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Supplemental Solubility Data for SRAT Processing of Sludge Batch 3 with H-Canyon Slurry Containing Precipitated Pu and Gd in DWPF

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1.0 SUMMARY

The Savannah River Technology Center (SRTC) was requested to investigate the effects of the addition of Pu and Gd from H-Canyon to Sludge Batch 3 (SB3). The effects on Sludge Receipt and Adjustment Tank (SRAT) processing were discussed in WSRC-TR-2002-00322 [1], which also addressed iron and gadolinium solubility criticality concerns in the presence of sodium oxalate. Since this work was completed, SRTC was requested to provide additional data for solubility testing at higher levels of sodium oxalate. This report supplements WSRC-TR-2002-00322 [1] and addresses testing at higher levels that are considered bounding for DWPF SB3 “sludge-only” processing, as well as “SB3 with Actinide Removal Product” processing.

The specific sodium oxalate levels tested to meet the objective were 75% and 125% of the anticipated amount (i.e., 660,000 pounds) of sodium oxalate in Tank 7. Lab-scale SRAT processing was performed at each sodium oxalate level to address the impacts on iron solubility during SRAT processing. The products were then used to study lower pH effects on iron solubility at the two levels. No surrogates were added for the Pu, since a sufficient surrogate for Pu in the +4 state was not available and was not determined to be necessary based on earlier studies [1].

The solubility measurements during SRAT processing are a subject of this report, whereas, the results of SRAT testing will be discussed in a separate report. The impacts of sodium oxalate on solubility during SRAT processing were as follows:

- Small amounts of iron and gadolinium became soluble with sodium oxalate at 75% of the amount anticipated in Tank 7 (i.e., ~495,000 pounds). The maximum fraction of iron dissolved was 4.91×10^{-2} (4.91% of total Fe), while the maximum fraction of gadolinium dissolved was 3.12×10^{-2} (3.12% of total Gd).
- Although the SRAT process with 125% sodium oxalate did not meet the nitrite destruction objectives and processing of this level of sodium oxalate would require higher levels of acid addition, iron and gadolinium solubility were calculated based on the data available. The studies reported in WSRC-TR-2002-00322 showed that more iron and gadolinium were dissolved in the lower pH testing than in SRAT processing. Therefore, the lower pH testing would be considered more bounding for solubility calculations. For the SRAT run with 125% of the anticipated amount in Tank 7 (i.e., ~825,000 pounds), a small fraction of iron was again dissolved, 4.37×10^{-2} (4.37% of total Fe). However, all of the gadolinium was dissolved during the SRAT process. The calculated gadolinium results are conservatively high since the gadolinium detected in the SRAT product (i.e., ~0.006%) was approximately a fourth of what it was targeted to be based on the amount added (i.e., ~0.02%)
- Soluble iron was similar in the 75% and 125% cases and was approximately ten times higher than the 50% sodium oxalate runs [1]. Soluble Gd, on the other hand, was comparable to the 50% results for the 75% sodium oxalate run, but it was much greater for the 125% run [1].

In the testing to support solubility determinations at pH levels below those expected in typical SRAT processing (i.e., 2<pH<4), the following was observed:

- Higher levels of the available iron and gadolinium became soluble. In the lower pH testing, up to 9.75% iron and 56.2% gadolinium were dissolved from the SRAT product with 75% of the anticipated sodium oxalate, while up to 15.68% iron and 100% gadolinium were dissolved from the SRAT product containing 125% of the anticipated sodium oxalate. Therefore, ~90% of the iron and ~44% of the gadolinium remained insoluble in testing with 75% sodium oxalate, while ~84% of the iron and no gadolinium remained insoluble for the testing with 125% sodium oxalate. The gadolinium results for the 125% test have the same caveat as the SRAT tests since the same gadolinium number for the SRAT product was used to perform the calculation.
- Soluble iron was higher in both the 75% and 125% cases compared to the 50% and no sodium oxalate cases previously reported [1]. Soluble gadolinium for the 75% case was comparable to the 50% case data, while the 125% case had much higher soluble gadolinium [1].

2.0 INTRODUCTION AND BACKGROUND

Currently, DWPF is operating using a sludge-only processing flowsheet. Sludge Batch 2 (SB2) was being fed to the DWPF before the current outage. The next batch to be qualified for DWPF processing is SB3. For each sludge batch, SRTC has performed non-radioactive and radioactive sludge runs to evaluate potential chemical processing issues. SRTC has been and is performing studies to evaluate processing of SB3. Sludge Batch 3 is primarily Tank 7 sludge, but is expected to contain several components that are considered non-typical to DWPF sludge and also higher levels of noble metals than previously processed sludge batches. In addition to the Tank 7 contents, an H-Canyon slurry containing precipitated Pu with Gd has already been transferred to Tank 51 to be fed as part of SB3 and it has been proposed to add Tank 18, Tank 19, and Am/Cm feed. The studies discussed in this report concentrate on the effects of high levels of sodium oxalate when combined with the H-Canyon slurry in the SRAT. Preliminary information on SRAT processing with the sodium oxalate and the H-Canyon slurry, as well as some of the effects of the other non-typical components of Tank 7 (sand and coal), have already been reported [(1), (2), and (3)]. The data in this report supplement the data reported in WSRC-TR-2002-00322 [1] by testing the effects of higher levels of sodium oxalate on iron solubility. The supplemental data in this report was performed under the guidance of WSRC-RP-2002-00320 [4].

Historical information indicates that Tank 7 may contain sodium oxalate at levels up to 660,000 pounds [5]. This level is much higher than other tanks processed in the DWPF, therefore its impacts on processing have to be fully understood or researched before it can be processed. Issues related to criticality are of utmost concern with regards to the ability to process the H-Canyon precipitated slurry since it is believed that the oxalate may solubilize iron contained in SB3 to the tris-oxalato ion, $Fe(C_2O_4)_3^{3-}$. Since iron is considered the primary neutron poison in the DWPF feed and is normally present in the sludge solids, any impacts on its behavior due to the presence of the sodium oxalate must be understood before SB3 can be processed in DWPF. Initial results of studies performed to address these issues have been reported [(1) and (2)], but SRTC was requested by DWPF to perform additional studies at higher sodium oxalate levels to help address criticality concerns. The two levels of sodium oxalate selected were 75% and 125% of the anticipated amounts in Tank 7. These values correspond to 495,000 and 825,000 pounds of sodium oxalate in Tank 7. It is anticipated that these two levels will bound SB3 processing and SB3 processing with the addition of the Actinide Removal Product (if no washing of Tank 7 sludge is performed).

3.0 EXPERIMENTAL

The testing was performed at the Aiken County Technology Laboratory (ACTL) using the same configuration as earlier testing (see reference [1] for details). In summary, the equipment consisted of a four-liter kettle to replicate the SRAT, the SRAT Condenser, the Formic Acid Vent Condenser, the Mercury Water Wash Tank, and the Slurry Mix Evaporator Condensate Tank (SMECT). Run plans were written for each SRAT test to provide operational guidance and trim chemical and acid addition amounts [(6) and (7)].

The same simulated sludge as used in earlier studies was used in this testing. The sludge was made for processing of SB2 and is representative of Tank 8 material. The composition of the Tank 8 surrogate and the projected SB3 compositions [8] are given in Table 1. The composition of the Tank 8 simulant did not exactly match the composition of the projected SB3 sludge; however, the small deviations in composition were expected to have minimal impact on processing with regards to the Pu/Gd precipitate.

To closer match the anticipated components of the SB3 sludge, sand, coal, mercury, noble metals, and Gd were added to the Tank 8 simulant. On a dried sludge solids basis (free of any sodium oxalate additions), sand was added at 1.12 wt% and coal was added at 0.72 wt% [8]. Both the sand and coal were received from the manufacturer of the sand filter material that was transferred to Tank 7 and were of the specification particle size. Mercury was added at the anticipated level of 0.076 wt% (dried solids basis) [8]. Noble metals were added at two different levels during the runs. The run with 75% sodium oxalate contained 10% of the nominal anticipated amount, while the run with 125% sodium oxalate contained the nominal anticipated amount of noble metals [8]. The reason for the difference was that the 75% sodium oxalate SRAT product with low noble metals was readily available for additional testing. The noble metals level should not have a significant impact on the solubility of the Fe and Gd. Gd was added to the sludge at 0.037 wt% to represent the Gd contribution from the H-Canyon slurry.

As mentioned above, two levels of sodium oxalate were used in the testing. For each SRAT run, sodium oxalate was blended with the sludge in the necessary amounts. Again, the basis amounts used were 495,000 or 825,000 pounds of sodium oxalate remaining.

Table 1 – Sludge Compositions (Wt% Calcined Basis with Calcine Factor of 0.80)

Element	Tank 8 Simulant	Projected SB3 [8]
Al	11.8	11.02
Ba	0.26	0.26
Ca	2.82	2.96
Ce	N/A	0.34
Cr	0.27	0.29
Cu	0.17	0.18
Fe	33.3	32.4
K	0.01	0.41
La	N/A*	0.20
Mg	0.16	0.13
Mn	3.24	6.40
Na	7.58	9.08
Ni	3.57	1.45
Pb	0.12	0.32
Si	1.12	1.13
Zn	0.28	0.38
Zr	0.47	0.66

*La was not added to the Tank 8 simulant.

The target sludge solids content was approximately 18.5 wt% air-dried total solids. Due to the additions of sodium oxalate, the total solids were adjusted using distilled water to match the nominal target. Acid additions were based on (1) total acid to achieve the acid stoichiometry and (2) acid mix to produce redox target (0.2 $Fe^{2+}/\Sigma Fe$ redox ratio) by the modified redox correlation [9]. Concentrated formic acid (90-wt%) and nitric acid (50-wt%) were used during processing. After acid addition was completed, the temperatures of the slurries were ramped to boiling and remained at boiling for $\geq$ 12 hours depending on the run. Slurry samples were pulled throughout the SRAT testing and at the end of testing to monitor cation solubility and oxalate concentrations.

In the low pH solubility testing, the SRAT products were adjusted to low pH levels to simulate upset conditions in DWPF that could indeed lower the pH. An example would be transfer of a portion of the SRAT contents to the SMECT. The specific issue was the effect of lowering the pH on the solubility of Fe and of Gd during such an upset. Moving a large fraction of Fe to the supernate phase has the potential to remove a key neutron poison for the Pu from the insoluble solids.

The testing apparatus was the same as used during previous investigations for solubility testing [1]. In summary, the apparatus was a smaller version of the SRAT set-up. A temperature adjustable calibrated pH probe was used to monitor the pH throughout the testing and the experiment was conducted at 85°C to minimize evaporation losses. Throughout the testing, pH was adjusted using ~10M nitric acid. The nitric acid was metered in until the pH reached approximately 6, 5, 4, 3.5, 3, 2.5, and 2. The process was held near the target pH levels for 15 minutes to 2 hours depending on the test and the corresponding pH. In some cases, additional acid was added to offset upward drift in the pH and to return the pH to the target value for that hold period. Usually, acid was added when the drift was greater than 0.1 pH units.

Samples were taken upon stabilization at each pH level for supernate and solids analyses. Supernate samples were obtained by centrifuging a slurry sample and decanting the supernate fraction. For longer hold times at lower pH levels, additional samples were taken prior to dropping the pH to the next target. Solids samples were analyzed for weight percent total and dissolved solids, and weight percent soluble and insoluble fractions were determined based on this analysis. Density measurements were also performed on the slurry and supernate samples. A combination of sample results and material balance data permitted determination of the masses of supernate and insoluble solid phases throughout the test. This, combined with the compositional analysis, permitted the determination of the dissolved mass of Fe and Gd.

4.0 ANALYTICAL METHODS

As stated earlier, samples were generated throughout the runs and at the end of the runs for analyses to quantify the SRAT processing behavior. The SRAT samples were analyzed by the Savannah River Technology Center/Immobilization Technology Section Mobile Lab (SRTC-ML) to determine the chemical composition of the soluble and insoluble fractions. The SRAT product samples were prepared by calcining a portion of the samples at 900°C and then dissolving the calcined product using Na_2O_2/NaOH fusion, lithium metaborate fusion, and aqua regia dissolution. Cation analyses were performed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Anion analyses were performed using weighted dilutions and Ion Chromatography (IC). Supernate samples were obtained by centrifuging the slurry samples and removing the supernate. The SRAT product was also submitted for calcined, total, insoluble, and soluble wt% solids determinations. Total and dissolved solids were measured and insoluble and soluble solids were calculated based on the results. The dissolved cations and anions in the supernate were analyzed using ICP-AES and IC.

All analyses for this task were governed by Analytical Study Plan WSRC-RP-2002-00342 [10]. A sample request form accompanied each sample. A unique lab identification number was assigned to each sample for tracking purposes. Analyses were performed using approved analytical and QA procedures.

5.0 RESULTS

5.1 SRAT Processing

The main objective of the SRAT processing studies, as related to this task, was to monitor the solubility of Fe, Gd, and oxalate during and after completion of SRAT processing. This information will help DWPF determine if criticality will be an issue, especially with regards to formation of tris-oxalato iron complexes. Two levels of sodium oxalate were studied; 75% (Run SB3-20) and 125% (Run SB3-24) of the anticipated sodium oxalate in Tank 7. During the runs, hydrogen generation, foaming, slurry pH, and nitrite destruction were also monitored to help determine the impact of oxalate on the process. However, data from the runs related to SRAT processing will be reported elsewhere.

The 125% sodium oxalate SRAT run (Run SB3-24) had poor nitrite destruction. While this is important from a SRAT processing perspective, the main goal of the testing was to produce product for the lower pH testing and this level of sodium oxalate would not expected to be processed in the DWPF. While insight provided into Fe solubility during processing is beneficial, results of previous testing have shown that the lower pH studies result in more Fe becoming soluble [1]. Therefore, even though the SRAT processing goal was not met, insight into solubility was provided.

As mentioned earlier, samples were taken throughout the runs for supernate cation and anion analysis. Table A1 in Appendix A presents the results from the analyses of the supernate samples. Table A1 indicates the sample IDs, the time the samples were taken relative to the end of acid addition, and the pH of the SRAT slurry at the time of sampling. Table 2 contains the Fe and Gd supernate data from the runs. In this table, data is reported as the fraction of the total available Fe and Gd dissolved. The values were obtained as follows:

1. The analyzed Fe concentration in the supernate was divided by the density of the supernate to give the amount of Fe in the supernate.
2. The grams of supernate in the sampled SRAT slurry were calculated based on the insoluble solids concentration in the SRAT product and the mass of slurry available at the time of sampling.
3. The grams of supernate were multiplied by the result from step 1 to give the total grams of soluble Fe.
4. The grams of Fe available for dissolving were calculated by multiplying the mass of slurry available at the time of sampling by the total (dried) solids of the SRAT product and the Fe concentration in the total (dried) solids from the SRAT product.
5. The ratio of dissolved Fe was then calculated based on the grams of soluble Fe (step 3) divided by the total grams of Fe available (step 4).

The same method was followed for calculating the amount of Gd dissolved.

Table 2 – Fraction of Fe and Gd Dissolved during SRAT Processing

75% Sodium Oxalate Run (SB3-20)	**Sample ID**	**ICP-0**	**ICP-5**	**ICP-9**	**ICP-15**	**Product[2]**
	Time (min)[1]	14	362	602	1023	N/A
	pH	4.31	4.72	4.75	4.80	4.80
	Fraction Fe Dissolved	4.91E-02	2.15E-02	1.87E-02	1.70E-02	1.35E-02
	Fraction Gd Dissolved	3.12E-02	2.84E-02	2.74E-02	2.97E-02	1.70E-02
125% Sodium Oxalate Run (SB3-24)	**Sample ID**	**ICP-0**	**ICP-2**	**ICP-8**	**ICP-11**	**Product[2]**
	Time (min)[1]	7	184	541	745	N/A
	pH	6.60	6.93	7.05	7.08	7.08
	Fraction Fe Dissolved	4.37E-02	4.52E-03	2.31E-03	1.78E-03	1.52E-03
	Fraction Gd Dissolved	0.875	1.06	1.07	1.04	0.801

[1] Elapsed Time from End of Acid Addition
[2] Sample taken after product cooled to room temperature.

The solubility of Fe and Gd were both affected by the amount of sodium oxalate present in the feed. In both cases, the "Product" samples, which were taken after the SRAT product cooled to room temperature, contained less soluble Fe and Gd than samples taken at the end of the SRAT process while the contents were at boiling. This was consistent with the results of earlier testing [1]. Fe appeared to be more soluble during the testing with 75%, whereas Gd was much more soluble during the testing with 125% sodium oxalate. The higher Fe in the 75% case could be an artifact of the lower pH seen during the 75% SRAT run, but the low pH solubility testing will provide more insight since pH levels were specifically targeted. It should be noted that SRAT product results were used to determine the total amounts of Fe and Gd available in the feed. For the 125% sodium oxalate product, detected Gd was ~35% (or ~0.006% wt%) of what was found in the 75% sodium oxalate product (or ~0.016 wt%). However, the actual amount added to the 125% sodium oxalate feed was ~80% of that added to the 75% sodium oxalate feed. Therefore, some error in the total amount of Gd available exists for the 125% case, and the results provided for the fraction of Gd dissolved would therefore be conservative. When only the amount of Gd in the supernate is compared for both runs versus the fraction of Gd dissolved (which takes into account the amount of Gd detected in the product), the numbers are only ~10x higher for the soluble Gd in the 125% case versus the ~25 to 50x higher reported in Table 2. In any case, the amounts of Gd dissolved were much higher in the 125% run. Both of these tests indicate that higher levels of Fe can be dissolved when higher levels of sodium oxalate are present (see reference [1] for 50% and 25% sodium oxalate cases). For Gd, comparable results were seen for the 75% sodium oxalate test and the previously tested 50% sodium oxalate test [1]. However, the 125% sodium oxalate test had much higher dissolved Gd. In the previous tests, SRAT processing with 25% sodium oxalate resulted in no Fe or Gd being dissolved within the detection limits [1].

The fractions of Fe and Gd dissolved during SRAT processing are shown in Figures 1 and 2. Product data is also shown in the figures. For clarity, the product data is arbitrarily represented as +10 minutes to the last sample pulled during processing. Corresponding pH plots for the runs are given in Appendix B as Figure B1. Figure 1 shows that the largest amount of Fe was dissolved when the SRAT process was at the minimum pH (i.e., the end of acid addition). After this, the fraction of Fe dissolved drastically decreased and remained relatively low to the end of the run. For Gd, the dissolved Gd remained relatively constant after acid addition for the 75% sodium oxalate run. In the 125% run, Gd continued to dissolve after the end of acid addition. After concentration was completed, the level remained the same until the test was completed.

Figure 1 - Fraction of Fe Dissolved during SRAT Processing

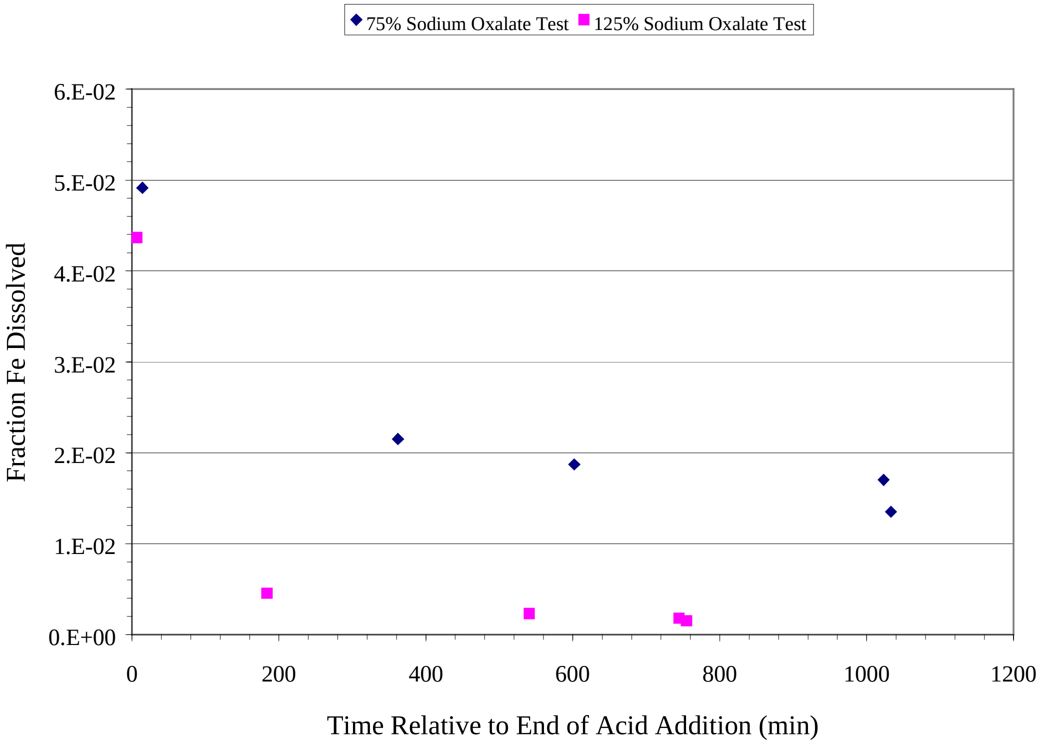
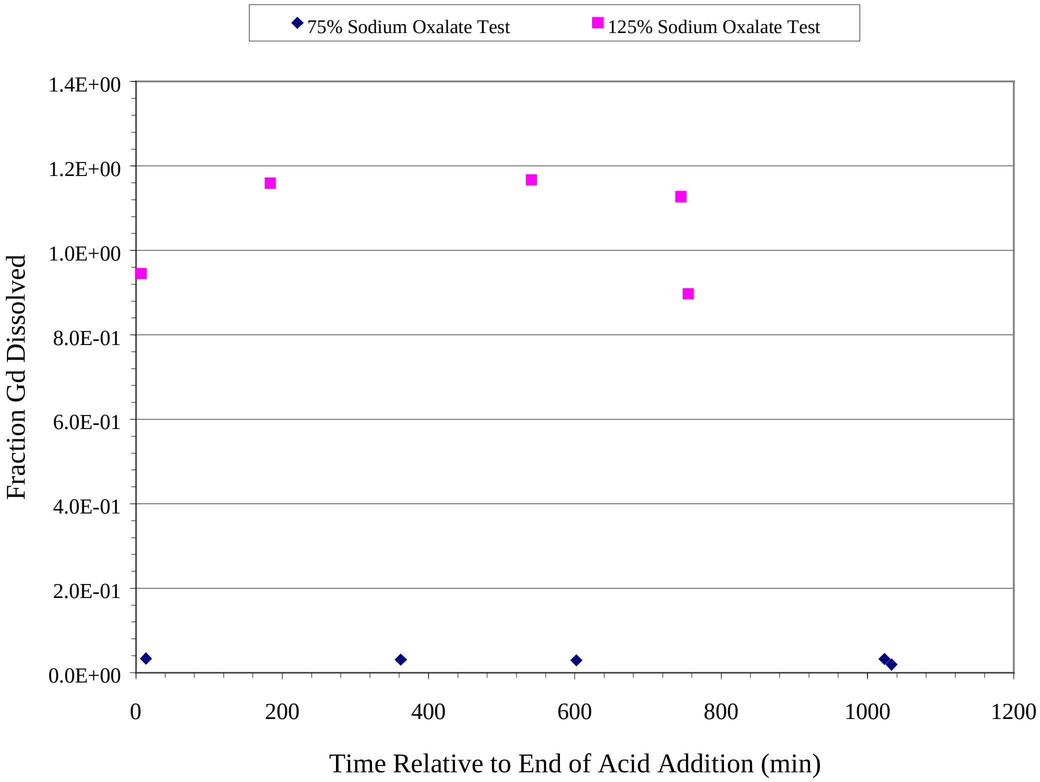


Figure 2 - Fraction of Gd Dissolved during SRAT Processing



The anion samples during the runs and the SRAT products were analyzed for oxalate concentration. Samples during the runs were the same as the ones used for cation analyses so they were centrifuged and decanted. The product samples, on the other hand, were analyzed using a weighted dilution. These samples were adjusted for density to compare to the in-process samples. The oxalate concentrations are given in Table 3. During the SRAT process, samples indicate that >50% of the oxalate added was in the supernate for the 75% SRAT run, while >80% of the oxalate added was in the supernate for the 125% SRAT run. About 85% of the oxalate was detected in the 75% SRAT run product, while almost all of the oxalate added was detected in the 125% SRAT run product.

Table 3 – Oxalate Concentration in Supernate Samples from SRAT Processing

75% Sodium Oxalate Run (SB3-20)	**Sample ID**	**ICP-0**	**ICP-5**	**ICP-9**	**ICP-15**	**Product[2]**
	Time (min)[1]	14	362	602	1023	N/A
	pH	4.31	4.72	4.75	4.80	4.80
	Oxalate (mg/L)	26,600	33,200	33,300	33,000	46,995
125% Sodium Oxalate Run (SB3-24)	**Sample ID**	**ICP-0**	**ICP-2**	**ICP-8**	**ICP-11**	**Product[2]**
	Time (min)[1]	7	184	541	745	N/A
	pH	6.60	6.93	7.05	7.08	7.08
	Oxalate (mg/L)	62,400	78,500	71,500	70,000	68,320

[1] Elapsed Time from End of Acid Addition
[2] Sample taken after product cooled to room temperature.

5.2 Low pH Studies

Two pH adjustment tests were performed to determine fractions of Fe and Gd dissolved at low pH values as might be experienced if some of the SRAT material were inadvertently transferred to the SMECT. One used the 75% sodium oxalate SRAT product (Run SB3-20); the other used the 125% sodium oxalate SRAT product (Run SB3-24).

As described in Section 3 and in WSRC-TR-2002-00322 [1], the SRAT products were heated to 85°C with a goal of adjusting the pH to a target of ~2 by adding additional nitric acid. During the process, samples were taken at each pH level, along with additional samples at some of the pH levels to account for upward drift in the pH. These samples were analyzed to determine the soluble species at the pH levels and throughout the testing. The amounts of soluble Fe and Gd for each sample were then used to determine the fraction of Fe and Gd soluble. The same methodology used to calculate the fractions during SRAT processing were used to perform these calculations. However, total solids and insoluble solids data was available on each sample taken throughout the lower pH testing. Table 4 contains the percent of Fe and Gd dissolved as the pH was lowered to 2 and with respect to time. Supernate results for all elements analyzed are given as Tables A2 and A3 of Appendix A. Once again, the Gd percentage fractions are a little high because of the low amount of Gd found in the 125% sodium oxalate SRAT product. In general, more uncertainty exists in the Gd values for fraction dissolved than for Fe, because of the lower Gd concentrations being measured. Figures 3 and 4 show the percent of Fe and Gd, respectively, dissolved versus the test pH.

In general, the percent total Fe dissolved increased as pH decreased for both products. In the 125% sodium oxalate test, a large amount of Gd was dissolved at the beginning of the test. This is likely due to the higher starting pH (i.e., ~7) and the solubility of Gd at this pH. The amount of Fe and Gd in solution at each pH level changed with time in both tests; however the trend was not consistent between runs or with the specific element. The changes with time at the pH levels may indicate that equilibrium was not completely achieved between the insoluble solids and the supernate.

Table 4 – Percentage Fraction of Fe and Gd Dissolved in Low pH Testing at 85°C

75% Sodium Oxalate (SB3-20 Product)				125% Sodium Oxalate (SB3-24 Product)			
Elapsed Time (min)	**pH**	**% Total Fe Dissolved**	**% Total Gd Dissolved**	**Elapsed Time (min)**	**pH**	**% Total Fe Dissolved**	**% Total Gd Dissolved**
0	4.66	1.25	1.56	0	7.00	0.178	70.9
48	3.99	2.62	4.40	21	6.11	4.16	86.4
73	3.49	4.06	7.28	40	5.04	9.49	20.1
100	2.99	5.94	13.3	67	4.01	11.40	6.74
130	3.05	5.60	16.6	89	3.58	13.47	7.65
142	2.41	7.24	32.4	112	3.07	13.33	23.0
171	2.55	8.19	32.9	137	3.02	13.58	25.9
185	1.99	9.75	49.9	152	2.65	13.86	41.3
245	1.99	7.84	56.2	167	2.58	14.25	47.9
305	2.03	6.11	49.4	187	2.06	15.68	87.0
				229	2.15	14.33	106
				261	2.03	13.40	103

Figure 3 - Iron Dissolution with pH Adjustment

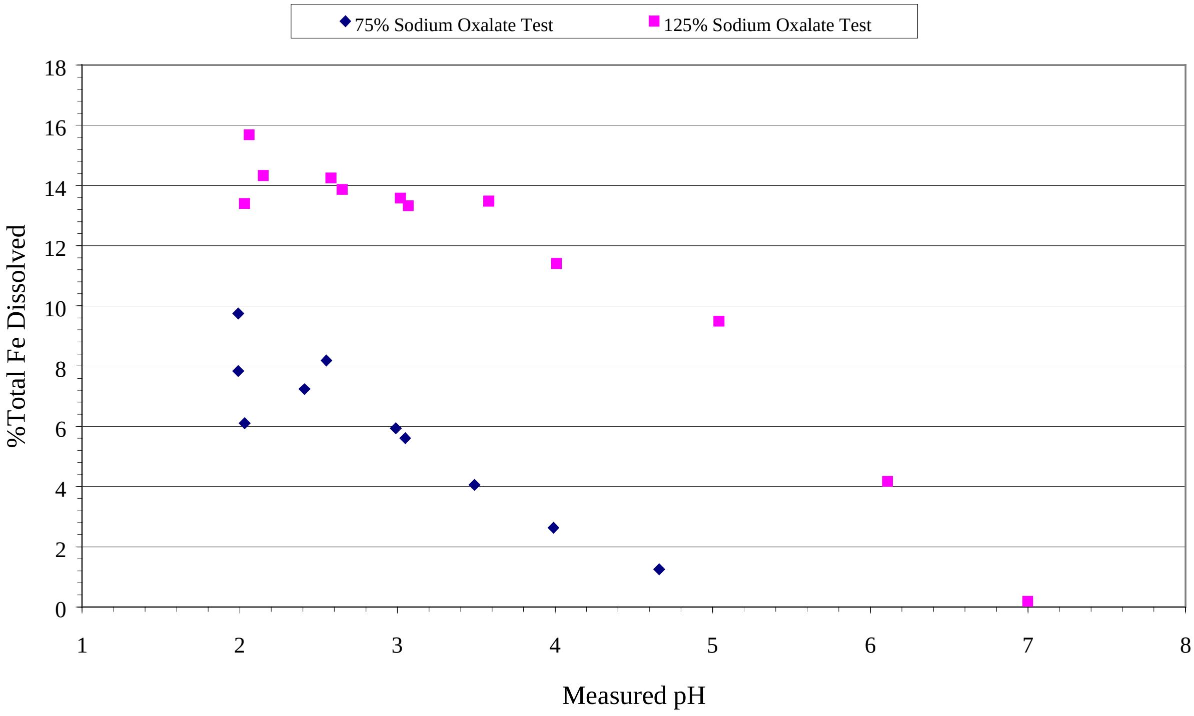
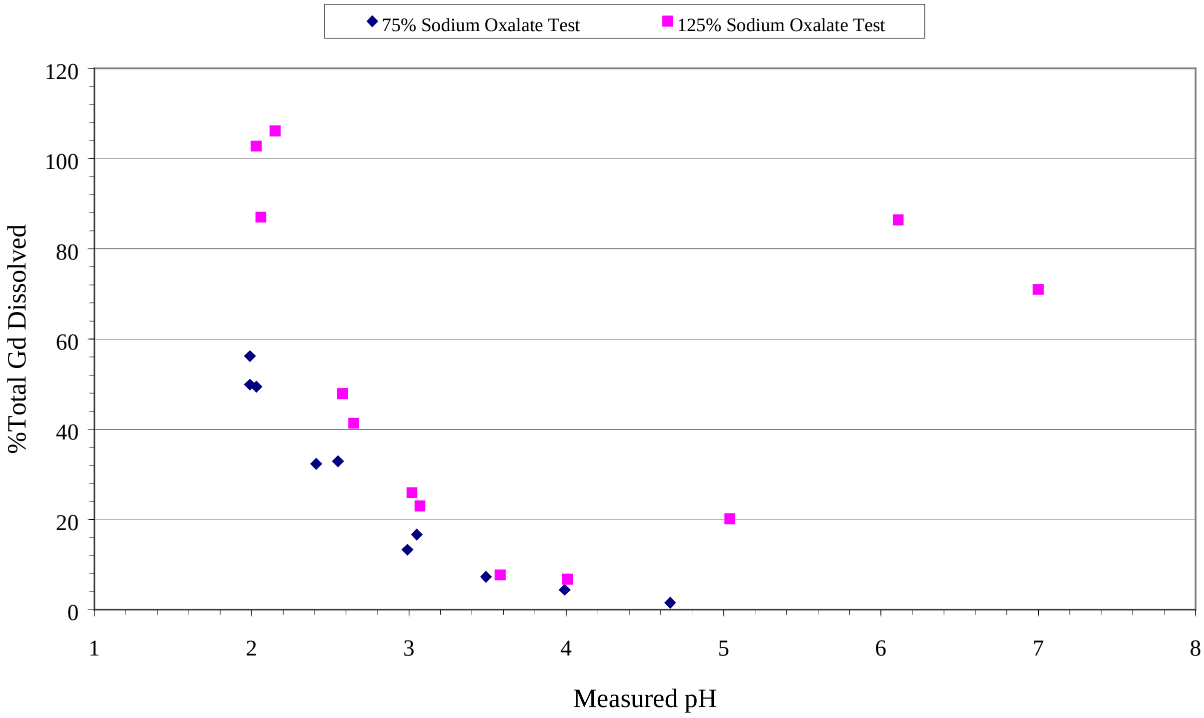


Figure 4 - Gadolinium Dissolution with pH Adjustment



The lower pH testing showed that the amounts of dissolved Fe remained relatively small. Overall, the maximum Fe dissolved in the 75% sodium oxalate containing feed was ~10%, while it was ~16% for the 125% sodium oxalate containing feed. Gadolinium continued to dissolve during this test with higher concentrations in the slurry with higher levels of sodium oxalate. The maximum Gd dissolved was ~56% for the 75% sodium oxalate test and was ~100% for the 125% sodium oxalate test. These bounding tests showed that slightly more Fe can become soluble at higher sodium oxalate concentrations; however, ~84% of the Fe still remained in the solids. For Gd, the 75% sodium oxalate case produced similar results to those seen in the 50% sodium oxalate testing [1], whereas the results for the 125% sodium oxalate case were much greater than those seen in the other tests. Once again, this may be an artifact of the relatively low Gd number obtained in the analyses of the SRAT product. When only the amount of soluble Gd is considered (i.e., the amount available for dissolving is not considered), the amounts of soluble Gd were comparable between the runs. If the product actually contained all that was added to the SRAT feed, then the percentage of Gd dissolved would be closer to the results from the other tests. Literature data indicates that Fe and Pu (IV) have similar solubilities in weak nitric acid solutions, and therefore Fe and Pu would not be separately dissolved over the pH range of 0 to 4 [11].

6.0 CONCLUSIONS

Bounding testing for Fe and Gd solubility has been completed for 75% and 125% of the anticipated sodium oxalate level in Tank 7. During SRAT processing, the maximum Fe fraction that became soluble was 4.91×10^{-2} for the 75% sodium oxalate test and 4.37×10^{-2} for the 125% sodium oxalate test. Gd, on the other hand, had a maximum soluble fraction of 3.12×10^{-2} for the 75% sodium oxalate test and 1.07 for the 125% sodium oxalate test. For the lower pH solubility testing, the amounts of Fe and Gd that became soluble increased at the lower pH levels tested. Iron present in the supernate still represented a small portion of the total amount in the sludge, whereas Gd concentration was more significant. The maximum amount of Fe was dissolved with the 125% sodium oxalate product and was ~16%, and the highest Gd was also dissolved with the 125% sodium oxalate product and was ~100%. It should be noted that the Gd fractions and percentages dissolved for the 125% sodium oxalate testing are conservatively high because of the relatively small amount of Gd detected in the SRAT product. This number was used to calculate the total Gd available and was about a fourth of what it was anticipated to be based on the amount added. Therefore, the fraction of Gd dissolved could be up to a fourth lower.

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Appendix A – Supernate Analyses from 75% and 125% Sodium Oxalate Testing

Table A1 – Supernate Results during Processing (mg/L)

Run	Sample ID	Time Relative to End of Acid Addition (min)	pH	Al	Ba	Ca	Cr	Cu	Fe	Gd	K	Mg	Mn	Na	Ni	Pd	Rh	Ru	Si	Zn	Zr
75% Sodium Oxalate (SB3-20)	ICP-0	14	4.31	1910	6.44	73.7	2.65	77.8	1490	1.19	76.9	25.3	445	22600	64.0	3.99	7.03	6.69	24.8	16.8	0.204
	ICP-5	362	4.72	3880	4.14	75.9	3.16	91.9	664	1.10	125	71.3	1430	35000	6.97	0.182	4.73	4.70	30.9	18.4	0.142
	ICP-9	602	4.75	3740	3.35	67.4	2.75	81.0	577	1.06	122	63.0	1330	34200	4.42	0.173	4.94	3.44	27.9	12.2	0.128
	ICP-15	1023	4.80	3760	3.68	76.3	2.88	86.1	525	1.15	126	66.0	1270	33300	4.83	0.186	5.47	3.06	30.7	11.4	0.129
	Product	N/A	4.80	4000	1.65	50.6	2.71	79.9	436	0.689	131	61.4	2190	35000	2.40	0.185	5.15	2.90	45.5	10.3	0.118
125% Sodium Oxalate (SB3-24)	ICP-0	7	6.60	1470	10.6	4.62	1.41	99.6	1300	11.9	97.7	71.1	1530	32500	1060	29.5	40.5	6.23	17.2	95.6	<0.200
	ICP-2	184	6.93	1860	11.5	5.95	1.69	123	136	14.6	107	94.2	2000	36300	1370	0.430	38.2	2.90	50.3	104	<0.200
	ICP-8	541	7.05	1640	12.5	6.37	1.33	121	69.2	14.7	112	94.0	2050	38400	1440	0.263	29.0	1.51	49.7	84.0	<0.200
	ICP-11	745	7.08	1450	11.6	5.57	1.22	119	53.4	14.2	115	96.3	2080	30100	1470	0.186	25.3	1.11	53.1	81.0	<0.200
	Product	N/A	7.08	1720	10.6	10.1	1.21	120	46.8	11.3	123	97.9	932	39300	1570	<0.010	24.8	1.00	11.8	79.7	<0.010

Table A2 – Supernate Results for Low pH Test with 75% Sodium Oxalate Product (mg/L)

Measured pH	4.66	3.99	3.49	2.99	3.05	2.41	2.55	1.99	1.99	2.03
Al	3610	3900	4040	4340	4540	5210	4990	5810	6400	6870
Ba	1.49	4.06	4.50	5.43	5.97	9.78	8.98	13.8	19.3	20.9
Ca	61.7	183	325	644	730	1640	1540	2470	2490	2440
Cr	2.20	2.26	2.35	2.43	2.45	2.51	2.47	2.66	2.49	2.55
Cu	70.8	81.7	76.4	75.6	76.6	78.2	77.2	78.8	76.3	68.7
Fe	357	3500	1160	1730	1600	2150	2370	2950	2380	1890
Gd	0.561	1.59	2.61	4.86	5.58	12.1	11.3	18.9	20.4	19.2
K	186	124	192	190	193	192	193	197	189	191
Mg	51.3	52.8	53.1	53.4	54.2	57.1	55.5	64.8	65.7	71.9
Mn	1220	1200	1290	1300	1310	1340	1320	1490	1560	1640
Na	32200	37900	28800	27000	21100	28000	29700	23700	26900	30400
Ni	3.29	17.6	27.6	45.2	49.9	103	93	231	300	310
Pb	<0.200	1.51	3.92	8.06	7.98	16.0	16.5	26.1	27.5	22.8
Pd	0.111	0.087	0.112	0.107	0.108	0.110	0.119	0.195	1.51	0.434
Rh	5.49	5.76	5.55	5.62	5.64	5.89	5.93	6.40	6.85	7.04
Ru	2.33	2.51	2.75	3.12	3.27	3.75	3.66	4.42	4.75	5.15
Si	41.1	42.6	41.8	42.2	42.4	43.4	43.0	45.3	42.3	41.1
Zn	9.10	17.1	20.8	25.5	28.1	38.7	35.4	53.6	63.8	68.6
Zr	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

Table A3 – Supernate Results for Low pH Test with 125% Sodium Oxalate Product (mg/L)

Measured pH	7	6.11	5.04	4.01	3.58	3.07	3.02	2.65	2.58	2.06	2.15	2.03
Al	1600	1960	2430	3200	2980	3290	3500	3940	4200	4730	5660	6100
Ba	10.1	22.4	10.4	9.35	16.4	16.4	15.4	18.1	17.5	29.9	36.6	39.9
Ca	4.08	5.89	6.03	83.2	166	290	350	750	967	1850	2400	2400
Cr	1.31	1.58	1.90	2.27	2.61	2.21	2.35	2.28	2.11	2.32	2.44	2.39
Cu	116	123	101	100	95.1	76.2	70.6	66.3	55.2	59.8	54.1	51.7
Fe	52.1	1240	2920	3530	4160	4190	4200	4370	4460	5130	4680	4490
Gd	9.49	11.8	2.83	0.954	1.08	3.30	3.42	5.95	6.41	13.0	15.0	15.7
K	169	171	167	127	200	172	179	180	163	174	175	174
Mg	83.7	59.5	13.7	7.87	12.5	18.8	24.1	32.2	33.4	45.0	54.0	57.4
Mn	2010	1450	285	203	230	366	435	605	696	946	1150	1220
Na	31900	36700	32900	37900	36700	38000	36200	36800	35500	36900	34000	35500
Ni	1400	1070	204	33.6	30.8	45.2	43.9	77.1	84.2	211	256	274
Pb	<0.200	<0.200	<0.200	<0.200	<0.200	1.50	1.85	4.96	6.22	17.0	18.7	21.0
Pd	0.350	0.354	0.715	11.7	24.6	28.4	16.2	23.2	29.2	32.9	33.1	32.5
Rh	25.4	28.6	33.9	43.8	50.0	46.0	48.8	49.6	46.2	51.3	52.6	53.4
Ru	1.04	3.74	10.2	24.5	37.9	38.6	41.9	44.2	42.5	50.4	54.3	54.9
Si	61.9	53.5	108	124	157	177	215	251	222	194	157	120
Zn	83.6	83.9	13.5	6.91	9.20	14.5	15.2	24.3	25.5	46.0	59.1	63.7
Zr	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

Appendix B – pH Plot for SRAT Processing

Figure B1 - pH Plots for SRAT Runs containing 75% and 125% Sodium Oxalate