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Melt Rate Testing for Sludge Batch 6

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was requested to provide Savannah River Remediation (SRR) with a recommended frit composition for Sludge Batch 6 (SB6) to optimize processing at the Defense Waste Processing Facility (DWPF). This report discusses the results of a series of melt rate experiments that were completed in support of the frit recommendation and the preparation of the feed used in the testing. The objective of the work was to identify the impact of individual frit component concentrations on melt rate for both SB6 and for DWPF sludge batches in general. The dry fed, Melt Rate Furnace (MRF) was used to compare the relative melt rate performance of several candidate frit compositions. Sludge composition projection changes and variation led to the fabrication and testing of several new frits along with Frit 418, which is currently utilized at the DWPF for Sludge Batch 5 (SB5) processing.

The melt rate testing results show that changes in the frit composition, such as increases in B_2O_3 or Li_2O concentrations, can provide a faster melt rate for SB6 relative to Frit 418. However, the composition of SB6 as currently projected (February 2010 blended with a 40 inch heel of SB5) does not allow for significant changes in frit composition relative to Frit 418 without compromising the projected operating windows. Only one of the new frits tested, Frit IS7, remains viable for SB6 processing based on the current composition projections. The melt rate results also demonstrated that a low Na_2O concentration frit (particularly Frit IS7) can provide reasonable melt rates if the concentrations of Li_2O or B_2O_3 in the frit are increased.

The measured melt rate for Frit IS7 with the simulated SB6 feed was about 15% faster than that for Frit 418. The projected operating windows for Frits 418 and IS7 are very similar with the current SB6 projections. However, waste loadings with Frit IS7 are limited by low viscosity predictions, while waste loadings with Frit 418 are limited by predictions of nepheline crystallization. It is recommended that SRNL reevaluate the final SB6 composition once washing and blending are complete to determine whether a change in frit composition could provide improved operating windows, improved sulfate solubility, and/or increased waste throughput.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
MAR	Measurement Acceptability Region
MRF	Melt Rate Furnace
PCCS	Product Composition Control System
SB5	Sludge Batch 5
SB6	Sludge Batch 6
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

1.0 Introduction

The Savannah River National Laboratory (SRNL) was requested to provide Savannah River Remediation (SRR) with a recommended frit composition for Sludge Batch 6 (SB6) to optimize processing at the Defense Waste Processing Facility (DWPF).[1, 2] This report discusses the results of a series of melt rate experiments that were completed in support of the frit recommendation[3] and the preparation of the feed used in the testing. The objective of the work was to identify the impact of individual frit component concentrations on melt rate for both SB6 and for DWPF sludge batches in general. The dry fed, Melt Rate Furnace (MRF)[4] was used to compare the relative melt rate performance of several candidate frit compositions. Sludge composition projection changes and variation led to the fabrication and testing of several new frits[5] along with Frit 418, which is currently utilized at the DWPF for Sludge Batch 5 (SB5) processing.

A small number of preliminary melt rate tests were completed earlier in the SB6 frit optimization process, using earlier SB6 composition projections as a basis.[6] These tests showed that higher concentrations of B_2O_3 in the frit relative to that of Frit 418 appeared to improve melt rate. However, when a higher concentration of B_2O_3 was coupled with a lower concentration of Na_2O relative to Frit 418, melt rate did not appear to improve. The results also showed an inverse relationship between melt rate and waste loading, which is consistent with trends previously identified for DWPF processing.[4, 7, 8] The melt rate testing described here builds on those results by further investigating the impact of the concentrations of individual frit components on melt rate for SB6, utilizing a more recent SB6 composition projection.

2.0 Experimental Procedure

2.1 Feed Preparation

Simulant was prepared and processed through the DWPF Sludge Receipt and Adjustment Tank (SRAT) process to prepare feed for melt rate testing. The SB6 simulated sludge composition target (designated SB6-F) was developed based on the best available projections of the SB6 blended feed in November 2009. The projected composition was renormalized after removal of radioactive species from the elemental compositions and adjusted for charge balance as required. The recipe development and simulant preparation process is documented separately.[9]

Two identical SRAT runs (designated SB6-19 and SB6-20) were performed in 22 L vessels at the Aiken County Technology Laboratory (ACTL). The laboratory testing was conducted in accordance with procedure ITS-0094 of the L29 manual: “Laboratory Scale Chemical Process Cell Simulations”. The experimental apparatus was set up using a 22 L SRAT/SME vessel. At the conclusion of the SRAT cycles, the SRAT products from the duplicate runs were blended and one 125 ml sample was pulled from the composite batch (designated as SB6-19/20) for analysis.

As per the current protocol for feed preparation for melt rate studies, no mercury or noble metals were added to the sludge prior to SRAT processing. This allows for running without online gas chromatography to detect hydrogen thus reducing the cost and complexity of the runs, and is not expected to significantly influence measured melt rates.

Acid calculations for Chemical Process Cell (CPC) process simulations were completed based on the SB6-F sludge simulant analysis. These runs utilized the Koopman acid equation[10] with a stoichiometric factor of 125%. The formic acid destruction and nitrite to nitrate conversion assumptions were 14% and 18% respectively. These values were chosen based on SB5 feed preparation runs without noble metals and mercury.

2.2 MRF Testing

The MRF installed at the ACTL is utilized to compare the melting behavior of different feed formulations for the DWPF. The furnace inner chamber is a cylindrical volume, approximately 14.2 L (0.5 ft^3) in size, with heating coils winding around the chamber walls. The diameter of the chamber is ~17.8 cm (7 in). The testing was conducted in accordance with ITS-0010 of the L29 manual, "Preparing Batches and Melting in the Dry-Feed Melt Rate Furnace." Samples are prepared by mixing SRAT product with frit in the proper ratio to obtain the desired waste loading. The material is dried and then screened through a 10 mesh (1.7 mm) screen before being poured into a 1200 ml stainless steel beaker. The beaker is placed in an insulating sleeve and covered with a vented, insulating cover. The furnace is heated to approximately 1150 °C with the top opening covered. Once the furnace reaches the set point, the cover is removed and the beaker containing sufficient product to produce 525 g of glass is inserted. When inserted, the beaker bottom is approximately flush with the top of the uppermost chamber coil. After 50 minutes, the beaker is removed from the furnace. There is a 20 minute period between successive tests for the furnace to return to a stable temperature. For control purposes, a beaker containing a Frit 418 standard is fired along with each series of test beakers. After cooling, each beaker is sectioned and the linear melt rate determined by measuring the height of the glass formed along the bottom of the beaker.

3.0 Results and Discussion

3.1 SRAT Product Results

Blended (SB6-19/20) SRAT product elemental, anion and solids results are reported in the tables below. Nitrite was successfully destroyed to below the detection limit. Formate destruction was 12% compared to an estimated 14%. Nitrite to nitrate conversion was 23% compared to a predicted 18%. These data can be used to further refine processing assumptions for sludges with no mercury or noble metals.

Table 3-1. SB6-19/20 Elemental Composition.

Element	wt % (calcined basis)		Element	wt % (calcined basis)
Al	14.0		Na	14.4
Ba	0.142		Ni	2.82
Ca	1.56		P	<0.100
Ce	0.213		Pb	0.022
Cr	0.184		S	0.286
Cu	0.102		Si	1.27
Fe	20.4		Sn	0.057
K	0.090		Ti	0.033
Mg	0.538		Zn	0.100
Mn	6.31		Zr	0.287

Table 3-2. SB6-19/20 Anions and Solids Results.

Analyte	Result	Units
F	<100	mg/kg slurry
Cl	255	mg/kg slurry
NO_2	<100	mg/kg slurry
NO_3	34000	mg/kg slurry
SO_4^{2-}	134	mg/kg slurry
HCO_2	65100	mg/kg slurry
C_2O_4	<100	mg/kg slurry
PO_4^{3-}	<100	mg/kg slurry
Total Solids	24.5	wt %
Soluble Solids	12.2	wt %
Insoluble Solids	12.2	wt %
Calcined Solids	14.8	wt %
pH	3.86	no units
Density	1.18	g/mL

An updated SB6 composition projection was received in February 2010 before the processing of SB6-19/20 in the MRF. This updated projection was higher in sodium and sulfur than previous projections. To better match the new composition, sulfur and sodium were added to the blended SRAT product as trim chemicals prior to MRF testing. Sulfur was added as Na_2SO_4. The balance of the sodium was added as NaCl. Trim chemicals were added to target 19 wt % Na and 0.46 wt % S on a calcined solids basis. The chemical composition of the SRAT product was not re-analyzed after the trim addition. The trim addition changed the total and calcined solids to 26.3 and 15.8 wt %, respectively.

3.2 MRF Testing

The MRF testing was intended to provide data on the impacts of individual frit components on melt rate for SB6 based on composition projections updated in February 2010.[5] The concentrations of each of the frit components were varied to develop the seven frit compositions shown in Table 3-3, along with Frit 418. As described in Section 2.1, a large quantity of blended SB6 SRAT material was produced to support this series of melt rate testing. This allowed for each of the eight frit compositions to be tested in triplicate at 36% waste loading, providing some gauge of reproducibility for the measured melt rate of each sludge and frit combination. The time necessary to fabricate the quantity of frits needed for testing on this scale dictated that the compositions be selected a few months before the MRF testing would begin. Therefore, not all of the frit compositions tested would currently be considered viable for use with SB6 based on the most recent sludge composition projections. However, the frits selected are still useful for identifying compositional effects on melt rate in general, and for the SB6 system in particular. Frits containing CaO were included as this component may be beneficial for improved sulfate retention in SB6 and future sludge batches.

Table 3-3. Target Frit Compositions (wt %) for the Fourth Series of SB6 Melt Rate Tests.

Frit ID	B_2O_3	CaO	Li_2O	Na_2O	SiO_2
IS1	12	3	9	6	70
IS2	14	0	9	6	71
IS3	8	3	11	6	72
IS4	8	0	11	6	75
IS5	10	0	12	6	72
IS6	8	0	11	8	73
IS7	8	0	12	2	78
418	8	0	8	8	76

The MRF testing was carried out over a period of four days, with the frits being tested in the order of the run numbers shown in Table 3-4. Each of the individual, measured melt rates is given in Table 3-4, along with an average melt rate for each frit composition. The measured melt rates for the frit standard were consistent with previous studies.[11, 12]

Table 3-4. Results of the Fourth Series of MRF Testing.

Frit ID	Run Number	Measured Melt Rates (in/hr)	Average Melt Rate (in/hr)
IS1	2, 10, 18	0.8, 0.8, 0.9	0.8
IS2	3, 11, 19	0.8, 0.8, 0.9	0.8
IS3	4, 12, 20	0.8, 0.8, 0.7	0.8
IS4	5, 13, 21	0.7, 0.7, 0.8	0.7
IS5	6, 14, 22	0.8, 0.8, 0.9	0.9
IS6	7, 15, 23	0.7, 0.8, 0.7	0.7
IS7	8, 16, 24	0.5, 0.7, 0.6	0.6
418	1, 9, 17	0.5, 0.5, 0.6	0.5
Frit Standard	A,B,C,D	1.6, 1.6, 1.5, 1.6	1.6

The results in Table 3-4 show that, to varying degrees, all of the frit compositions tested have an improved average melt rate relative to that of Frit 418. The following general conclusions can be made about the effects of frit component concentrations on melt rate with the SB6 feed material:

- Higher concentrations of B_2O_3 improved melt rate.
    - Frits IS1, IS2 and IS5, with the highest B_2O_3 concentrations, also had the highest average melt rates.
- The addition of CaO resulted in a marginal improvement in melt rate.
    - Compare the results for Frit IS3 to the results for Frits IS4 and IS6
- Higher concentrations of Li_2O appeared to improve melt rate.
    - Compare the results for Frits IS4 and IS6 to the results for Frit 418.
- Higher concentrations of Na_2O appeared to improve melt rate.
    - Compare the results for Frits IS4 and IS6 to the results for Frit IS7.
- Lower concentrations of SiO_2, resulting from increased concentrations of other frit components, generally improved melt rate.

After completion of this series of MRF testing, the predicted performance (i.e., projected operating windows) of the frit compositions used was reevaluated with the most recent (February 2010) SB6 composition projections.[3] Nominal and Variation Stage assessments using the DWPF Product Composition Control System (PCCS) Measurement Acceptability Region (MAR) showed that, based on these updated projections, only Frits IS7 and 418 are now candidates for SB6 processing at a target waste loading of 36%. The other frits do not provide projected operating windows that are sufficient for targeting 36% waste loading. A comparison of the melt rate data between Frits IS7 and 418 shows a marginal improvement for Frit IS7, which has a lower Na_2O concentration and a higher Li_2O concentration relative to Frit 418.

4.0 Conclusions and Recommendations

The melt rate testing results show that changes in the frit composition, such as increases in B_2O_3 or Li_2O concentrations and decreases in SiO_2 concentrations, can provide a faster melt rate for SB6 relative to Frit 418. These observations are consistent with previous melt rate testing in support of DWPF. However, the composition of SB6 as currently projected does not allow for significant changes in frit composition without compromising the projected operating windows. Only one of the new frits tested, Frit IS7, remains viable for SB6 processing based on the current composition projections.

The melt rate results demonstrated that a low Na_2O concentration frit (particularly Frit IS7) can provide reasonable melt rates if the concentrations of Li_2O or B_2O_3 in the frit are increased. This may become of additional importance should the compositions of future sludge batches continue to drive frit compositions toward lower Na_2O concentrations to provide useful projected operating windows. Frits that include CaO, which may be beneficial for improved sulfate retention, also showed improved melt rates.

The measured melt rate for Frit IS7 with the simulated SB6 feed was about 15% faster than that for Frit 418. The projected operating windows for Frits 418 and IS7 are very similar. However, waste loadings with Frit IS7 are limited by low viscosity predictions, while waste loadings with Frit 418 are limited by predictions of nepheline crystallization. It is recommended that SRNL reevaluate the final SB6 composition once washing and blending are complete to determine whether a change in frit composition could provide improved operating windows, improved sulfate solubility, and/or increased waste throughput.

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