

Downstream Impacts of Sludge Mass Reduction via Aluminum Dissolution on DWPF Processing of Savannah River Site High Level Waste - 9382

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ABSTRACT

The SRS sludge that was to become a major fraction of Sludge Batch 5 (SB5) for the Defense Waste Processing Facility (DWPF) contained a large fraction of H-Modified PUREX (HM) sludge, containing a large fraction of aluminum compounds that could adversely impact the processing and increase the vitrified waste volume. It is beneficial to reduce the non-radioactive fraction of the sludge to minimize the number of glass waste canisters that must be sent to a Federal Repository. Removal of aluminum compounds, such as boehmite and gibbsite, from sludge can be performed with the addition of NaOH solution and heating the sludge for several days. Preparation of SB5 involved adding sodium hydroxide directly to the waste tank and heating the contents to a moderate temperature through slurry pump operation to remove a fraction of this aluminum. The Savannah River National Laboratory (SRNL) was tasked with demonstrating this process on actual tank waste sludge in our Shielded Cells Facility. This paper evaluates some of the impacts of aluminum dissolution on sludge washing and DWPF processing by comparing sludge processing with and without aluminum dissolution. It was necessary to demonstrate these steps to ensure that the aluminum removal process would not adversely impact the chemical and physical properties of the sludge which could result in slower processing or process upsets in the DWPF.

INTRODUCTION AND BACKGROUND

The Savannah River Site (SRS) is currently immobilizing High Level Waste (HLW) sludge in the Defense Waste Processing Facility (DWPF). The sludge is a waste product from production of nuclear materials. At the SRS, aluminum-clad nuclear fuel assemblies and targets were irradiated in the reactors and dissolved in the chemical separations facilities. Isotopes of uranium, plutonium, and other elements were then extracted from the dissolution. The resulting acidic waste, consisting of fission products and dissolved metals was mixed with caustic to raise pH and inhibit corrosion of the carbon steel waste tanks prior to discharge to the SRS HLW Tank Farm. Caustic addition resulted in precipitation of the metals and many of the fission products.

A significant fraction of the sludge solids is aluminum. Removal of a portion of the aluminum reduces the total mass of sludge processed by the DWPF. The aluminum is instead processed in the SRS saltstone facility, where liquid waste is mixed with cement and fly ash and cured into a grout waste form. Since the operational cost of producing grout in the saltstone facility is less than the cost of vitrification, aluminum dissolution can represent a substantial cost savings if no other impacts in the vitrification facility are realized.

A study of low temperature (55 °C) aluminum dissolution and its downstream impacts has been completed using a sample of radioactive sludge [1,2]. Aluminum dissolution consists of the addition of caustic to sludge, heating and mixing the sludge for a period of time to allow the aluminum to dissolve, and settling of the insoluble sludge solids to allow the now aluminum rich supernate to be decanted. Following aluminum dissolution, the sludge is washed and then processed in the DWPF.

Sludge washing involves the addition of water (or other chemicals as needed for corrosion control) to the sludge followed by settling and decanting. The purpose of sludge washing is to lower the sodium salt

content of the sludge. Typically, a sludge is washed two to five times to lower sodium concentration to 1 M in the supernate and to increase insoluble solids content to as high as possible based upon the rheological properties.

DWPF processing includes two main cycles. During the Sludge Receipt and Adjustment Tank (SRAT) cycle, nitric and formic acids are added to the sludge. The purpose of the acidification is to destroy nitrite and carbonate and to improve rheological properties. Formic acid is used to reduce oxides of mercury in the sludge to metallic mercury. Following acid addition, the sludge is boiled and water is removed to increase solids content. Finally, the sludge is boiled under reflux conditions to steam strip the metallic mercury.

During the Slurry Mix Evaporator (SME) cycle, glass frit is added to the sludge as a slurry. Water is removed by boiling to increase solids content (and reduce water fed to the melter). Additional formic acid may be added to improve the slurry's rheological properties. The resulting SME product is then sent to the Melter Feed Tank for subsequent vitrification in the DWPF melter.

This paper evaluates some of the impacts of aluminum dissolution on sludge washing and DWPF processing by comparing sludge processing with and without aluminum dissolution.

EXPERIMENTAL

Three cases were evaluated in this paper. They are designated as SC-3, SC-4, and SC-6. SC designates the SRNL Shielded Cells, the facility where the demonstrations were performed. Table I provides a brief description of each case. Note that SRS has two main types of sludge from its separations processes: HM sludge and PUREX sludge. HM sludge, relative to PUREX sludge, is high in aluminum, and it is the primary "target sludge" for aluminum dissolution.

Table I. Description of Evaluated Cases

SC-3	<ul style="list-style-type: none">• HM Sludge (relatively high aluminum and mercury)• Tank Farm Washed
SC-4	<ul style="list-style-type: none">• HM Sludge• Aluminum dissolution and washing performed in the SRNL Shielded Cells facility with a 3 L sludge sample
SC-6	<ul style="list-style-type: none">• HM Sludge + PUREX Sludge (high in iron relative to HM sludge)• Aluminum dissolution performed in SRS HLW tank with 2×10^6 L of sludge (note that the PUREX sludge was added following aluminum dissolution of the HM sludge)• Washing performed in the SRNL Shielded Cells facility with a 3 L sludge sample

Sludge Washing

Sludge washing involves the addition of wash water or chemicals to dilute the sludge supernate, followed by settling of the sludge and decanting of the resultant supernate. Sludge washing removes soluble components from the sludge. The typical washing endpoint is a nominal sodium concentration of 1 M in the supernate. The final decant sets the percent of insoluble solids ultimately sent to DWPF for processing. Higher insoluble solids generally correlate to more sludge and less water which must be removed either during processing or in the melter itself. However, high insoluble solids results in a more viscous sludge (i.e., a sludge that is more difficult to pump/transfer). Therefore the target insoluble solids content is a balance between the desire to send less supernate (mainly water) to DWPF and the ability to

pump the sludge. Given in Table II is a brief summary of the washing for each sludge processing case evaluated.

Table II. Summary of Sludge Washing

SC3	SC-4	SC-6
<ul style="list-style-type: none"> • Four washes • First three washes utilized water • Final wash utilized supernate from another waste tank. • Unlike most washing scenarios, there was no decant following the final wash. 	<ul style="list-style-type: none"> • Three washes using water. 	<ul style="list-style-type: none"> • Four washes One wash utilized supernate from another waste tank; the other washes utilized water. • Addition of a Pu bearing high nitrate stream to simulate a planned SRS Separations Facility discharge. • Addition of sodium nitrite to maintain a high nitrite to nitrate ratio for corrosion control.

During Cases SC-4 and SC-6, where the sludge was washed on a small scale in the SRNL Shielded Cells facility, sludge level was periodically monitored during the settling steps of washing.

Simulation of DWPF Processing of Sludge

DWPF processing of the sludges include the Sludge Receipt and Adjustment Tank (SRAT) cycle and the Slurry Mix Evaporator (SME) cycle. A summary of each cycle is presented in Table III below.

Table III. Summary of CPC Processing

SRAT Cycle	SME Cycle
<ul style="list-style-type: none"> • Acid Calculation • Heating of SRAT Receipt to 93 °C • Addition of nitric and formic acids per acid calculation • Heat to boiling • Concentration (water removal) to a target wt% total solids • Reflux to steam strip mercury 	<ul style="list-style-type: none"> • Addition and removal of water to simulate addition and removal of water from the decontamination of five glass canisters • Addition of frit and dilute formic acid • Concentration (water removal) to target 45-50 wt% total solids.

In the SRAT cycle, acid is added to destroy nitrite and lower the pH to improve rheology. Formic acid is used to reduce Hg(II) to metallic mercury for steam stripping. The split between nitric and formic acids also has an impact on the glass redox ratio, as measured by the Fe(II) to Fe(III) ratio (glass oxidation state impacts glass processing and properties). To determine the acid amounts, the sludge is characterized to determine required inputs to the acid addition calculation such as nitrite, nitrate, and total acid. A stoichiometric factor is also a required acid calculation input. The stoichiometric factor is determined from SRAT cycle simulations using nonradioactive simulant sludge.

The primary purpose of the SME cycle is to add the glass formers to the sludge in the form of glass frit. Frit is fed to the SME vessel as a frit/formic acid slurry. In the small scale experiments, frit and formic acid are added separately by pouring each into the vessel rather than pumping. The SME cycle is also used to evaporate water used to decontaminate the final glass canisters.

The DWPF has separate vessels for the SRAT and SME cycles. For the SRNL small scale experiments, a single apparatus is used to simulate both cycles with approximately 1 L of sludge. The glass kettle is connected to the SRAT Condenser and the Mercury Water Wash Tank (MWWT). Depending on valve configuration, condensed water can be removed from the system or sent back (refluxed) to the kettle. Because the DWPF Formic Acid Vent Condenser (FAVC), a secondary condenser, does not directly impact SRAT and SME chemistry, it is not included in the SRNL Shielded Cells apparatus. Instead, a simple “cold finger” condenser is used to cool offgas to approximately 20 °C below ambient to remove excess water before the gas reaches a micro gas chromatograph for characterization. The Slurry Mix Evaporator Condensate Tank (SMECT) is represented by a sample bottle that is used to remove condensate through the MWWT. A sketch of the experimental apparatus is given in Figure 1.

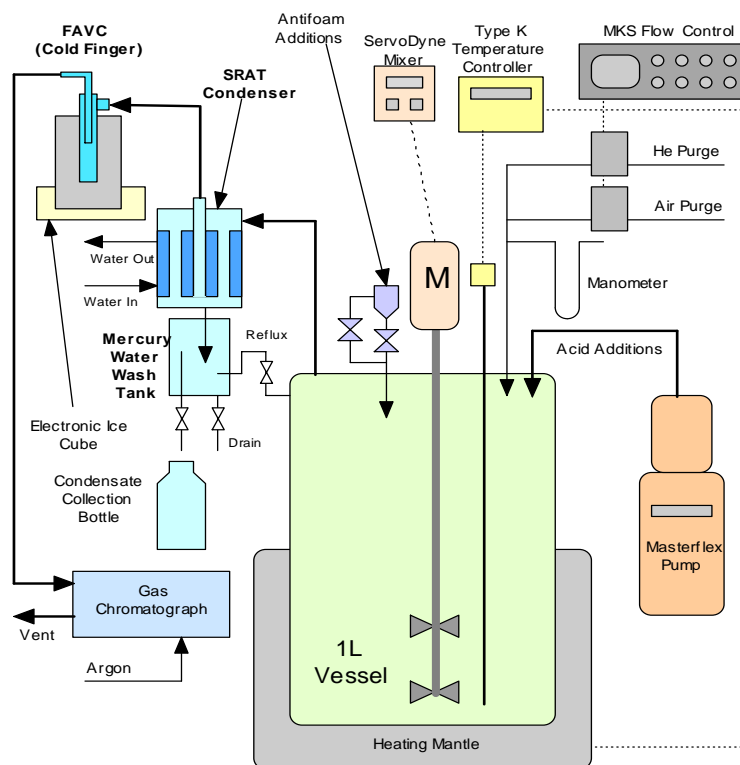


Figure 1. Schematic of SRAT Equipment Set-Up

Offgas from the SRNL DWPF simulations is characterized using an Agilent M200 micro gas chromatograph (GC). The GC is used to quantify helium, hydrogen, oxygen, nitrogen, nitrous oxide, and carbon dioxide emissions. Helium is introduced at a concentration of 0.5% of the total apparatus air purge as an inert tracer gas. The measured helium concentration and helium flow rate are used with the measured concentrations of other gasses to calculate generation rates.

During simulations, the vessel contents are monitored with a camera to observe reactions that may be occurring, slurry air entrainment, and rheology changes. Evidence of reactions or air entrainment include

excessive foaming. Evidence of rheology change includes changes in sludge appearance and inadequate mixing.

Rheology

Rheological properties of the slurries and the DWPF process products were determined using a Haake M5/RV30 rotoviscometer. The M5/RV30 is a Searle sensor system, where the bob rotates and the cup is fixed. The torque and rotational speed of the bob are measured. Heating/cooling of the cup/sample/bob is through the holder that holds the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses. The shear rate is geometrically determined using the equations of change (continuity & motion) and is that for a Newtonian fluid. This assumption also assumes that the flow field is fully developed and the flow is laminar. The shear rate can be calculated for non-Newtonian fluid using the measured data and fitting this data to the rheological model or corrected as recommended by Darby [3]. In either case, for shear thinning non-Newtonian fluids typical of Savannah River Site (SRS) sludge wastes, the corrected shear rates are greater than their corresponding Newtonian shear rates, resulting in a thinner fluid. Correcting the flow curves will not be performed in this task, resulting in a slightly more viscous fluid.

The bob typically used for measuring tank sludge or SRAT product is the MV I rotor. For SME product, the MV II rotor is used to perform the measurements, due to the larger frit particles that are present in the SME product. The MV II has a larger gap to accommodate the larger frit particles. The shape, dimensions, and geometric constants for the MV I and MV II rotors are provided in Figure 2.

Prior to performing the measurements, the rotors and cups are inspected for physical damage. The torque/speed sensors and temperature bath are verified for functional operability using a bob/cup combination with a National Institute of Standards and Technology (NIST) traceable Newtonian oil standard, using the MV I rotor. The resulting flow curves are then fitted as a Newtonian fluid and this calculated viscosity must be within $\pm 10\%$ of the reported NIST viscosity at a given temperature for the system to be considered functionally operable. A N10 oil standard was used to verify system operability prior to the sludge measurements.

The flow curves for the sludge are fitted to the down curves using the Bingham Plastic rheological model, Equation 1, where τ is the measured stress (Pa), τ_0 is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa-sec), and $\dot{\gamma}$ is the measured shear rate (sec^{-1}). During all these measurements, typically the sample remained in the cup for the second measurement, due to the sample availability. If thixotropic properties or unique flow behavior were obvious on the first sample, efforts were made to perform additional measurements by reloading the sample.

$$\tau = \tau_0 + \mu_\infty \dot{\gamma} \quad (\text{Eq. 1})$$

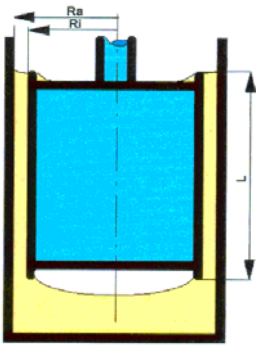
Rotor Design	Dimensions and Flow Curve Program		
	Rotor Type	MV I	MV II
	Rotor radius - R_i (mm)	20.04	18.40
	Cup Radius - R_a (mm)	21.0	21.0
	Height of rotor - L (mm)	60	60
	Sample Volume (cm^3) minimum	40	55
	A factor (Pa/%torque)	3.22	3.76
	M factor ($\text{s}^{-1}/\% \text{RPM}$)	11.7	4.51
	Shear rate range (s^{-1})	0 – 600	0 – 300
	Ramp up time (min)	5	5
	Hold time (min)	1	1
	Ramp down time (min)	5	5

Figure 2. MV I and MV II Rotor Specifications and Flow Curve Program

RESULTS AND DISCUSSION

Sludge Washing

Presented in Table IV is a comparison of the compositions of the three evaluated cases after washing (and aluminum dissolution where applicable). One of the more significant differences in the cases is the calcine factor. The calcine factor is a ratio of the weight percent calcined solids to the weight percent total dried solids. The weight percent calcined solids are determined by heating a slurry sample to constant weight at 1100 °C. At this temperature, the slurry of nitrites, nitrates, and hydroxides is essentially converted to oxides. The calcine factor gives a qualitative indication of the anions present in a given slurry. That is, a lower calcine factor indicates more nitrite and nitrate. With the large addition of sodium hydroxide, nitrite and nitrate content is significantly lower in the sludge following aluminum dissolution.

Table IV. Comparisons of Slurry Compositions

	SC-3 ^a	SC-4 ^a	SC-6 ^b
Wt% Total Solids (% of slurry)	19.5	19.1	17.1
Wt% Insoluble Solids (% of slurry)	12.5	12.0	11.2
Calcine Factor (mass of calcined solids/mass of total dried solids)	0.73	0.87	0.82
Slurry Density (kg/L)	1.14	1.20	1.14
Supernate Density (kg/L)	1.06	1.07	1.06
Na (mol/L supernate)	1.08 ^c	1.42	1.14
Al (mol/L supernate)	0.02 ^d	0.095	0.073
NO ₂ ⁻ (mol/L supernate)	0.46 ^c	0.11	0.22
NO ₃ ⁻ (mol/L supernate)	0.23 ^c	0.051	0.13
Al (wt% of total dried solids)	16 ^e	13.9	8.91
Fe (wt% of total dried solids)	8 ^e	9.97	16.3
Hg (wt% of total dried solids)	2.57	2.84	2.22
Mn (wt% of total dried solids)	1.94	2.44	3.66
Na (wt% of total dried solids)	11.8	22.6	15.2
U (wt% of total dried solids)	2 ^e	2.77	5.33
NO ₂ ⁻ (mg/kg slurry)	20,500	6,550	8,660
NO ₃ ⁻ (mg/kg slurry)	15,400	4,550	6,220
Total Base (mol/L slurry)	0.316	1.5/2.1 ^f	0.74

^a Reference 4.

^b Reference 5.

^c From Tank Farm corrosion control program sample results.

^d Tank Farm estimate.

^e Estimate based on a previous sample (Reference 6).

^f Total base was measured by diluting the sample with water, followed by autotitration (1.5 M) and by a direct titration of undiluted slurry (2.1 M).

Another significant difference between pre and post aluminum dissolution sludge is the aluminum concentration in the supernate (0.02 M in SC-3 and 0.095 and 0.073 in SC-4 and SC-6, respectively). The soluble aluminum likely complicates the total base measurement since aluminum in caustic can contribute up to three hydroxides (Al(OH)₃⁻) and aluminum has non-labile equilibrium chemistry.

One issue with aluminum during washing is its semi-solubility. Unlike sodium or nitrate, it is partially soluble, making it difficult to predict aluminum content in a washed sludge. This was investigated during washing of the Case SC-6 sludge. The concentration of aluminum was compared to the concentration of sulfur in the supernate during washing. The ratio of aluminum to sulfur dropped from thirteen in the as-received sludge to nine in the washed sludge [5]. This may indicate aluminum precipitation as washing progressed since a constant ratio would indicate soluble aluminum and sulfur being removed in the same proportions. Note that aluminum and sulfur cannot be compared to other soluble species (sodium, nitrite, nitrate) since these species were added during the washing process.

The impact of aluminum dissolution on the sludge elemental composition can be seen most clearly by comparing the major cations in the sludge on a calcine solids basis. The weight percent of aluminum, iron, manganese, sodium, and uranium on a calcined solids basis is calculated using Equation 2. The results are given in Table V.

$$\text{wt\% of element } i \text{ in calcined solids} = \frac{\text{wt\% of element } i \text{ in total dried solids}}{\text{Calcine Factor}} \quad (\text{Eq. 2})$$

As can be seen, in both aluminum dissolution cases (SC-4 and SC-6) aluminum is indeed significantly less than in case SC-3. However, in comparing SC-3 and SC-6, the other major elements increase significantly. (Note that the other major elements in case SC-4 would have shown an increase if the sludge were washed more.) The increase in the concentrations of these elements may have impacts on the final DWPF glass, glass frit composition and processability.

Table V. Comparison of Aluminum, Iron, Manganese, Sodium, and Uranium on a Weight % Calcined Solids Basis

	SC-3	SC-4	SC-6
Al	22	16	11
Fe	11	11	20
Mn	2.7	2.8	4.5
Na	16	26	19
U	3	3.2	6.5

Sludge Settling

The settled sludge solids level was recorded during washing for each case. The results of settling prior to the final decant are presented graphically in Figure 3. Note that only one data point was taken for Case SC-3. In all three cases, the sludge solids height dropped to 70% of the starting height within a week. Based strictly on the final wash step, it would appear that settling behavior may be improved with the aluminum dissolution, but the settling rate throughout washing remained erratic so there does not appear to be enough data to draw a definitive conclusion. In fact, during washing in all cases, settling rates were unpredictable [4,5]. Settling during washing of the Case SC-6 sludge is shown in Figure 4 as an illustration.

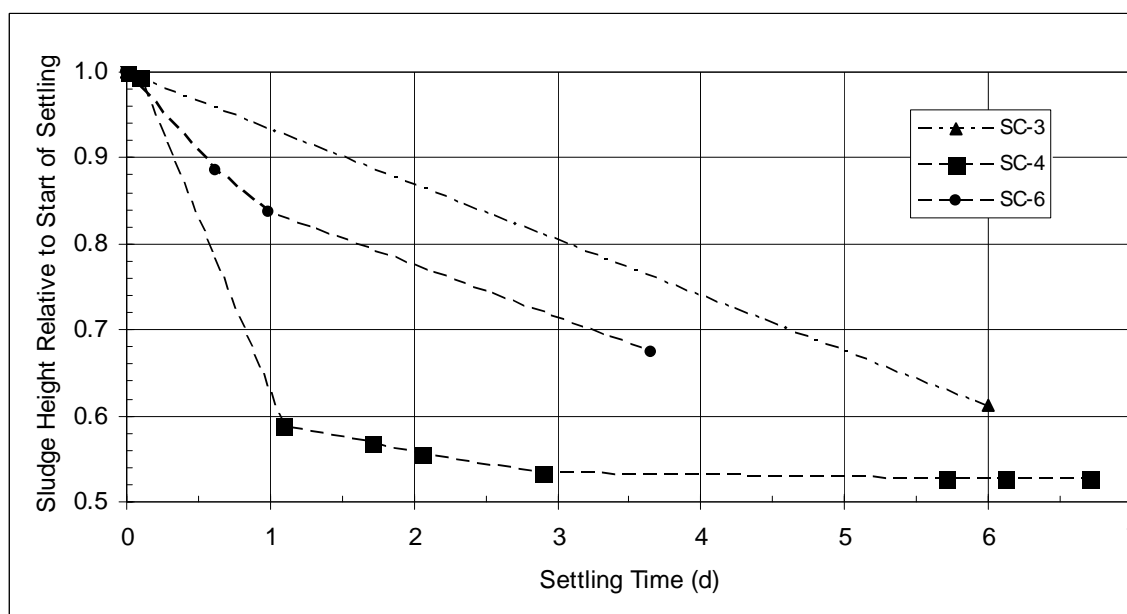


Figure 3. Sludge Settling Prior to Final Decant

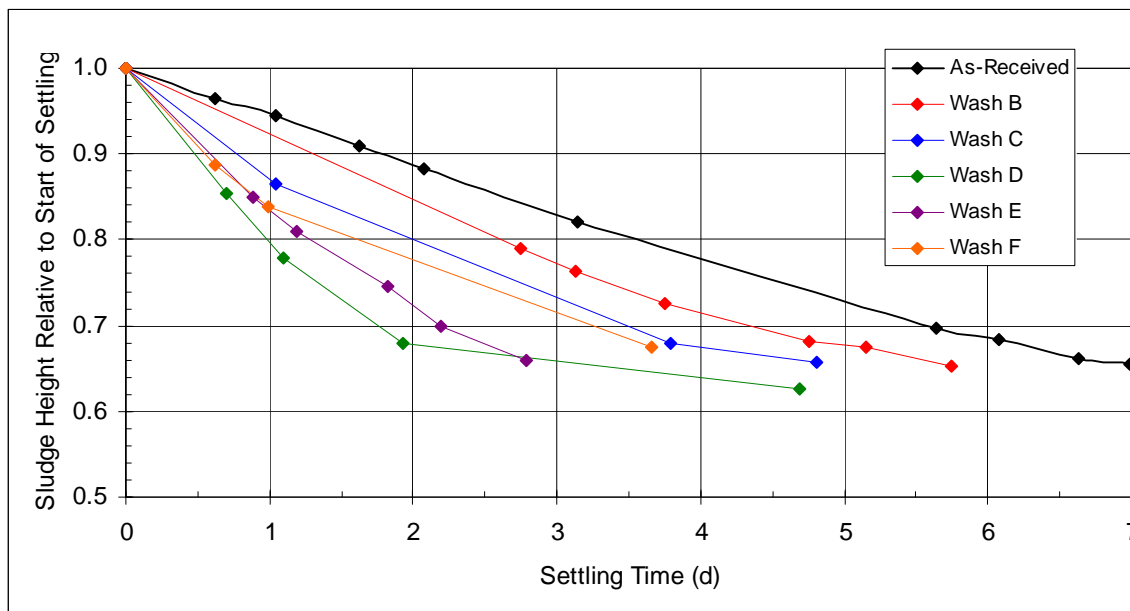


Figure 4. Sludge Settling During Washing of SC-6 Sludge

Simulation of DWPF Sludge Processing

DWPF processing of sludge utilizes an acid calculation to estimate the acid required to accomplish specific goals. Acid is added to destroy nitrite and lower the pH to improve rheology. Both nitric and formic acids are used. Formic acid is used to reduce mercury from Hg (II) to Hg (0) for steam stripping. The split between nitric and formic acids also has an impact on the glass redox as measured by the Fe (II) to Fe (III) ratio (Fe oxidation state impacts glass processing and properties). A stoichiometric factor is also a required acid calculation input. The stoichiometric factor is determined from DWPF simulations using non radioactive simulant sludge.

The primary acid calculation inputs for the three evaluated cases are given in Table VI. Errors or inaccuracies in the acid calculation inputs can result in too little acid being added resulting in incomplete reactions or too much acid being added resulting in excess formic acid causing high hydrogen generation rates via a noble metals catalyzed formic acid destruction reaction. Note that there are additional inputs, such as assumed nitrate and formate destruction factors, which are not included in this paper.

Table VI. Comparison of Primary Acid Calculation Inputs

Input	SC-3^a	SC-4^a	SC-6^b
Total Solids (wt% of slurry)	19.5	19.1	17.1
Insoluble Solids (wt% of slurry)	12.5	12.0	11.2
Soluble Solids (wt% of slurry)	7.0	7.2	5.9
Calcined Solids (wt% of slurry)	14.3	16.6	14.0
Slurry Density (kg/L)	1.14	1.20	1.14
Supernate Density (kg/L)	1.06	1.07	1.06
Mercury (wt% of total solids)	2.57	2.84	2.22
Manganese (wt% of calcined solids)	2.65	2.81	4.48
Nitrite (mg/kg slurry)	20,500	6,550	8,660
Nitrate (mg/kg slurry)	15,400	4,550	6,220
Total Inorganic Carbon (mg/kg slurry)	2,510	1,060	1,280
Total Base (mol/L slurry) ¹	0.316	1.50 / 2.10 _c	0.739

^a Reference 4.

^b Reference 5.

^c Two values for total base are given. The first is a titration of diluted slurry. The second is a titration of undiluted slurry.

The primary results of the acid calculation (the acid requirements) are presented in Table VII. The stoichiometric acid amount is the minimum (theoretical) acid amount required to accomplish the processing goals (nitrite destruction, mercury reduction, etc.). The acid amount is then adjusted based on simulant runs to a level that accomplishes the processing goals without significant excess acid which can result in excess hydrogen generation. Note that for the SC-4 SRAT cycle, two stoichiometric acid amounts are given based on the two titration results (see discussion above). The actual amount of acid added for the SC-4 cycle was based on the lower total base result. Acid amounts using both titration results were calculated and prepared. At the conclusion of acid addition, the SRAT pH was measured and found to be less than 4. Based on this measurement, it was determined that no additional acid was required. However, post cycle analytical results (nitrite and mercury in the SRAT product) indicate that insufficient acid was added.

Table VII. Acid Calculation Results

	SC-3 ^a	SC-4 ^b	SC-6 ^c
Calculated Stoich. Acid (mol/L slurry)	1.30	1.99/2.59 ^d	1.32
Actual Acid Added (mol/L slurry)	1.46	2.29	1.72
Ratio of Formic Acid to Total Acid (mol basis)	0.99	0.83	0.85

^a Reference 7.

^b Reference 4.

^c Reference 5.

^d The two values correspond to 1.5 mol total base/L and 2.1 mol total base/L, respectively. The actual amount of acid added was 115% of the lower acid amount.

During both SRAT and SME processing the most significant difference between the cases was foaming. In both aluminum dissolution cases (SC-4 and SC-6) the sludge foamed more during acid addition and during reflux boiling than in Case SC-3. This foaming may be due to changes in particle morphology following aluminum dissolution.

Following the SRAT and SME cycles, samples of the resulting products were characterized for each case. Key results are presented in Table VIII and Table IX. As shown in Table VIII, nitrite was not adequately destroyed to the required <1,000 mg/kg, and mercury was not removed to below the DWPF requirement of 0.45% of the total solids for Case SC-4, demonstrating that acid was under-added. This under-addition may be attributed to the difficulty in measuring the slurry total base. The analytical results of the Case SC-4 SME product again emphasize the under-addition of acid with the relatively high nitrite result.

Table VIII. SRAT Product Characterization Results

	SC-3 ^a	SC-4 ^b	SC-6 ^c
Wt % Total Solids (slurry basis)	21.3	22.6	26.5
Wt % Insoluble Solids (slurry basis)	11.1	10.0	14.9
Slurry Density (g/mL)	1.22	1.17	1.22
Supernate Density (g/mL)	1.09	1.10	1.09
Formate (mg/kg slurry)	33,400	51,900	57,400
Nitrite (mg/kg slurry)	<1,000	2,710	<800
Nitrate (mg/kg slurry)	26,100	25,000	39,100
Mercury (wt % of total solids)	0.23	0.79	0.18

^a Reference 7.

^b Reference 4.

^c Reference 5.

Table IX. SME Product Characterization Results

	SC-3 ^a	SC-4 ^b	SC-6 ^c
Wt % Total Solids (slurry basis)	49.6	48.3	48.8
Wt % Insoluble Solids (slurry basis)	40.8	37.6	40.4
Slurry Density (g/mL)	1.44	1.46	1.44
Supernate Density (g/mL)	1.12	1.13	1.10
Formate (mg/kg slurry)	36,000	46,600	31,000
Nitrite (mg/kg slurry)	<1,000	1,360	<800
Nitrate (mg/kg slurry)	30,400	22,400	21,400

^a Reference 7.^b Reference 4.^c Reference 5.

Rheology

A comparison of rheological properties is summarized in Table X. In comparing Tank 51 rheology (without aluminum dissolution), to the SC-4 sludge, it appears that the aluminum dissolution process caused an increase in yield stress. Case SC-6 sludge cannot be directly compared to the other cases; SC-6 sludge contained material (PUREX sludge) with significantly different rheological properties compared to the Tank 51 sample and the Case SC-4 sludge. It is difficult to draw conclusions as to the effect of aluminum dissolution on SRAT and SME rheology. The high yield stress of Case SC-4 for both the SRAT and SME products may be further evidence that acid was under added and may not be a result of aluminum dissolution. The rheology of the SC-3 and SC-6 SRAT and SME products cannot be directly compared due to the addition of PUREX sludge to SC-6, which is known to exhibit lower yield stress and consistency than HM sludge.

Table X. Rheological Properties of Sludges and DWPF Processing Products

Sample	Wt% Insoluble Solids	Yield Stress (Pa)	Consistency (Pa·s)
Tank 51 Sample (no Al Dissolution) ^a	11.7	11.7	10.8 X 10 ⁻³
SC-4	12.0	19.9	18.2 X 10 ⁻³
SC-6	11.2	6.8	8.6 X 10 ⁻³
SC-3 SRAT Product	11.10	7.2	10.2 X 10 ⁻³
SC-4 S SRAT Product	12.0	13.4	16.5 X 10 ⁻³
SC-6 SRAT Product	14.9	9.9	14.3 X 10 ⁻³
	11 ^b	6.4	6.1 X 10 ⁻³
SC-3 SME Product	40.8	10.9	19.8 X 10 ⁻³
SC-4 SME Product	37.6	21.6	29.2 X 10 ⁻³
SC-6 SME Product	40.4	16.7	13.8 X 10 ⁻³

^a Rheological properties of Sludge SC-3 were not measured. The results of this sample (see Reference 8), however, are comparable.^b Because the rheological properties of the 14.9% sample exceeded DWPF processing limits, a sample was diluted to 11% insoluble solids (20% total solids).

CONCLUSIONS

General observations about the downstream impacts of aluminum dissolution include:

- The unpredictable settling behavior of SRS sludges during washing was not changed as a result of aluminum dissolution.
- The relationships between the major sludge elements (aluminum, iron, and sodium) are impacted by aluminum dissolution, which has potential downstream impacts to DWPF melter operations such as the final glass composition, frit composition, and melt rate.
- Aluminum dissolution complicates slurry total base measurements. This could result in under or over addition of acid in DWPF processing. Under addition of acid yields a product with out-of-specification nitrite and mercury content and a product with rheological properties that cannot be processed. Over addition of acid can increase hydrogen generation during processing.
- Aluminum dissolution impacts on sludge rheology are not clear; however, slurries from aluminum dissolution appear to be foamier during processing than slurries that have not undergone dissolution.

REFERENCES

1. M. S. HAY, J. M. PAREIZS, C. J. BANNOCHIE, M. E. STONE, D. R. CLICK, and D. J. MCCABE, "Characterization and Aluminum Dissolution Demonstration With A 3 Liter Tank 51H Sample," WSRC-STI-2007-00697, Rev. 0, Savannah River National Laboratory, Aiken, SC (2008).
2. M. T. KEEFER, B. A. HAMM, and J. A. PIKE, "Low Temperature Aluminum Dissolution of Sludge Waste," Waste Management 2008, Phoenix AZ (2008).
3. R. DARBY, *Chemical Engineering Fluid Mechanics, 2nd edition*. Marcel Dekker: (2001).
4. J. M. PAREIZS, C. J. BANNOCHIE, D. R. CLICK, E. K. HANSEN, D. P. LAMBERT, and M. E. STONE, "Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells Using Post Aluminum Dissolution Tank 51 Sludge Slurry," WSRC-STI-2008-00086, Savannah River National Laboratory, Aiken, SC (2008).
5. J. M. PAREIZS, C. J. BANNOCHIE, D. R. CLICK, D. P. LAMBERT, M. E. STONE, B. R. PICKENHEIM, A. L. BILLINGS, and N. E. BIBLER, "Sludge Washing And Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 5 Qualification," SRNS-STI-2008-00111, Savannah River National Laboratory, Aiken, SC (2008).
6. J. M. PAREIZS, C. J. BANNOCHIE, M. J. BARNES, N. E. BIBLER, D. R. CLICK, E. K. HANSEN, D. P. LAMBERT, and M. E. STONE, "Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells in Support of Sludge Batch 4 Qualification," Technical Report WSRC-STI-2007-00053, Savannah River National Laboratory, Aiken, SC (2007).
7. D. C. KOOPMAN, J. M. PAREIZS, D. P. LAMBERT, and C. J. BANNOCHIE, "Sludge Batch 4 Follow-up Qualification Studies to Evaluate Hydrogen Generation," WSRC-STI-2007-00212, Savannah River National Laboratory, Aiken, SC (2007).

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8. E. K. HANSEN, "Tank 51 Sludge Batch 4 Transfer to Tank 40," WSRC-STI-2006-00218, Rev. 0, (2006).