in all tubes except Tests #3 and #8, which exhibited a cloudy supernatant liquid. Again each tube was inverted, put back on the shaker and shaken at 200 rpm. After 48 hours, the sludge solids in all tubes except Tests #3 and #8 had settled producing a clear supernatant liquid above the solids. For Tests #3 and #8, the supernatant liquid above the solids was cloudy, although the cloudiness was significantly less than that previously observed. Each tube was inverted to resuspend the solids, placed back on the shaker and shook at 200 rpm for an additional 24 hours. This produced a total contact time of 14 days.

After 14 days of contact the mixtures were filtered through a Nalgene® disposable filter equipped with a 0.45-micron nylon filter membrane. Two 50:1 dilutions were prepared from each filtrate of for chemical and radiochemical analyses. The first dilution used a solution of 0.015 molar sodium hydroxide and 0.015 molar sodium nitrite (referred to as inhibited water), whereas the second dilution used a 1.0 molar solution of high purity nitric acid (Fisher Scientific Lot #120110). Approximately 5 mL of the diluted samples were pipetted into a shielded plastic sample bottle and removed from the Shielded Cells. The inhibited water dilutions were submitted to the Analytical Development Section (ADS) for determination of anions using ion chromatography. The nitric acid dilutions were submitted to ADS for elemental analysis by inductively coupled plasma emission spectroscopy (ICP-ES) and actinides by inductively coupled plasma mass spectroscopy (ICP-MS) and alpha counting.

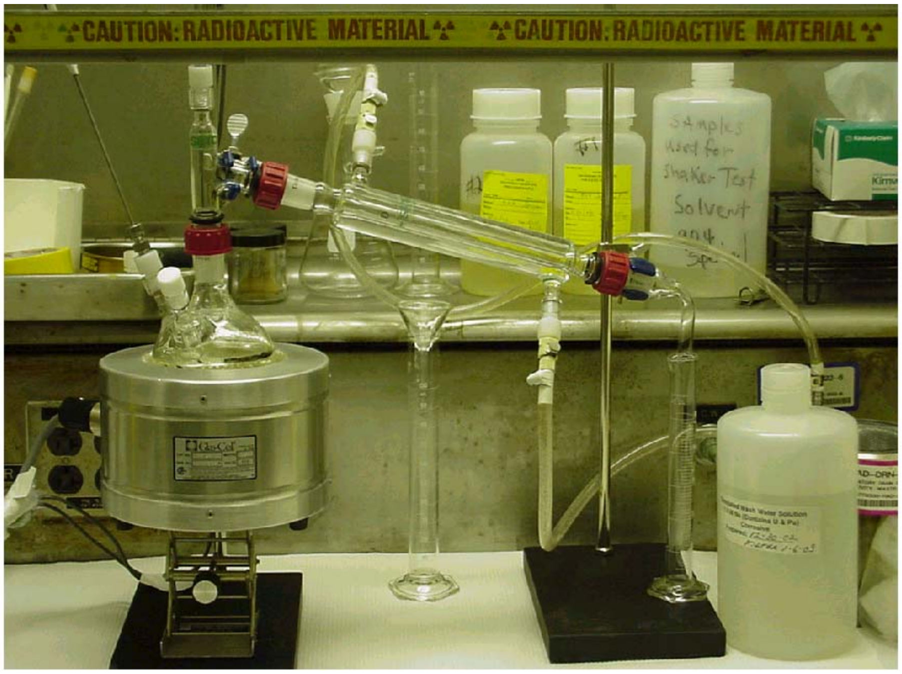
3.2 Tasks 2 and 3

These tests featured the evaporation of two simulated waste solutions containing uranium, plutonium, aluminum and silicon with and without 0.1-M oxalate. Table 3.2.1 provides the composition of the solutions. The solution composition is based on the composition of decant from the second stage of Sludge Batch 3 washing estimated by Elder.[4] This composition represents an intermediate salt solution composition approximating an average of all wash waters generated from preparing Sludge Batch 3. Both solutions were prepared using reagent grade chemicals and a nitric acid solution of weapons-grade plutonium supplied by the Actinide Technology Section of SRTC. Figure 3.2.1 provides a photograph of the system used for the evaporation tests. The SRTC glass shop fabricated the glassware comprised on a 500 mL round bottom flask with connections for temperature sensor, solution inlet and condenser head, the condenser head with connection for temperature sensor, water-cooled condenser and overheads collector (graduated cylinder). A 115-volt 250-watt Glas-Col heating mantle (Part #TM560) and Glas-Col controller (Part #U-36225-91) provided controlled heating to the evaporation flask. A calibrated (MTE# WP-924, WP-844A and WP-844E) thermistor thermometer (Omega Model #5831A) and thermistor probes (Omega Part #OL-703-PP) provided temperature measurements of the evaporating liquid in the round bottom flask and the heated vapor prior to entering the condenser.

Table 3.2.1 Composition of Simulated Wash Water Solution

	Concentration			
	Without Oxalate		With Oxalate	
Component	Gravimetric	Measured	Gravimetric	Measured
NaOH (M)	0.35		0.35	
$NaNO_3$ (M)	0.21		0.21	
$NaNO_2$ (M)	0.21		0.21	
$NaAl(OH)_4$ (M)	0.030	0.030	0.030	0.029
Na_2CO_3 (M)	0.035		0.035	
NaF (M)	0.020		0.020	
Si (M)	0.00090	0.0019	0.00090	0.0019
$Na_2C_2O_4$ (M)	0		0.10	
Total Na (M)	0.90 M	0.96	1.0	1.05
U (µg/L)	15,000	16,800 ± 2600	15,000	15,500 ± 2000
Pu (µg/L)	200	131 ± 1.76	200	(see Table 4.2.2)

Figure 3.2.1 Photograph of the Equipment Used in the Evaporation Testing



The evaporation test consisted of placing 350 mL of the salt solution (Table 3.2.1) in the evaporator pot, flowing water to the condenser, energizing the heating mantle to heat the evaporator pot solution to boiling and collecting condensed overheads. After collecting approximately 150 mL of overheads, 150 mL of fresh salt solution were added to the evaporator pot. The evaporation was stopped each day by de-energizing the heating mantle, cooling the evaporator pot to ambient laboratory temperature and shutting off flow of the cooling water to the condenser. The following day the evaporation resumed by energizing the heating mantle to return to boiling conditions and flowing cooling water to the condenser.

each test continued until evaporating between 1500 and 1550 mL of fresh salt solution and collecting between 1230 and 1340 mL of condensed overheads. All of the collected overheads were combined into a single preweighed plastic bottle for each test. At the completion of the evaporation test, the concentrated salt solution remaining in the evaporator pot was cooled to ambient laboratory temperature. Additional white solids formed. The solids from the walls of the flask were loosened and the mixture was poured into a 150-mL Nalgene® filter with 0.2-micron nitrocellulose membrane (Part #138-4020). The solids were air-dried for 48 hours and transferred into preweighed wide-mouth glass jars. The filtered concentrated salt solutions were collected and stored in preweighed plastic storage bottles.

The densities, metals and actinide contents for the condensed overheads and concentrated salt solutions were determined for each test. ADS determined crystalline phases in the solids by X-ray diffraction (XRD) analysis. ADS also determined metals, actinides and oxalate content of the solids by ICP-ES, ICP-MS, alpha counting methods and ion chromatography following a dissolution in a combination of nitric and hydrofluoric acids.

An additional test determined if mixing wash water with a concentrated salt solution would produce a solid precipitate. For these tests small portions of simulated wash water solutions having the compositions reported in Table 3.2.1 were added slowly to a more concentrated salt solution consistent with that in an evaporator feed tank. Table 3.2.2 provides the composition of the solution used in this test representing an evaporator feed solution. The composition of this solution is based on the highest reported concentration for each component, with the exceptions of silicon, uranium and plutonium, in the most recently recorded and completely analyzed sample from Tanks 26F, 32H and 43H.[5] For silicon, the concentration is that measured in the tank sample having the highest aluminum concentration (Tank 32H). The uranium and plutonium concentrations were selected to be near their respective solubility limits.

Table 3.2.2 Composition of Simulated Evaporator Feed Solution

Component	Concentration Value[a]	Unit
NaOH	7.3	M
$NaNO_3$	2.6	M
$NaNO_2$	2.2	M
$NaAl(OH)_4$	0.54	M
Na_2CO_3	0.17	M
NaF	0.012	M
NaCl	0.011	M
$Na_2C_2O_4$	0.0063	M
Na_3PO_4	0.012	M
KNO_3	0.069	M
Na_2SiO_3	0.001	M
U	10,000 (5930)	μg/L
Pu	1000 (401)	μg/L

[a] Values in parenthesis are those measured by ICP-MS.

Table 3.2.3 provides a listing of the conditions we used for the solids formation tests. In addition to performing tests with and without oxalate in the wash water solutions, the volume ratios of evaporator feed solution to wash water were varied. After adding the wash water solution to the evaporator feed solution, the two-phase mixture was allowed to stand undisturbed at ambient laboratory temperature. Periodically the test solutions were inspected for evidence of solids formation. For tests with precipitated solids, the mixture was filtered through a 150-mL Nalgene® filter with 0.2-micron nitrocellulose membrane (Part #138-4020) to separate the solids from the salt solution. The solids were washed briefly three times each with approximately 1 mL of inhibited water followed by air-drying for 48 hours at ambient laboratory temperature. XRD analysis featured the solids isolated from Test #1 (3:1 v/v). Due to the small quantity of precipitated solids, elemental and actinide analyses featured a composite of all solids isolated from Tests # 2 – 5.

Table 3.2.3 Solids Formation Testing Conditions

Test #	Wash Water Solution	Evaporator Feed Solution to Wash Water Volume Ratio
0	without oxalate	3:1
1	with oxalate	3:1
2	with oxalate	4:1
3	with oxalate	6:1
4	with oxalate	10:1
5	with oxalate	20:1

3.3 Task 4

This testing featured a salt solution having the targeted composition provided in Table 3.3.1. Note that analysis of the salt solution indicated only about one-third of the mercury dissolved in the alkaline salt solution. Figure 3.3.1 provides a photograph of the experimental apparatus used for this test. Heating and temperature measurement in this test is that previously described in the Tasks 2/3 evaporation tests. No attempt was made to scrub vapors that passed beyond the top of the reflux condenser. The round bottom flask was charged with approximately 250 mL of the Hg-spiked salt solution followed by an appropriate amount of reagent grade solid sodium oxalate to produce an oxalate concentration of 0.0 M, 0.01 M, 0.02 M and 0.04 M assuming all of the sodium oxalate dissolved. After adding the solid sodium oxalate, the heating mantle was energized and the solution heated to boiling. Prior to boiling all of the sodium oxalate dissolved in each of the tests featuring addition of sodium oxalate. Boiling conditions were maintained for 4 hours during each test. After 4 hours, the heating mantle was de-energized and solution allowed cooling to ambient laboratory temperature. The flask was inspected for evidence of elemental mercury. Samples of the solution from each test were submitted to ADS for determination of mercury content by cold vapor atomic absorption spectroscopy.

During the workup of Test #2, 0.29 grams of white solids was collected onto a Nalgene® disposable filter (0.45-micron nylon membrane). The solids were washed with several small portions of deionized, distilled water and air-dried for 48 hours at ambient laboratory temperature. All of the solids from Test #2 were submitted to ADS for XRD analysis. Subsequent tests produced a white film on the wall of the flask in contact with the salt solution. However, there were insufficient solids in these films to isolate and characterize. The white film was easily removed after each test by rinsing the flask with several small portions of 2M nitric acid solution.

Table 3.3.1 Composition of Task #4 Simulated Evaporator Feed Solution

Component	Concentration Value	Unit
NaOH	0.70	M
$NaNO_3$	0.42	M
$NaNO_2$	0.42	M
$NaAl(OH)_4$	0.060	M
Na_2CO_3	0.14	M
NaF	0.040	M
Si	0.0018	M
$Hg(NO_3)_2$	0.00043[a]	M

[a] added 0.0012 M Hg during preparation of solution, however, analysis of the filtered solution measured 0.00043 M Hg

Figure 3.3.1 Photograph of Testing Equipment Used for the Mercury Vaporization Testing

3.4 Task 5

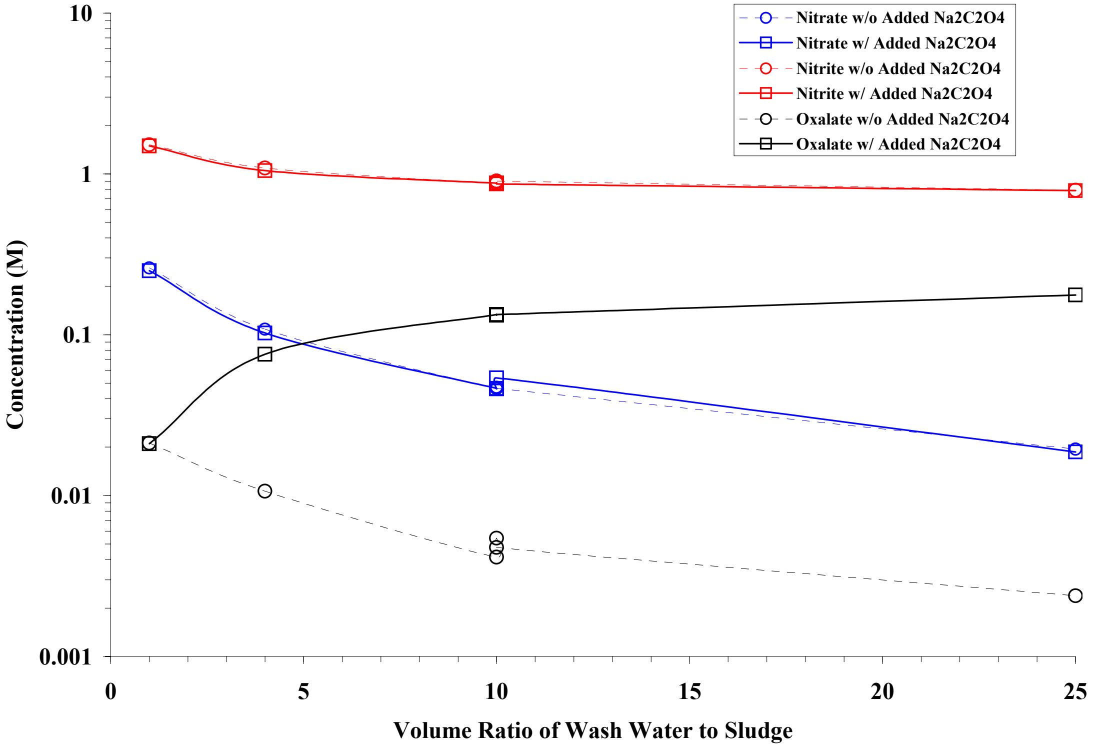
The experimental method used to evaluate the impact of oxalate on MST performance for strontium and actinide removal from alkaline salt solutions was previously reported in another technical report.[6] This report detailed the effects of solution composition including that of oxalate on MST performance.

4.0 Results and Discussion

4.1 Task 1

Analysis of the wash waters from contacting the Tank 8F sludge with inhibited water provided an assessment of the impact of a large amount of solid oxalate during washing of sludge slurries. In this test the volume ratio of wash water to sludge slurry volume was varied from 1:1 to 25:1. Figure 4.1.1 presents a semi-log graph of the concentrations of nitrite, oxalate and nitrate versus volume ratio of wash water to sludge as determined by ion chromatography for each test. Note that the tests at a volume ratio of 10:1 were conducted in triplicate.

Figure 4.1.1 Nitrite, Oxalate and Nitrate Concentrations in Wash Waters Contacted with Tank 8F Sludge

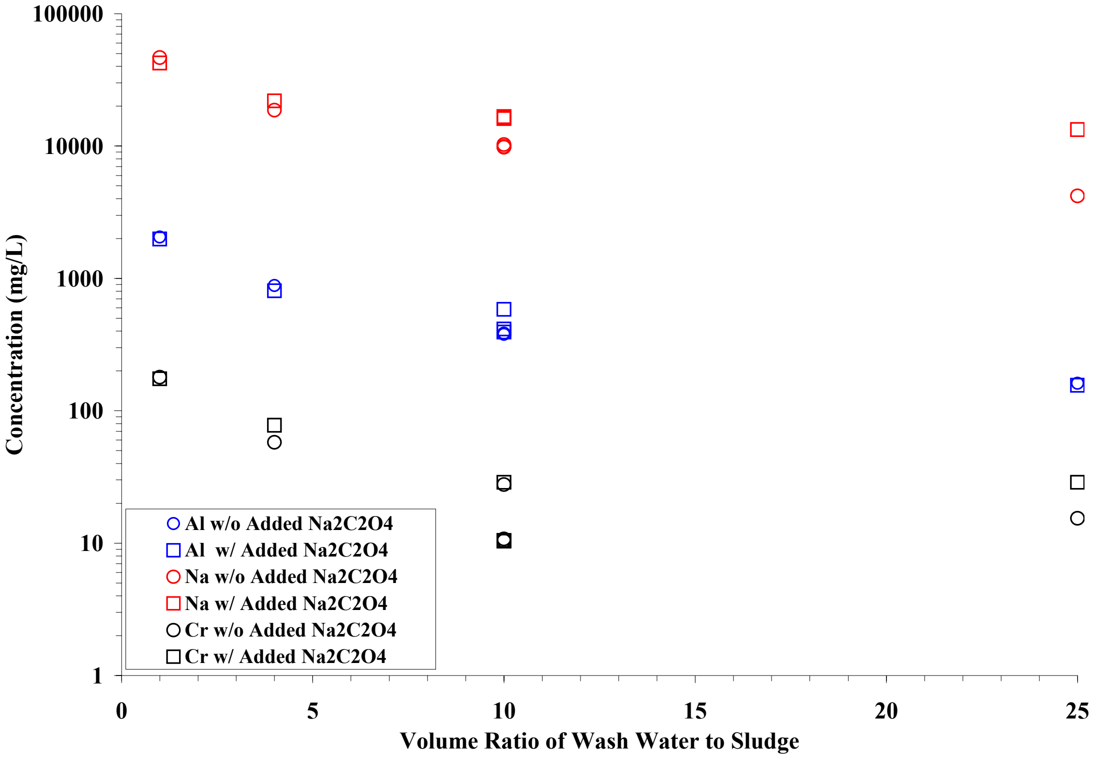


The blank test, which contained no sludge or sodium oxalate, is not shown in the graph. The nitrite concentration in the blank test sent through the same experimental processing steps as the other tests measured 0.0137 M, which is in good agreement with the as-prepared value of 0.0150 M. This result suggests no measurable cross-contamination or dilution errors occurred with respect to the major anions. Appendix 1 provides a complete list of the nitrate, nitrite and oxalate concentrations after contact with Tank 8F sludge for 14 days.

Nitrate and oxalate (w/o added sodium oxalate) concentrations decreased with increasing volume ratio of wash water to sludge. This is the expected trend based on simple dilution. Note that in the tests with added oxalate, the concentration of oxalate increases with increased wash water. I attribute the increase to more of the solid sodium oxalate dissolving as the concentration of the other salts decreases. At a volume ratio of 25:1, the oxalate concentration measured 0.177 M, which is slightly lower than the estimated maximum value of 0.250 M, based on previous testing by J. Pareiz and others.[7]

ICP-ES analyses provided a list of elements detected in the wash water solutions. Appendix 2 provides a complete listing of all elements for each of the test solutions corrected for dilution and for elements found in the blank solution. The blank solution measured 831 mg/L or 0.036 M in sodium, which is 20% higher than the targeted as-prepared value of 690 mg/L or 0.030 M. ICP-ES analyses measured only three elements for each volume ratio after correcting for the blank solution. These elements included sodium, aluminum and chromium. Figure 4.1.2 provides a semi-log plot of the sodium, aluminum and chromium concentrations for the test set arranged by whether the test contained added sodium oxalate or not.

Figure 4.1.2 Concentrations of Selected Elements in Wash Water Solutions from Contacting Tank 8F Sludge with Inhibited Water for 14 Days



The results indicate that the sodium and aluminum concentrations decreased upon an increase in the wash water to sludge ratio in the absence of added sodium oxalate. Initially the data indicates a similar trend for chromium. At the highest wash water volume ratio, the chromium concentration increased slightly. However, the measured concentration is just above the detection level and may just reflect a greater analytical variance at the higher ratio of wash water to sludge.

I observed similar trends with these three elements in the tests with added sodium oxalate. The higher sodium concentration at the 25:1 volume ratio reflects higher concentration of sodium oxalate resulting from the dissolution of the solid sodium oxalate added in this test compared to the test without added sodium oxalate.

ICP-ES analytical results identified only four other elements, calcium, potassium, molybdenum and strontium, in the 1:1 volume ratio wash water solutions for tests with and without added sodium oxalate. At the higher volume ratios of wash water to sludge, the measured concentrations fell below the detection limits after correcting for dilution and the test blank (see Appendix 2). The measured concentrations of potassium, molybdenum and strontium in the wash waters with added sodium oxalate fell below those measured without added oxalate. For calcium the calcium concentration in the test with added oxalate (2.29 mg/L) was about a factor of two higher than that measured in the same test condition without oxalate (1.54 mg/L). Based on the elemental measurements obtained from ICP-ES I conclude that the presence of added sodium oxalate does not significantly increase the dissolution of metals from the sludge solids upon contact with a range of inhibited water solution volumes.

We measured plutonium and uranium concentrations in the wash water solutions by radiochemical counting and ICP-MS, respectively. In principle, ICP-MS should provide the concentrations for selected plutonium isotopes as well. However, the concentrations of plutonium in the wash water solutions isolated from these tests fell below the minimum detection limits of the ICP-MS instrument.

Table 4.1.1 provides a complete table of the plutonium and uranium concentrations in the wash water solutions obtained from the tests with and without added sodium oxalate. Plutonium measurements for all but one of the test conditions proved below the minimum detection level after correcting for dilution and contamination in the test blank solution. Uranium concentrations also proved low, but above minimum detection limits in all but one test.

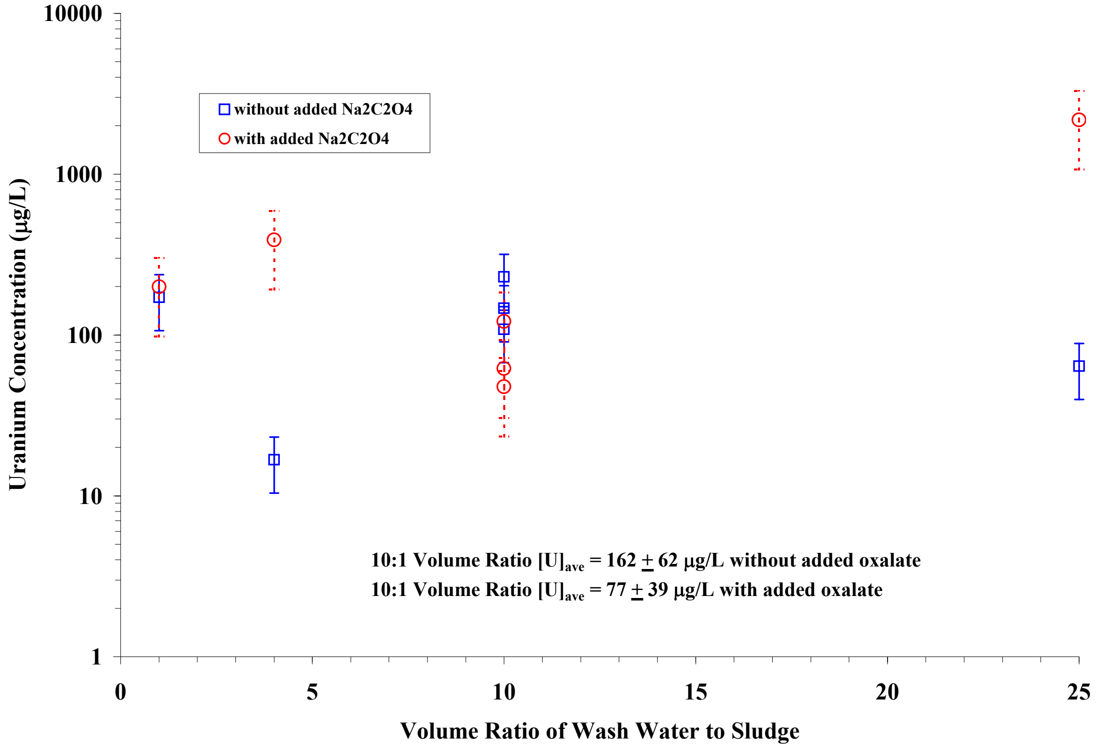
Table 4.1.1 Plutonium and Uranium Concentrations in Wash Water Solutions upon Contact with Tank 8F Sludge

Wash Water Volume Ratio	Added Oxalate	[Pu] (μg/L)	[U] (μg/L)
1:1	no	<6.83	172
1:1	yes	<6.83	200
4:1	no	<6.83	17
4:1	yes	<6.83	391
10:1	no	<6.83	230
10:1	no	<6.83	<147
10:1	no	<6.83	109
	Average	<6.83	≤162 ± 62
10:1	yes	<6.83	109
10:1	yes	1.52	122
10:1	yes	<6.83	48
	Average	≤5.06 ± 3.07	77 ± 39
25:1	no	<6.83	64
25:1	yes	<6.83	2175

The low plutonium concentrations in the wash water solutions in all of the test solutions suggest that oxalate does not enhance dissolution of plutonium from the Tank 8F sludge. However, since all but one of the measured plutonium concentrations fell below the detection limit, I cannot conclusively quantify the effect of oxalate on plutonium dissolution with the existing dataset. I recommend that the archived wash water samples be prepared with a lower dilution factor as a means to better quantify plutonium dissolution.

Figure 4.1.3 shows a graph of the uranium concentrations in the wash water solutions versus the volume ratio. Included in the graph are the one standard deviation error bars based on the replicate tests at the 10:1 volume ratio. The uranium concentrations at the 1:1 and 10:1 volume ratios suggest that oxalate do not enhance uranium dissolution. However, the results at the 4:1 and 25:1 volume ratios exhibit much higher uranium concentrations in the tests with added sodium oxalate. This suggests that oxalate is enhancing uranium dissolution. I speculate that the difference in the uranium concentrations for the 4:1 volume ratio solutions largely reflects the variance associated with the acid-dilution subsamples. I suspect that the uranium measurement at the 25:1 volume ratio may be in error or represents a subsample of the Tank 8F sludge that had a much higher uranium concentration than the other subsamples. With the exception of the 25:1 test with added oxalate, the uranium concentrations in the acid-diluted subsamples are very low and range from about 2 to 10 μg/L. For the 25:1 test, the measured uranium concentration in the acid-diluted subsample measured 42 µg/L. This high value could be the result of sample contamination. I recommend that the archived wash water samples be prepared with a lower dilution factor as a means to better quantify uranium dissolution across the range of wash water contacts.

Figure 4.1.3 Uranium Concentrations in Wash Water Solutions



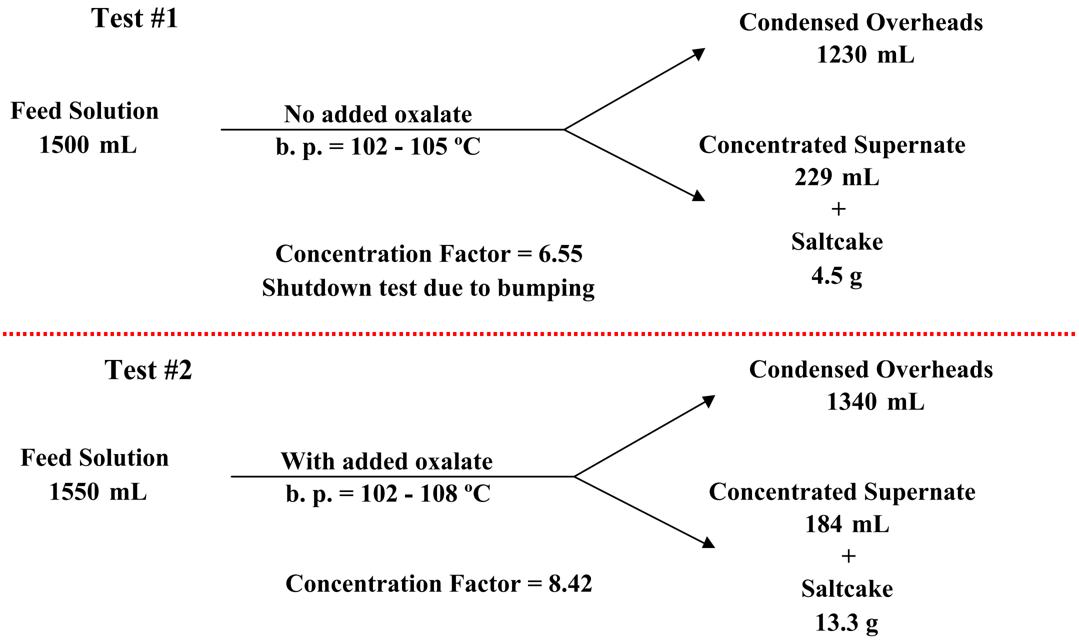
4.2 Tasks 2/3

Evaporation Tests

Testing featured the evaporation and mixing of salt solutions with and without oxalate to determine effects of oxalate on evaporation characteristics and the possible formation of solids phases. For the evaporation tests we prepared a salt solution spiked with uranium and plutonium, evaporated the solution to produce a quantity of concentrated supernate, saltcake and condensed overheads and characterized these products to determine the mass balance of uranium and plutonium. One evaporation test featured no oxalate, whereas the second test featured a solution containing 0.01-M oxalate in addition to the other salts. Table 3.2.1 provides a composition of the solutions used for this testing.

Figure 4.2.1 provides a schematic diagram of the quantities of salt solution evaporated as well as the quantities of condensed overheads, concentrated supernate and air-dried saltcake recovered from the tests. Evaporation test #1 featured a solution without sodium oxalate, whereas Test #2 featured the solution with added sodium oxalate. The addition of sodium oxalate increased the ionic strength of the starting evaporator feed solution as measured by sodium concentration from 1.0 M to 1.2 M.

Figure 4.2.1 Evaporator Test Schematic Diagram



Test #1 evaporation completed in 28.4 hours over 6 workdays in a nine-day period. We observed an initial haziness to the solution and fine white solids in the evaporator pot during Test #1 after evaporating for almost 5 hours and collecting 300 mL of condensed overheads (evaporator pot charged with a total of 650 mL of feed solution). The quantity of white solids continued to increase with continued evaporation.

After evaporating for about 1 hour during the 4th day, the hot solution began eructing periodically instead of the usual smooth boiling action. Eventually the eructing sent the pot solution up into the condenser and over to the graduated cylinder that collected the condensed overheads. At this point, we stopped the evaporation, cooled the equipment to room temperature and cleaned the equipment with dilute nitric acid and deionized distilled water. The nitric acid dissolved the thin film of scale that had formed on the walls of the evaporator flask in contact with the feed solution being evaporated.

We returned the feed solution with solids to the evaporator pot and resumed evaporation. Shortly after returning to boiling temperature, the solution eructed again sending solution through the condenser and into the graduated cylinder. At this point we stopped the evaporation test, cooled the equipment to ambient laboratory temperature and removed the concentrated supernatant liquid and solids from the evaporator flask. We replaced the evaporator flask with a new flask and resumed the test the following day achieving another 5.3 hours of evaporation. At this point we terminated Test #1. During the final 5.3 hours, the solution generally boiled smoothly with an occasional small eructation. The small eructions did not send material out of the evaporator flask.

Evaporation Test #2 completed in 25.6 hours over 5 workdays during a six-day period. White solids first formed after 3.75 hours of evaporation and collecting 150 mL of condensed overheads (evaporator pot charged with 500 mL of feed solution). The quantity of white solids increased continuously throughout the test. Boiling continued smoothly throughout the remainder of the test. During the last 3.5 hours of evaporation the solution began to exhibit small eructions and the boiling temperature increased from about 105 to 108 °C. Note however that the eructions were small and never sent solution out of the boiling flask into the condenser. Based on visual and physical characteristics of the two evaporation tests, I conclude that the presence of oxalate does not adversely impact evaporation of alkaline salt solutions.

Test #2 featured a higher concentration factor (8.42) compared to Test #1 (6.55). Also, we isolated considerably more saltcake from Test #2 (13.5 grams) versus that from Test #1 (4.5 grams). The increased weight of saltcake in Test #2 is consistent with the deposition of the sodium oxalate in addition to that of the sodium aluminosilicates. XRD (see Figures 4.2.1 and 4.2.2) and elemental analyses (see Table 4.2.1) confirmed that the solids from Test #1 are predominantly cancrinite and sodalite and those of Test #2 are predominantly sodium oxalate with smaller amounts of cancrinite and sodalite. Elemental analysis of the Test #1 solids showed that the solids contained principally sodium, aluminum and silicon. Based on the elemental analysis data, I calculate a mole ratio of Na:Al:Si normalized to that of silicon for the Test #1 solids at 1.66:0.98:1.00. The equimolar quantities of aluminum and silicon are consistent with an aluminosilicate solid phase such as cancrinite, which was identified by XRD analysis (see Figure 4.2.1). The mole ratio of sodium to silicon (1.66:1.00) is higher than that calculated (1.33:1.00) for a pure nitrated cancrinite, $Na_8Al_6Si_6O_{24}(NO_3)_2 \cdot 4H_2O$. I attribute the higher sodium content to the presence of other sodium salts (e.g., sodium hydroxide) that are not detected by XRD.

Elemental analysis indicates much higher sodium content in the Test #2 solids compared to that in the Test #1 solids. From the elemental composition I calculate a mole ratio of Na:Al:Si normalized to that of silicon for the Test #2 solids at 10.0:1.07:1.00. The Al:Si mole ratio of close to 1:1 is consistent with these elements present as a cancrinite phase, which was identified by XRD analysis. We attribute the much higher mole ratio of sodium to aluminum and/or silicon to the presence of other sodium salts, principally sodium oxalate. This is consistent with XRD analysis, which indicated sodium oxalate as the principle crystalline phase in the Test #2 solids (see Figure 4.2.2). Furthermore, ion chromatographic analysis indicated that the solids had a high oxalate content (0.65 g $C_2O_4^{2-}$/g of solid).

Figure 4.2.1 X-Ray Diffraction Patter of Evaporator Test #1 Solids

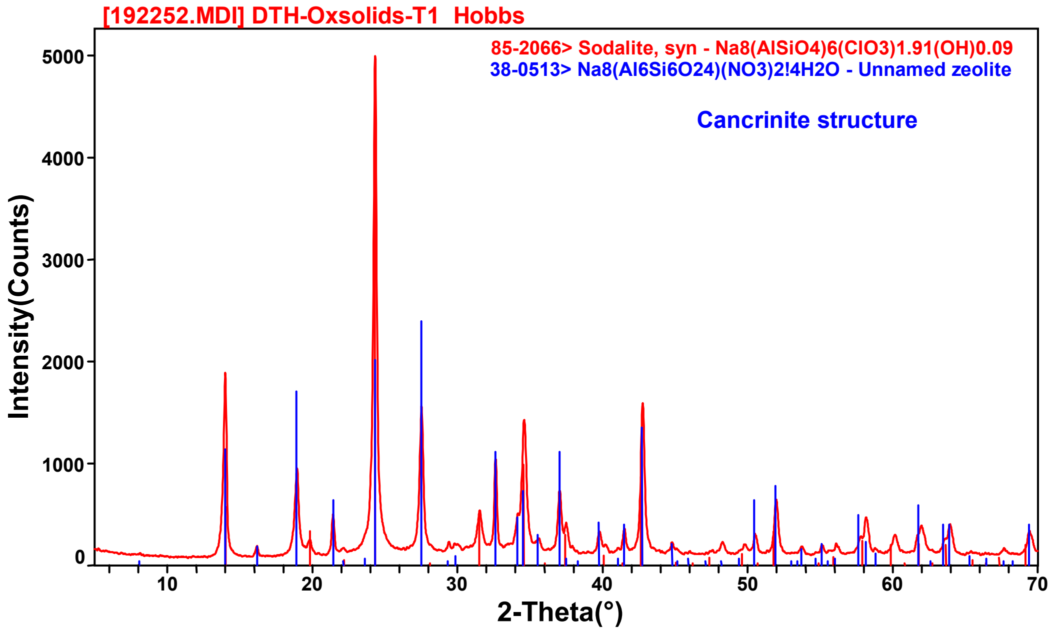


Figure 4.2.2 X-Ray Diffraction Patter of Evaporator Test #2 Solids

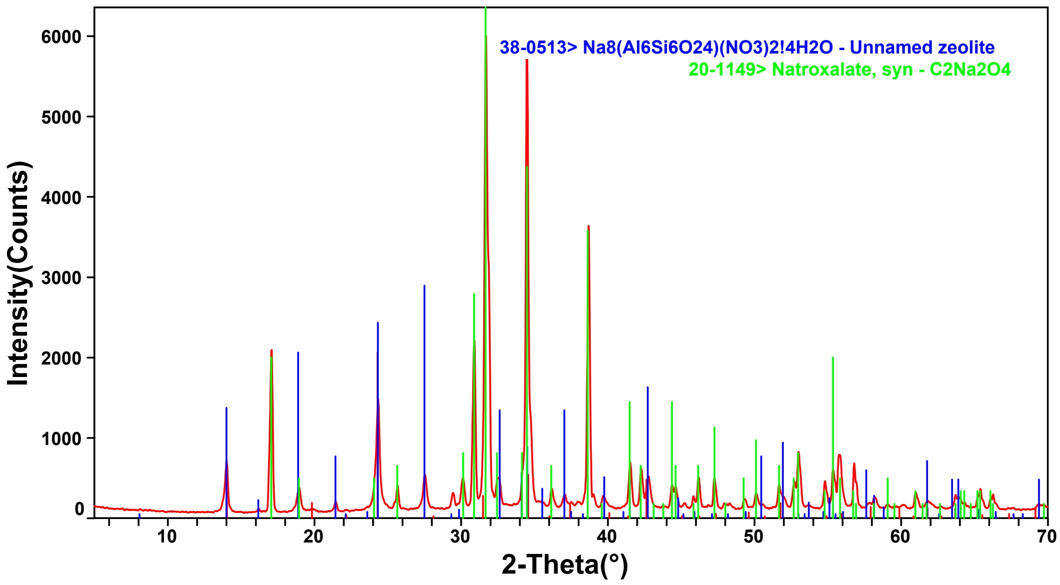


Table 4.2.1 Elemental Concentrations in Solids Isolated from Evaporator Tests

Element	Evaporation Test #1 Solids (µg/g)	Evaporation Test #2 Solids (µg/g)
Ag	<56.3	<66.3
Al	136000	39200
Ba	<134	<157
Ca	<162	<191
Cd	<29.6	<34.8
Ce	<190	<224
Cr	<42.2	<49.7
Cu	160	181
Fe	<25.3	<29.8
Gd	<165	<194
K	<6600	<7780
La	<50.7	<59.7
Li	<303	<356
Mg	<37.3	<43.9
Mn	<5.63	<6.63
Mo	<373	<439
Na	196000	311000
Ni	<95.0	<112
P	<486	<572
Pb	<225	<264
Sb	<2660	<3130
Si	144000	37800
Sn	9240	10400
Sr	<53.5	<63.0
Ti	<54.2	<63.8
U	<1600	<1880
Zn	<22.5	<26.5
Zr	235	<189

Table 4.2.2 provides the measured concentrations of uranium and plutonium in subsamples of the evaporator feed, condensed overheads, the concentrated supernate solutions as well as the solids isolated from the evaporator experiments. The concentrations of uranium and plutonium in the condensed overheads are much higher than expected. I believe that the majority of the uranium and plutonium measured in the condensed overheads resulted from the residual materials deposited on the glassware when eructions sent a portion of the evaporator pot solution into the condenser and condensate collection flask during Test #1. Although the glassware was cleaned after these events, residual materials could have remained and rinsed out of the glassware and

collected in the condensed overheads collection flask upon resumption of the testing. Some carryover of uranium and plutonium is possible due to the short vapor path length and lack of a demister in the testing equipment. Overall, the quantities of uranium and plutonium in these overheads are small measuring 1.7 and 3.6 wt % of the uranium and 1.4 and 16 wt % of the plutonium fed to the evaporator in Tests #1 and #2, respectively.

XRD and ICP-ES analyses indicate that the solids isolated from the evaporation tests are principally sodium aluminosilicate for Test #1 and sodium oxalate and sodium aluminosilicate for Test #2. Thus, the solids in Test #1 and non-oxalate solids in Test #2 are more representative of the aluminosilicate solids deposited in the 2H-Evaporator pot and gravity drain lines[8,9,10] than bulk saltcake[11,12,13] deposited upon cooling concentrated supernate in tanks that receive concentrated supernates from HLW evaporators.

Table 4.2.2 Uranium and Plutonium Concentrations in Evaporation Test Feed Solution, Condensed Overheads, Concentrated Supernate and Saltcake Solids

Test & Solution/Solid ID	[Uranium]	[Plutonium]	Unit
#1 Feed Solution	16800 ± 2760	131 ± 1.76[a]	μg/L
#1 Condensed Overheads	388	0.149	μg/L
#1 Concentrated Supernate	70200 ± 14100	8.61 ± 0.81	μg/L
#1 Saltcake solids	220	29.3	μg/g
#2 Feed Solution	15600 ± 2050	200 (est.)[b]	μg/L
#2 Condensed Overheads	957	0.584	μg/L
#2 Concentrated Supernate	88500 ± 12300	32.2 ± 1.31	μg/L
#2 Saltcake Solids	64.7	25.7	μg/g

[a] Analysis of a sample of the remaining feed solution for Test #1 after completing both evaporation tests indicated a plutonium concentration of 8.9 μg/L (Pu-TTA method) or 16 μg/L (ICP-MS method). This result suggests that a large fraction of the plutonium originally in solution precipitated from the solution during approximately 46 days of storage. Thus, there is considerable uncertainty in the total quantity of plutonium fed to the evaporator since the evaporation test initiated 8 days after sampling the feed solution. The quantity of plutonium measured in the saltcake solids is consistent with the feed solution having an effective concentration of about 100 μg/L.

[b] Analysis of a sample of the remaining feed solution for Test #2 after completing both evaporation tests indicated a plutonium concentration of 32μg/L (Pu-TTA method) or 52 μg/L (ICP-MS method). This result suggests that a large fraction of the plutonium originally in solution precipitated from the solution during approximately 46 days of storage. Thus, there is considerable uncertainty in the total quantity of plutonium fed to the evaporator. Note that a sample of the feed solution for Test #2 was not taken and analyzed as in the case of Test #1. The quantity of plutonium measured in the saltcake solids is consistent with the feed solution containing close to the target (gravimetric) concentration of 200 μg/L.

The measured quantities of uranium and plutonium in the solids isolated from the two evaporation tests are very low and do not present a criticality safety concern. The measured uranium and plutonium concentrations in the solids resulting from the feed solution with oxalate (0.05 M) are below that measured for the solids without added oxalate. The total quantities of uranium deposited in Tests #1 and #2 are 981 μg and 859 μg, respectively. Even though Test #2 experienced a greater concentration factor, less total uranium deposited into the solids in this test compared to Test #1. Thus, I conclude that the presence of oxalate does not enhance the precipitation of uranium during evaporation.

Due to the uncertainty in the effective quantity of plutonium fed to each of the evaporation tests (see Table 4.2.1), I cannot conclude whether oxalate has an impact on the precipitation of plutonium during evaporation. Note that in these tests the uranium concentration was about 75 times that of the plutonium. In solubility tests with both uranium and plutonium present, the concentration of uranium measured on average 112 times that of the plutonium.[14] Wilmarth reported analytical results for supernate samples taken from a variety of SRS waste tanks, which indicate that, the average uranium concentration ranged from 114 to 908 times that of plutonium.[15] Given the low concentration of plutonium in the saltcake solids measured in these tests and the low solubility of plutonium in SRS waste solutions, I conclude that the impact, if any, of oxalate on the accumulation of plutonium during evaporation will be minor and not present a significant concentrating mechanism for plutonium.

Solids Formation Tests

For solids formation tests, we mixed two different salt solutions and inspected for solids formation. The two solutions included a dilute solution representing wash waters with and without sodium oxalate and a concentrated solution representing the supernatant liquid present in SRS HLW evaporator feed tanks. Tables 3.2.1 and 3.2.2 provide the compositions of the dilute salt solution and evaporator feed solution, respectively.

Table 4.2.3 provides a summary table of the testing results. We varied the volume ratio of the evaporator feed to wash water solutions from 3:1 to 20:1. We observed solids formation in all of the tests with wash water solutions containing dissolved sodium oxalate. From Test #1, we isolated 0.134 grams of solids or 3.35 g solids/L of combined solutions. XRD analysis of the air-dried solids revealed that the predominant crystalline phase is a zeolite (sodium aluminosilicate) with smaller amounts of sodium oxalate, sodium nitrate, sodium carbonate and sodium nitrite. Calculations indicate that the concentrations of aluminum, silicon and oxalate exceed the expected solubilities upon combining the two solutions. Thus, the identification of aluminosilicate and sodium oxalate phases is not unexpected.

Solids precipitated in Tests #2 – #5 were isolated as a single composited material and analyzed by ICP-ES and ICP-MS. Table 4.2.4 provides a summary of these results. Analysis indicates that the solids are principally comprised of sodium, aluminum and silicon with very small concentrations of uranium (26.0 μg/g) and plutonium (71.0 μg/g).

Note that the sodium concentration in these solids is much higher than those isolated from the Evaporation Test #1 and identified as predominantly the sodium aluminosilicate material, cancrinite (see Section 4.2 –Evaporation Tests). The solids also exhibit a higher aluminum to silicon weight ratio (2.12) than that measured for that measured for the solids isolated from Evaporation Test #1 (0.94) and for sodium aluminosilicate solids produced from SRS waste evaporation studies (1.0).[16] These results suggest that the composited solids are predominantly sodium salts (e.g., sodium oxalate) other than sodium aluminosilicate as identified by XRD analysis in the Test #1 solids.

Table 4.2.3 Solids Formation Testing Conditions and Findings

Test #	Volume Ratio	Oxalate in Wash Water	Solids Formed	Other Findings/Comments
0	3:1	no	no	
1	3:1	yes	yes	Principal crystalline phase is zeolite with smaller amounts of sodium oxalate, sodium nitrate, sodium carbonate and sodium nitrite. Isolated 0.134 g of dried solids - 3.35 g solid/L combined solutions.
2	4:1	yes	yes	Isolated a total of 0.294 g of solids upon combining Tubes #2 – 5 (2.86 g of solids/L combined solutions).
3	6:1	yes	yes	
4	10:1	yes	yes	
5	20:1	yes	yes	
6	3:1	no	no	
7	20:1	no	no	

Analysis of the precipitated solids did confirm the presence of small amounts of uranium and plutonium. The concentration of the uranium and plutonium in the solids does not represent a criticality safety concern. The weight ratios of sodium to that of the uranium and plutonium measured 11,400 and 4170, respectively. The weight ratios of aluminum to uranium and plutonium measured 349 and 128, respectively. Note that the concentration of plutonium in these solids is about a factor of three higher than that of uranium. This is in contrast to the two solutions that were mixed together. The plutonium to uranium ratio measured 0.0676 in the evaporator feed solution and 0.000929 in the wash water solution with dissolved sodium oxalate. I attribute the increased removal of plutonium relative to uranium to a greater impact of the change of the solution composition on plutonium solubility and perhaps to the sorption and/or coprecipitation of plutonium with the bulk precipitated solids.

Table 4.2.4. Analytical Data for the Solids Isolated from the Solids Formation Tests #2 – #5

Element	Concentration (μg/g)
Ag	<104
Al	9070
Ba	<247
Ca	<299
Cd	<54.6
Ce	<351
Cr	<78.0
Cu	283
Fe	<46.8
Gd	<304
K	<12200
La	<93.6
Li	<559
Mg	<68.9
Mn	<10.4
Mo	<689
Na	296000
Ni	<175
P	<897
Pb	<415
Sb	<4910
Si	4270
Sn	16500
Sr	<98.8
Ti	<100
U	<2950
Zn	<41.6
Zr	<296
Pu	71.0
U	26.0

4.3 Task 4

Washing of sludge from Tank 7F containing solid oxalate salts should provide elevated levels of oxalate in feed solution sent to high-level waste evaporators. Based on standard electrochemical reduction potentials, oxalate may serve as reductant to mercuric ion resulting in the formation of elemental mercury. Thus, elevated oxalate levels in evaporator feed solutions may produce increased elemental mercury upon evaporation resulting in the release of more mercury to the evaporator overheads.

Task 4 testing determined if oxalate increased the reduction of mercuric species in alkaline solution at boiling conditions as evidenced by visual observation of elemental mercury and loss of mercury from the liquid phase. This testing featured a dilute salt solution containing 86.2 mg/L mercury added as mercuric nitrate, which was refluxed for 4 hours in the absence and presence of varying amounts of sodium oxalate (0, 0.01, 0.02, and 0.04 M). After 4 hours of refluxing, and the salt solution was cooled to ambient laboratory temperature (ca. 20 °C) and sample for determination of mercury content.

Throughout the reflux period and after cooling the salt solution to ambient laboratory temperature I observed no evidence of elemental mercury formed in any of the tests. Table 4.3.1 provides a listing of the measured mercury concentrations for the as-prepared salt solution and samples of the solutions from each of the reflux tests with varying amounts of added sodium oxalate. Mercury levels changed in the solution refluxed without added oxalate, but did not change in the solutions with added sodium oxalate. Thus, I conclude that elevated levels of oxalate do not appear to serve as a reductant for alkaline mercuric species resulting in increased release of elemental mercury during evaporation of alkaline salt solutions.

Table 4.3.1 Mercury Concentrations After Refluxing in the Presence of Varying Levels of Sodium Oxalate

Test Identification	Mercury Concentration (mg/L)
As-Prepared Salt Solution	86.2
Refluxed without $Na_2C_2O_4$	69.1
Refluxed with 0.01 M $Na_2C_2O_4$	82.5
Refluxed with 0.02 M $Na_2C_2O_4$	84.2
Refluxed with 0.04 M $Na_2C_2O_4$	86.6

4.4 Task 5

Testing conducted during FY2000 evaluated the effect of solution composition on the performance of MST to remove strontium and actinides from alkaline salt solutions.[6] Solution components evaluated in the these tests include hydroxide, nitrate, nitrite, aluminate, carbonate, and sulfate and minor components which included oxalate, phosphate, fluoride, chloride, silicate, molybdate, potassium and cesium. This testing featured an oxalate level of 0.008 M with a fixed ionic strength of 6.13 M (5.6 M Na^+ concentration). The planned solution concentration for the Sr/Actinide separation stage in both the Salt Waste Processing Facility (SWPF) and the Actinide Removal Project (ARP) facility is 5.6 M in sodium.

Solubility testing indicates that the solubility of sodium oxalate at this sodium concentration is <0.01 M.[17] Thus, this testing featured a sodium oxalate concentration near the a bounding oxalate concentration for processing waste in the SWPF and ARP. Testing results[6] indicated that the presence of oxalate and the other minor components did not exhibit a statistically significant impact on the performance of MST to remove strontium, plutonium, neptunium and uranium. Thus I conclude that oxalate will not adversely impact the performance of MST to remove strontium and actinides from SRS HLW solutions in the SWPF and ARP facility.

4.5 Scoping Tests

Uranium and plutonium form a number of oxalate complexes.[18] Precipitation of plutonium and uranium oxalates has been used to separate and purify these actinides in fuel reprocessing flowsheets.[19] In one instance a criticality accident occurred at the Mayak site from the inadvertent accumulation of enriched uranium due to precipitation of uranyl oxalate under acidic conditions.[20] Thus, oxalate may serve to concentrate uranium in alkaline waste solutions by forming insoluble uranyl oxalate precipitates. A literature review of uranyl oxalate chemistry provided few references dealing with uranyl oxalates under strongly alkaline conditions that exist in the SRS HLW system. Russian literature reported the following stability order for ligands complexing to the uranyl ion, UO_2^{2+}: $OH^- > CO_3^{2-} > F^- > C_2O_4^{2-}$.[21] Furthermore, the Russian work reported that uranyl oxalates react in strong base to produce sodium uranates.

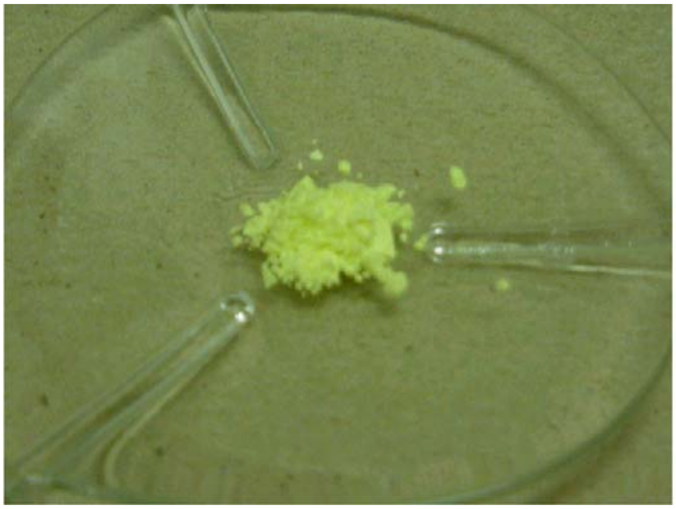
I confirmed the Russian testing by studying the behavior of solutions of uranyl nitrate upon addition of sodium hydroxide and oxalic acid or sodium oxalate. Additions of concentrated sodium hydroxide solution to uranyl nitrate solutions containing either oxalic acid or sodium oxalate produced yellow-orange precipitates consistent with that reported for sodium diuranate. I observed no evidence for the formation of a pale yellow precipitate reported for uranyl oxalate.

I successfully prepared crystalline solids of uranyl oxalate hydrate by adding an excess of oxalic acid to a concentrated solution of uranyl nitrate in dilute nitric acid. Figure 4.5.1a provides a photograph of the pale yellow solids. XRD analysis confirmed that the solids were uranyl oxalate (see Figure 4.5.2 for XRD pattern of the pale-yellow uranyl oxalate solids.

When I added the uranyl oxalate solids to a concentrated alkaline salt solution typical of HLW tank supernates, the pale yellow solids rapidly changed to a yellow-orange color typical of sodium diuranate (see Figure 4.5.1b). I isolated the yellow-orange solids from the salt solution, briefly rinsed with deionized distilled water to remove interstitial salt solution and air-dried the solids. XRD analysis of these solids revealed no evidence for diffraction peaks assigned to that of the original uranyl oxalate solids. The measured diffraction peaks were broad and located at 2θ positions consistent with those reported for sodium diuranate. This confirms that the uranyl oxalate solids had rapidly converted to a poorly crystalline sodium diuranate solid phase. Thus I conclude that formation of uranyl oxalate solids will not occur upon the addition of oxalate to alkaline solutions of uranium.

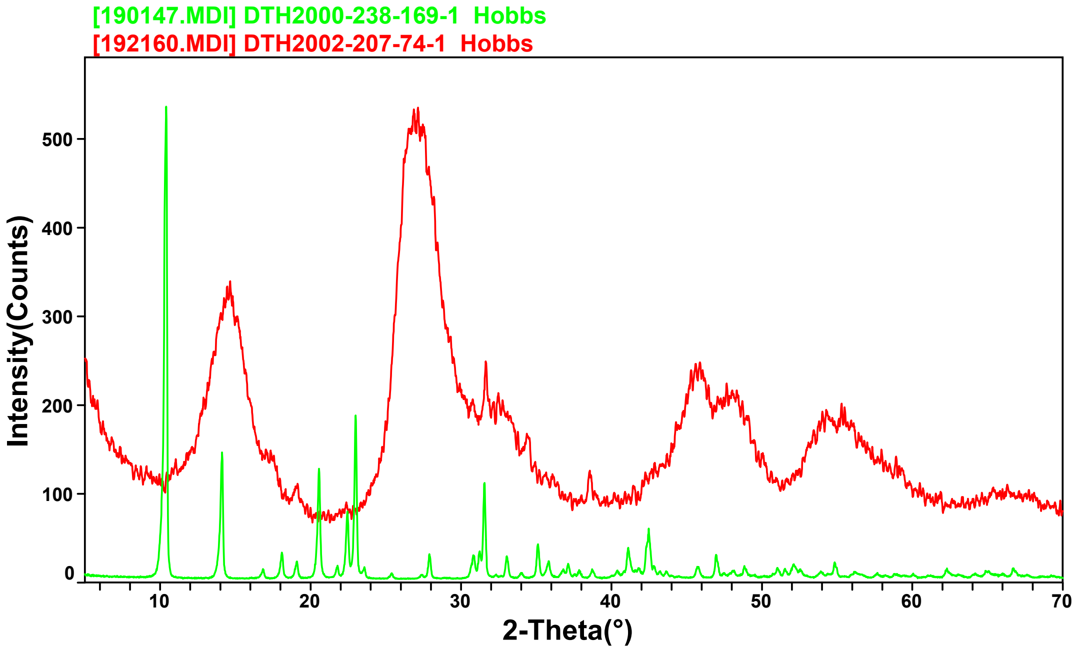
Figures 4.5.1 Photographs of Uranyl Oxalate and Solids Isolated upon Addition of Uranyl Oxalate to a Concentrated Alkaline Salt Solution

A. Pale yellow solids identified as $UO_2(C_2O_4)\cdot 3H_2O$



B. Yellow-orange solids identified as $Na_2U_2O_7$ produced upon addition of the pale yellow uranyl oxalate solids to a strongly alkaline salt solution.

Figure 4.5.2 XRD Patterns for Uranyl Oxalate and the Solids Isolated upon Addition of Uranyl Oxalate to a Concentrated Alkaline Salt Solution



Peaks in green are those measured for the pale yellow solids isolated from the nitric acid solution of uranyl oxalate upon addition of oxalic acid and match those reported in the literature for uranyl oxalate trihydrate. Peaks in red are those measured for the yellow-orange solids isolated from the strongly alkaline solution upon addition of the uranyl oxalate solids and mixing at ambient laboratory temperature for 1 hour. The red peaks match those reported in the literature for sodium diuranate.

5.0 Summary and Conclusions

This report documents results from tests conducted to evaluate the impacts, if any, of elevated levels of oxalate on operations within the SRS High-Level Waste System. These operations include sludge washing, evaporation, mixing of supernates and wash waters and pretreatment of supernates to remove strontium and actinides by monosodium titanate. Key findings of this testing include the following:

- oxalate appears to have little effect on the leaching of metals and actinides from sludges,
- the presence of dissolved oxalate did not exhibit an adverse impact upon the evaporation of wash water solutions,
- the presence of oxalate did not increase the deposition of uranium in saltcake produced from the evaporation of wash water solutions initially containing 0.05 M oxalate,
- the presence of dissolved oxalate did enhance the precipitation of solids upon mixing wash water solutions with a concentrated salt solution similar to that in evaporator feed tanks,
- the presence of between 0.01 and 0.04 M oxalate did not increase the release of elemental mercury during evaporation of alkaline salt solutions,
- the presence of 0.008 M oxalate and other minor solution components did not affect the performance of monosodium titanate to remove strontium and actinides from an alkaline, 5.6 M sodium salt solution and
- scoping tests confirmed that uranyl oxalate is not stable upon contact with strongly alkaline salt solutions such as those found throughout the SRS HLW System.

Based on these findings I conclude that the presence of sodium oxalate does not significantly impact uranium and plutonium chemistry within normal operations of the HLW system at the SRS. I recommend that the archived wash water samples be prepared with a lower dilution factor as a means to better quantify plutonium and uranium dissolution across the entire series of wash water contacts with the Tank 8F-sludge material. Alternatively, I recommend that SRTC conduct washing experiments with Tank 7F sludge materials to determine evidence for increased leaching of uranium and plutonium. Of particular interest are the final stages of washing when the supernatant liquids contain similar concentrations of free hydroxide and oxalate. I also recommend that SRTC conduct additional tests investigating the mixing of wash waters with evaporator feed solutions to better understand the extent of solids formation over the range of conditions spanned by the three HLW evaporator systems at the SRS.

6.0 Quality Assurance

Test results reported in this document followed the quality assurance requirements specified in the Task Technical and QA Plan for this activity,

> Hobbs, D. T.; "Task Technical and Quality Assurance Plan for Sodium Oxalate Impacts to HLW Processing," WSRC-RP-2002-00578, Rev. 0, November 27, 2002.

This report provides the final deliverable as specified the Technical Task Request,

> H. H. Elder, "Determine Sodium Oxalate in Sludge Batch 3 Impact on Washing, Evaporation and Waste Form Performance," HLW-TTR-2003-0054, October 10, 2002.

The scoping test results reported in section 4.5 dealing with uranyl oxalate chemistry fell outside the work scope detailed in the above Task Technical and QA Plan.

All experimental work is recorded in laboratory notebooks,

> Hobbs, D. T., "Uranium Chemistry Studies I," WSRC-NB-2000-00233 and
> Hobbs, D. T., "Uranium Chemistry Studies II," WSRC-NB-2002-00207.

7.0 Acknowledgements

The author thanks L. Thacker, M. Blume and T. Allen for their efforts in performing the experimental activities documented in this report as well as the technical staff of the Analytical Development Section, particularly D. Diprete, C. Diprete, M. Malek, W. Boyce, A. Jurgensen and D. Missimer, for the many analytical measurements performed in support of the testing.

8.0 References

---

[1] Bibler, N. E. and Click, D. R. "Measured Oxalate Concentrations in the First and Second Samples of Mixed Tank Seven Slurry Using an Acid Dissolution Technique," SRS-ITB-2003-0002, January 16, 2003.

[2] Elder, H. H.; "Determine Sodium Oxalate in Sludge Batch 3 Impact on Washing, Evaporation and Waste.
Form Performance," HLW-TTR-2003-0054, October 10, 2002.

[3] VanPelt, W. B.; Langton, C. A. "Impact of Sodium Oxalate on Saltstone Properties," SRT-LWP-2002-00130, November 21, 2002.

[4] Elder, H. H.; personal communication. Data recorded in laboratory notebook, "Uranium Chemistry Studies," WSRC-NB-2000-00233, p.87.

[5] Analytical results reported in Excel Files, "Ntank26.xls", "Ntank32.xls", and "Ntank43.xls" maintained on server WG08 by HLWE and accessed on November 27, 2002. Analytical results are those reported for the following sample dates: 2/6/02 (Tank 26F), 2/18/02 (Tank 32H) and 12/27/01 (Tank 43H).

[6] Barnes, M. J.; Edwards, T. B.; Hobbs, D. T.; Marshall, K. M.; "Strontium and Actinide Removal Testing with Monosodium Testing and Other Sorbents," WSRC-TR-2001-00436, Rev. 0, October 29, 2001.

[7] Pareizs, J. M. "Washing Demonstration Using Nonradioactive Simulated Tank 7 Sludge-Slurry," WSRC-TR-2002-00450, November 7, 2002.

[8] Wilmarth, W. R., Fink, S. D., Hobbs, D. T., Hay, M. S. "Characterization and Dissolution Studies of Samples from the 242-16H Evaporator Gravity Drain Line (U)," WSRC-TR-97-0326, Rev. 0, October 16, 1997.

[9] Wilmarth, W. R., Coleman, C. J., Jurgensen, A. R., Smith, W. M., Hart, J. C., Boyce, W. T., Missimer, D., Conley, C. M. "Characterization and Dissolution Studies of Samples from the 242-16H Evaporator," WSRC-TR-2000-00038, Rev. 0, January 31, 2000.

[10] Wilmarth, W. R., Coleman, C. J., Hart, J. C., Boyce, W. T. "Characterization of Samples from the 242-16H Evaporator Wall," WSRC-TR-2000-00089, Rev. 0, March 20, 2000.

[11] Hobbs, D. T. "Final Report: Analysis of Tank 41H Saltcake Sample #2 and Comparison to Sample #1 (U)," WSRC-TR-94-057, January 26, 1994.

[12] Martino, C. J. and Poirier, M. R. "Tank 31H Saltcake Dissolution Tests," WSRC-TR-2002-00388, Rev. 0, February 27, 2003.

[13] Hobbs, D. T. "Final Report on the Analytical Results for Tank Farm Samples in Support of Salt Dissolution Evaluations (U)," WSRC-TR-96-0410, Rev. 0, December 12, 1996.

[14] Hobbs, D. T., Edwards, T. B., Fleischman, S. D. "Solubility of Plutonium and Uranium in Alkaline Salt Solutions," WSRC-TR-93-056, February 12, 1993.

[15] Wilmarth, W. R. "High Level Waste Evaporator Analysis Results," WSRC-TR-98-00223, Rev. 0, June 16, 1998.

[16] Wilmarth, W. R.; Dukes, V. H.; Mills, J. T.; Edwards, T. B. "Results of Aluminosilicate Formation Testing," WSRC-TR-2001-00330, July 13, 2001.

[17] Wiley, J. R. "Sodium Oxalate Solubility in Simulated SRP Waste Solutions," DPST-78-480, August 23, 1978.

[18] *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press, London, 1973.

[19] *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Volume 2; Chapman and Hall, New York, 1986.

[20] McLaughlin, T. P.; Monahan, S. P.; Pruvost, N. L.; Frolov, V. V.; Ryazanov, B. G.; and Sviridov, V. I. "A Review of Criticality Accidents – 2000 Revision," LA-13638, May, 2000.

[21] *Complex Compounds of Uranium*, Chernyaev, I. I., ed., Translated from Russian by L. Mandel, Israel Program for Scientific Translation, Jerusalem, 1966.

Appendix 1
Nitrate, Nitrite and Oxalate Concentrations in Wash Water Solutions After 14-Day Contacts with Tank 8F Sludge

Test ID # (Tube ID)	Volume Ratio Inhibited Water to Sludge	Sodium Oxalate Added	Corrected Nitrate (M)	Corrected Nitrite (M)	Corrected Oxalate (M)
DTH8-1	25	yes	1.87E-02	7.86E-01	1.77E-01
DTH8-2	10	no	4.62E-02	8.75E-01	4.14E-03
DTH8-3	1	no	2.60E-01	1.52E+00	2.12E-02
DTH8-4	10	yes	4.63E-02	8.76E-01	1.34E-01
DTH8-5	4	no	1.08E-01	1.09E+00	1.07E-02
DTH8-6	10	yes	4.61E-02	8.78E-01	1.32E-01
DTH8-7	10	yes	5.39E-02	8.66E-01	1.34E-01
DTH8-8	1	yes	2.50E-01	1.49E+00	2.11E-02
DTH8-9	10	no	4.72E-02	9.01E-01	5.44E-03
DTH8-10	0	no	< 8.68E-03	1.37E-02	< 6.12E-03
DTH8-11	4	yes	1.02E-01	1.05E+00	7.56E-02
DTH8-12	25	no	1.94E-02	7.92E-01	2.38E-03
DTH8-13	10	no	4.65E-02	9.01E-01	4.77E-03

Appendix 2
Elemental Composition of Wash Water Solutions After 14-Day Contacts with Tank 8F Sludge

[Concentrations determined by ICP-ES and are corrected for dilution. For replicate tests, calculated average, standard deviation and relative standard deviation for those elements above detection limit.]

H2O:Sludge v:v		Oxalate?	Test ID # (Tube ID)		Ag		Al		B		Ba		Ca		Cd		Ce
					(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)
1		no	DTH8-3	<	8.69E-01		2.06E+03	<	3.04E+00	<	2.06E+00		1.54E+00	<	4.34E-01		1.11E+00
1		yes	DTH8-8	<	8.69E-01		1.98E+03	<	3.04E+00	<	2.06E+00		2.29E+00	<	4.34E-01	<	2.93E+00
4		no	DTH8-5	<	2.73E-03		8.84E+02	<	9.54E-03	<	6.48E-03	<	1.50E+01	<	1.36E-03	<	9.20E-03
4		yes	DTH8-11	<	8.69E-01		8.08E+02	<	3.04E+00	<	2.06E+00	<	1.50E+01	<	4.34E-01	<	2.93E+00
10		no	DTH8-2	<	8.69E-01		3.85E+02	<	3.04E+00	<	2.06E+00	<	1.50E+01	<	4.34E-01	<	2.93E+00
10		no	DTH8-9	<	4.53E-03		3.83E+02	<	3.04E+00	<	1.07E-02	<	1.50E+01	<	2.26E-03	<	1.53E-02
10		no	DTH8-13	<	3.72E-04		3.79E+02	<	1.30E-03	<	8.83E-04		3.32E+00	<	1.86E-04	<	1.25E-03
10		yes	DTH8-4	<	8.69E-01		4.14E+02	<	3.04E+00	<	2.06E+00	<	1.50E+01	<	4.34E-01	<	2.93E+00
10		yes	DTH8-6	<	8.69E-01		3.93E+02	<	3.04E+00	<	2.06E+00	<	1.50E+01	<	4.34E-01	<	2.93E+00
10		yes	DTH8-7	<	9.22E-03		5.83E+02	<	3.23E-02	<	2.19E-02		1.29E+01	<	4.61E-03	<	2.93E+00
25		no	DTH8-12	<	4.27E-02		1.61E+02	<	1.50E-01	<	1.01E-01	<	1.50E+01	<	2.14E-02	<	1.44E-01
25		yes	DTH8-1	<	1.58E-02		1.56E+02	<	5.52E-02	<	3.75E-02	<	1.50E+01	<	7.89E-03		1.60E+00
10		no	Average				3.82E+02										
10		no	Std Dev				2.97E+00										
10		no	% RSD				0.78%										
10		yes	Average				4.64E+02										
10		yes	Std Dev				1.04E+02										
10		yes	% RSD				22.49%										

Appendix 2 (continued)
Elemental Composition of Wash Water Solutions After 14-Day Contacts
with Tank 8F Sludge
[Concentrations determined by ICP-ES and corrected for dilution. For replicate tests, calculated average, standard deviation and relative standard deviation for those elements above detection limit.]

H2O:Sludge v:v		Oxalate?	Test ID # (Tube ID)		Cr		Cu		Fe		Gd		K		La		Li
					(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)
1		no	DTH8-3		1.79E+02		2.05E-02	<	1.24E+02	<	2.55E+00		2.06E+02	<	7.60E-01	<	1.09E+01
1		yes	DTH8-8		1.74E+02	<	1.90E+00	<	1.24E+02	<	2.55E+00		1.80E+02	<	7.60E-01	<	1.09E+01
4		no	DTH8-5		5.78E+01		1.69E-01	<	1.24E+02	<	8.01E-03	<	1.02E+02	<	7.60E-01	<	1.09E+01
4		yes	DTH8-11		7.76E+01		8.84E-02	<	1.24E+02	<	2.55E+00	<	1.02E+02	<	7.60E-01		9.67E+00
10		no	DTH8-2		1.04E+01	<	1.90E+00	<	1.24E+02	<	2.55E+00	<	1.02E+02	<	7.60E-01	<	1.09E+01
10		no	DTH8-9		1.07E+01	<	1.90E+00	<	1.24E+02	<	1.33E-02	<	1.02E+02	<	3.96E-03	<	1.09E+01
10		no	DTH8-13		2.77E+01	<	1.90E+00	<	1.24E+02	<	1.09E-03	<	4.37E-02	<	3.25E-04	<	1.09E+01
10		yes	DTH8-4		1.05E+01	<	1.90E+00	<	1.24E+02	<	2.55E+00	<	1.02E+02	<	7.60E-01	<	1.09E+01
10		yes	DTH8-6		1.04E+01	<	1.90E+00	<	1.24E+02	<	2.55E+00	<	1.02E+02	<	7.60E-01	<	1.09E+01
10		yes	DTH8-7		2.88E+01		3.15E+00	<	1.24E+02	<	2.71E-02	<	1.08E+00	<	8.07E-03		6.43E+01
25		no	DTH8-12		1.54E+01		3.65E-02		3.12E+01	<	1.25E-01	<	5.02E+00	<	3.74E-02	<	1.09E+01
25		yes	DTH8-1		2.88E+01	<	1.90E+00	<	1.24E+02	<	2.55E+00	<	1.85E+00	<	1.38E-02	<	1.09E+01
10		no	Average		1.63E+01												
10		no	Std Dev		9.87E+00												
10		no	% RSD		60.71%												
10		yes	Average		1.65E+01												
10		yes	Std Dev		1.06E+01												
10		yes	% RSD		64.15%												

Appendix 2 (continued)
Elemental Composition of Wash Water Solutions After 14-Day Contacts
with Tank 8F Sludge
[Concentrations determined by ICP-ES and are corrected for dilution. For replicate tests, calculated average, standard deviation and relative standard deviation for those elements above detection limit.]

H2O:Sludge v:v		Oxalate?	Test ID # (Tube ID)		Mg		Mn		Mo		Na		Ni		P		Pb
					(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)
1		no	DTH8-3	<	1.90E+00	<	2.26E+01		1.32E+00		4.67E+04	<	1.17E+01		1.06E+01	<	3.47E+00
1		yes	DTH8-8	<	1.90E+00	<	2.26E+01		1.12E+00		4.24E+04	<	1.17E+01		9.78E+00	<	3.47E+00
4		no	DTH8-5	<	1.90E+00	<	2.26E+01	<	1.81E-02		1.87E+04	<	1.17E+01		1.00E+00	<	1.09E-02
4		yes	DTH8-11	<	1.90E+00		2.03E-01	<	5.76E+00		2.20E+04	<	1.17E+01		2.45E+00	<	3.47E+00
10		no	DTH8-2	<	1.90E+00	<	2.26E+01	<	5.76E+00		9.82E+03	<	1.17E+01	<	7.49E+00	<	3.47E+00
10		no	DTH8-9	<	1.90E+00	<	2.26E+01	<	3.00E-02		9.92E+03	<	1.17E+01	<	3.90E-02	<	1.81E-02
10		no	DTH8-13	<	1.90E+00	<	2.26E+01	<	2.46E-03		1.02E+04	<	1.17E+01	<	3.21E-03	<	1.49E-03
10		yes	DTH8-4	<	1.90E+00	<	2.26E+01	<	5.76E+00		1.65E+04	<	1.17E+01		6.10E-01	<	3.47E+00
10		yes	DTH8-6	<	1.90E+00	<	2.26E+01	<	5.76E+00		1.61E+04	<	1.17E+01		1.20E+00	<	3.47E+00
10		yes	DTH8-7		1.17E+01		1.40E+01	<	6.11E-02		1.67E+04	<	1.17E+01		1.49E+01	<	3.69E-02
25		no	DTH8-12	<	1.90E+00	<	2.26E+01	<	2.83E-01		4.20E+03	<	1.17E+01	<	3.68E-01	<	1.71E-01
25		yes	DTH8-1	<	1.90E+00	<	2.26E+01	<	1.05E-01		1.33E+04	<	1.17E+01	<	1.36E-01	<	6.31E-02
10		no	Average								1.00E+04						
10		no	Std Dev								2.24E+02						
10		no	% RSD								2.25%						
10		yes	Average								1.64E+04				5.59E+00		
10		yes	Std Dev								2.90E+02				8.11E+00		
10		yes	% RSD								1.76%				145.29%		

Appendix 2 (continued)
Elemental Composition of Wash Water Solutions After 14-Day Contacts
with Tank 8F Sludge
[Concentrations determined by ICP-ES and are corrected for dilution. For replicate tests, calculated average, standard deviation and relative standard deviation for those elements above detection limit.]

H2O:Sludge v:v		Oxalate?	Test ID # (Tube ID)		Sb		Si		Sn		Sr		Ti		U		Zn		Zr
					(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)
1		no	DTH8-3	<	4.10E+01	<	1.57E+01	<	4.89E+00		1.06E+00	<	8.14E-01	<	2.46E+01	<	7.60E-01	<	2.50E+00
1		yes	DTH8-8	<	4.10E+01	<	1.57E+01		1.23E+00		1.05E+00	<	8.14E-01	<	2.46E+01	<	7.60E-01	<	2.50E+00
4		no	DTH8-5	<	1.29E-01	<	1.57E+01	<	1.53E-02	<	2.17E+00	<	2.56E-03	<	7.74E-02		2.39E-03	<	7.84E-03
4		yes	DTH8-11	<	4.10E+01	<	1.57E+01	<	4.89E+00	<	2.17E+00	<	8.14E-01	<	2.46E+01		4.22E-01	<	2.50E+00
10		no	DTH8-2	<	4.10E+01	<	1.57E+01	<	4.89E+00	<	2.17E+00	<	8.14E-01	<	2.46E+01	<	7.60E-01	<	2.50E+00
10		no	DTH8-9	<	2.14E-01	<	1.57E+01	<	2.55E-02	<	2.17E+00	<	4.24E-03	<	1.28E-01	<	7.60E-01	<	1.30E-02
10		no	DTH8-13	<	1.76E-02	<	1.57E+01	<	2.09E-03		7.07E-01	<	3.48E-04	<	1.05E-02	<	7.60E-01	<	1.07E-03
10		yes	DTH8-4	<	4.10E+01	<	1.57E+01	<	4.89E+00	<	2.17E+00	<	8.14E-01	<	2.46E+01	<	7.60E-01	<	2.50E+00
10		yes	DTH8-6	<	4.10E+01	<	1.57E+01	<	4.89E+00	<	2.17E+00	<	8.14E-01	<	2.46E+01	<	7.60E-01	<	2.50E+00
10		yes	DTH8-7	<	4.36E-01		4.99E+00	<	5.19E-02		2.71E+00	<	8.64E-03	<	2.62E-01		4.89E+00	<	2.65E-02
25		no	DTH8-12	<	2.02E+00	<	1.57E+01	<	2.40E-01	<	2.17E+00	<	4.00E-02	<	1.21E+00	<	7.60E-01	<	1.23E-01
25		yes	DTH8-1	<	7.45E-01	<	1.57E+01	<	8.87E-02	<	2.17E+00	<	1.48E-02	<	4.48E-01	<	7.60E-01	<	4.54E-02
10		no	Average																
10		no	Std Dev																
10		no	% RSD																
10		yes	Average																
10		yes	Std Dev																
10		yes	% RSD																