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SLUDGE BATCH 3 (DECANT #5)/FRIT 202 FLOWSHEET DEMONSTRATION (U)

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EXECUTIVE SUMMARY

Results of the test that demonstrated a "workable flowsheet" for a nominal Sludge Batch 3 (Decant #5)/Frit 202 feed are presented in this report. This workable flowsheet includes an acid addition strategy for the feed processing steps at the Defense Waste Processing Facility (DWPF) in the Sludge Receipt and Adjustment Tank (SRAT) and the Slurry Mix Evaporator (SME). Frit 202 was chosen due in part to its availability for the timing of this work. A waste loading (WL) of 35% was targeted (32% was the actual calculated WL from the final SME product) for this run to try and ensure that the glass produced was in the Property Acceptability Region (PAR) limits of the DWPF Product Composition Control System (PCCS). This test was the first that treated Sludge Batch 3 (SB3) simulant material via a small scale SRAT/SME and then vitrified the resultant material via slurry feeding in a melter (Slurry-fed Melt Rate Furnace or SMRF).

The results of the test did not indicate any major processing issues associated with the SRAT/SME or slurry feeding for this particular material. Melt rate as defined by SMRF pour rate was somewhat lower for this feed than for SB2/Frit 200 and SB2/Frit 320 (both previously tested in the SMRF at a lower 25% waste loading). However, the overall waste throughput (2.8 g/min) was less than SB2/Frit 320 (3.4 g/min) but greater than SB2/Frit 200 (2.4 g/min). Further development is needed to optimize the process with regards to melt rate, waste loading, acid/redox control strategy, and most importantly waste throughput. This development includes the slurry feed testing of other frits that have been documented elsewhere [Peeler and Edwards (2002)] to enhance the waste throughput of SB3 in the DWPF.

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ACRONYMS

ACTL	Aiken County Technology Laboratory
AES	Atomic Emission Spectroscopy
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
DWPF-PE	Defense Waste Processing Facility – Process Engineering
GC	Gas Chromatograph
HLW	high-level waste
IC	ion chromatography
ITS	Immobilization Technology Section
PAR	Property Acceptability Region
PCCS	Product Composition Control System
SB	sludge batch
SME	Slurry Mix Evaporator
SMRF	Slurry-fed Melt Rate Furnace
SRAT	Sludge Receipt and Adjustment Tank
SRS	Savannah River Site
SRTC	Savannah River Technology Center
WL	waste loading

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1.0 INTRODUCTION

Approximately 130M L of sludge/supernate high-level waste (HLW) is currently stored in underground carbon steel tanks at the Savannah River Site (SRS) in Aiken, South Carolina. The Defense Waste Processing Facility (DWPF) began immobilizing these wastes in borosilicate glass in 1996. Currently, the radioactive glass is being produced as a "sludge-only" composition by combining washed high-level sludge with glass frit and melting. The molten glass is poured into stainless steel canisters that will eventually be disposed of in a permanent geological repository.

Currently, the DWPF is processing Sludge Batch 2 (SB2) and is planning to start processing Sludge Batch 3 (SB3) in the spring of 2004 (WSRC 2001).[1] A sludge batch is defined as a single tank of sludge slurry or a combination of sludge slurries from different tanks that has been or will be qualified for eventual transfer to DWPF. SB3 will be primarily Tank 7 sludge (which also contains the heels from Tanks 18 and 19) mixed with the heel of Sludge Batch 1B (SB1B), an H-Canyon slurry containing precipitated Pu with Gd (Jilani 2002), and an Am/Cm precipitate from F-Canyon (Patel 2002). The sludge from Tank 7 is expected to contain several components that are considered atypical of DWPF sludge to date including higher levels of noble metals than previously processed sludge batches (Peeler et al. 2002) as well as sand, coal, sodium oxalate, and zeolite (Peeler and Edwards 2002). Based on the process history for Tank 7, it is estimated that significant quantities of sand/coal (~7723 kg) and sodium oxalate (~300,000 kg) have been added to this tank (Goslen 1984; Fowler 1980).

The quantities of sand, coal, and sodium oxalate may impact several processing parameters at the DWPF. DWPF Process Engineering (DWPF PE) has issued a Technical Task Request (TTR) requesting the Savannah River Technology Center (SRTC) to address these processing impacts (Rios-Armstrong 2002). Fellinger (2002) provided a list of the various tasks that are currently being addressed prior to DWPF's acceptance of SB3. Studies have been or are being performed by SRTC to assess the effects of sand, coal, sodium oxalate, the Pu/Gd stream, and the higher levels of noble metals on various SB3 issues [Herman et al. (2002a); Peeler et al. (2002); Bronikowski et al. (2002); Jantzen (2002); Herman et al. (2002b); Herman (2002a); Herman (2002b); Herman et al. (2003); Herman et al. (2003a); Peeler and Edwards (2002); Smith (2002); and Lorier et al. (2003)].

This report focuses on the first surrogate demonstration of a "workable flowsheet" for SB3 material. Two 15L glass Sludge Receipt and Adjustment Tank/Slurry Mix Evaporator (SRAT/SME) vessels at the Aiken County Technology Laboratory (ACTL) were used for the feed preparation portion of the test while the feed was vitrified in the ACTL Slurry-fed Melt Rate Furnace (SMRF). The flowsheet tested should not be considered final as further optimization is probable.

[1] Although the current HLW System Plan (WSRC 2001) projects the initiation of SB3 processing in the spring of 2004, plans to expedite processing of SB3 are currently being assessed. If proven feasible, processing of SB3 could begin sooner.

2.0 OBJECTIVE

The objective of this task was to demonstrate a "workable flowsheet" for a surrogate nominal SB3 (Decant #5) composition from which process improvements (optimizations) could be made. These improvements could include the use of alternative frits, acid addition/redox strategy changes, various levels of sludge washing, and higher or lower waste loadings in the melter feed. A determination of a "workable flowsheet" (or processable material) was to be based on no major issues associated with the SRAT/SME, no major foaming or problematic cold cap behavior during the melting process with slurry feeding, reasonable melt rate/waste throughput, and acceptable glass product (durability, predicted viscosity, and liquidus).

3.0 EXPERIMENTAL DESCRIPTION

3.1 22-L GLASS SRAT/SME

The sludge slurry for the SMRF runs was prepared using SB3 simulant from the Clemson Environmental Technologies Laboratory (CETL) as a starting sludge. Due to the large amount of feed required, two batches of sludge slurry were fabricated. Since the CETL simulant was a generic SB3 simulant, it had to be trimmed to match the Decant #5 composition (Lorier, et al. 2003). This was accomplished by measuring the total solids of the starting sludge and adding trim chemicals in the correct proportions to match the Decant #5 target composition. The addition chemicals required included sodium oxalate, potassium nitrate, and sodium salts. The target composition (not normalized) is given in Table 3-1. The sludge was not analyzed after the sodium and potassium compounds were added, and it was assumed that the composition was similar to previously batched and analyzed Decant #5 sludge simulants (Lorier, et al. 2003).

Table 3-1. Target Composition of the Decant #5 Sludge (calcined oxide basis, wt.%).

Species	Target Decant #5
Al_2O_3	16.0
BaO	0.216
CaO	3.17
CuO	0.181
Fe_2O_3	35.3
Gd_2O_3	0.037
K_2O	0.277
MgO	0.320
MnO	5.93
Na_2O	38.6
NiO	1.31
SiO_2	3.10
ZnO	0.359
ZrO_2	0.672
Sum	105.52

Approximately 60 liters of melter feed (SB3 (Decant #5) / Frit 202 at a targeted 35% WL) was generated for the experiments performed in the SMRF. Four separate SRAT/SME runs were performed over a 4-day period to generate this simulant (2 kettles per 2-day total cycle time). A schematic of the 22-liter vessel setup is shown in Figure A1 of Appendix A.

The SRAT cycle run plan consisted of adding sieved coal, sand, Gd, and noble metals to the batch; adding nitric and formic acids to acidify the sludge, concentrating the batch to the original volume, and then refluxing the batch for 12 hours. The additional trim components were added at the nominal values anticipated for the SB3 Decant #5 composition, which are given in Appendix A in the list of assumptions (item #15).

The acid addition strategy for the SRAT/SME runs was based on the Phase I simulant flowsheet runs in the lab-scale SRAT (i.e., 4-liter rig) (Herman et al. 2003a). In the Phase I flowsheet runs, Decant #5 simulant containing 10% of the nominal level of noble metals was processed with what was projected to be 100% of the stoichiometric addition of acid. The total moles of acid from the Phase I run were scaled to the batch size for the SMRF SRAT runs to estimate the amount of acid to add. Since the SMRF SRAT runs were being performed at nominal levels of noble metals and scoping SB3 simulant SRAT runs have shown more effective nitrite destruction at nominal levels of noble metals, it was assumed that acceptable nitrite destruction would be obtained for the SMRF runs with equivalent amounts of acid. The estimated necessary acid was 15.555 moles per trimmed sludge (~16,900 gms) used for each SRAT batch. The assumptions used to perform the acid calculation are given in Appendix A. The split of acid between nitric and formic was determined using the modified (preliminary) SB3 redox equation by Jantzen (not yet documented). A redox ratio of 0.2 was targeted and the equation was as follows:

$$Fe^{2+}/\Sigma Fe = 0.24 + 0.47\ (Formate) + 0.82\ (Oxalate) + 0.6\ (Coal) - 1.41\ (Nitrate + Nitrite)$$

The redox was calculated using molar concentrations of each species assumed to be present in the SME product. The split was determined to be 6.720 moles nitric acid and 8.835 moles formic acid per SRAT batch. This redox equation has subsequently been revised (not yet documented); however, at the time of the test, the above equation was felt to be the most appropriate for SB3.

During the SRAT/SME runs, samples of the in-process slurry were taken in select runs to monitor the anion behavior during processing. The in-process slurry samples were analyzed using Ion Chromatography (IC) by the Immobilization Technology Section (ITS)-Mobile Lab. Nitrate, nitrite, and formate analytical samples were prepped using a weighted dilution, whereas an acid addition strike had to be performed to measure the oxalate concentration. Samples of the SRAT and SME products were pulled from each SRAT/SME run to characterize the products of each run. The chemical composition of the cations in the sludge slurry were measured in duplicate on the Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy (AES) by the ITS-Mobile Lab. The samples for ICP were prepped by calcining the slurry at 1100°C followed by subsequent digestion of the solids using lithium metaborate fusion, sodium peroxide fusion, and aqua regia techniques. The anions in the sludge slurry were measured using the same techniques as for the in-process slurries. The physical properties of the products, including total solids, calcined solids, density, and dissolved solids, were also measured by the ITS-Mobile Lab. The soluble and insoluble solids were calculated from the total and dissolved solids results. The physical property measurements were also performed in duplicate.

The SME cycles immediately followed the SRAT cycles. This procedure consisted of adding Frit 202, formic acid, and the water associated with the frit solution, in two separate additions. Dewatering or concentration of the SME batch was performed after each frit addition. The target final SME total wt% solids was 45%.

A Gas Chromatograph (GC) was used to measure the generated gases in two of the four SRAT runs. Since the nominal levels of noble metals were being tested, it was anticipated that hydrogen would be generated during the runs. It was assumed that gases generated would be equivalent in all runs since the processing parameters were consistent. Therefore, two of the runs were monitored to determine the amount of hydrogen so that the flowsheet for SB3 could be better defined. Helium was used as a tracer gas at 0.5 volume percent of the scaled purge for the runs with the GC.

3.2 ACTL SLURRY-FED MELT RATE FURNACE (SMRF)

The SMRF installed in the high bay of the Aiken County Technology Laboratory (ACTL) has been utilized to compare the melting behavior and melt rate of different slurry feed formulations for the DWPF. The SMRF provides an opportunity for low cost, rapid analysis of process and chemistry alternatives that are under consideration as part of flow sheet improvements and enhancements.

The SMRF at the ACTL is designed to mimic the heat transfer characteristics of a large-scale joule-heated melter (Lorier et al., 2002). This is done by providing heating in one dimension through the bottom of an 8 inch diameter Inconel 690 crucible and insulating around the sides of the crucible in the melt pool area to minimize radial heat transfer to or from the melt pool and heat exchange with the plenum. This mimics the heat flow that would be present in a large melter that relies on convective and conductive heat transfer between the glass pool and cold cap. Sketches of the furnace are shown in Figures 3-1 and 3-2.

The glass temperature is controlled by a thermocouple mounted on the bottom of the crucible and is typically maintained within the temperature range of 1125-1150°C. Additional heating (separate from that supplied to the melt pool) is applied to the plenum above the melt pool through Globar heaters that surround the top of the crucible. These can be controlled to simulate different plenum conditions in the melter. The plenum temperature controller uses input from a thermocouple inserted into the vapor space of the crucible. Automated feed additions (typically 20 to 30 seconds in duration) to the melter are based on maintaining a plenum temperature set point. After each feed cycle, the controller will wait for the melter to return to the vapor space set point temperature (typically 600-800°C). Once the vapor space temperature setpoint has been reached and the temperature is increasing, the feed cycle will begin again.

Melt rate can be assessed by measuring the mass decrease of the feed vessel over a test period or by weighing the amount of glass poured over a test period. For these tests, glass pour rate was used to determine melt rate. The melt rate tests are conducted by feeding the slurry in controlled increments to the SMRF for a sufficient amount of time to establish the cold cap. These conditions are typically achieved after two hours. Melt rate data and observations relating to cold cap and feed behavior are then obtained.

An agitator is used to mix the contents of the melter feed tank and keep the solids in suspension. A peristaltic pump dispenses a predetermined quantity of slurry feed to the SMRF upon command by the Factory Link™ computer control system. A water-cooled feed tube directs the slurry feed onto the melt pool surface, eventually forming a cold cap.

As the automatic feed system dispenses slurry feed onto the melt surface, glass is continuously poured from the SMRF through the overflow pour tube. The break-over level for glass pouring from the SMRF requires 3½ inches of glass depth in the crucible. The poured glass is collected in a catch pan located beneath the pour tube discharge. Induction heating is applied to the lower portion of the pour tube that extends beyond the heated chamber of the SMRF to facilitate glass pouring.

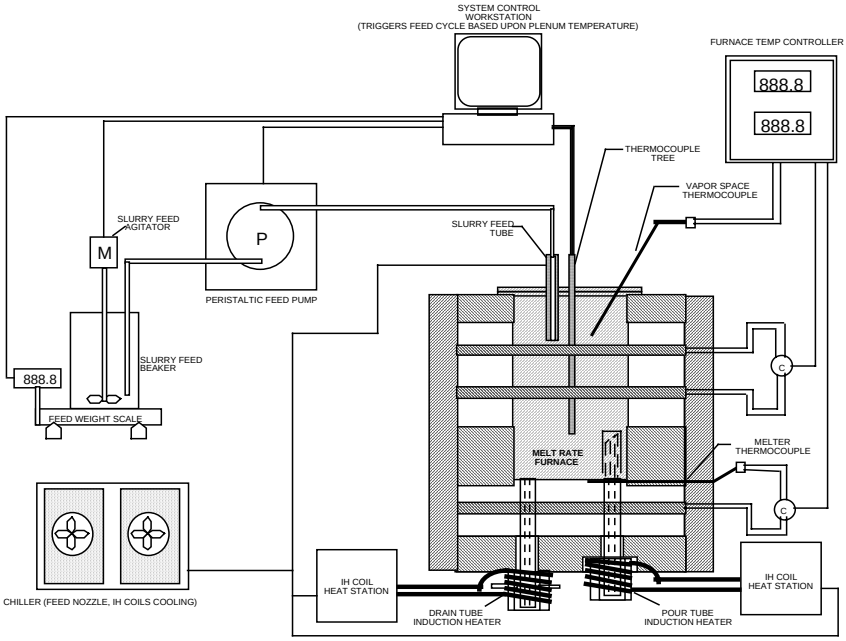

Figure 3-1. ACTL SMRF System Schematic

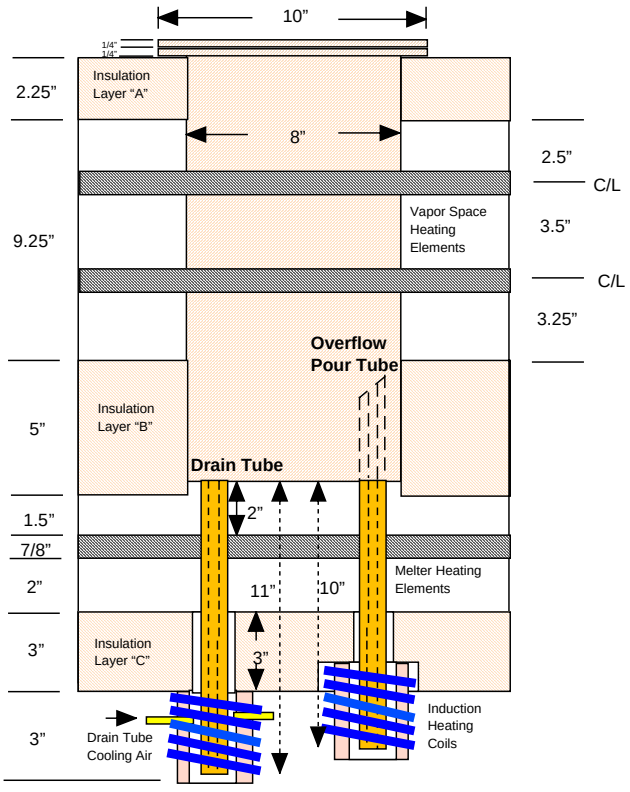

Figure 3-2. ACTL Slurry-fed Melt Rate Furnace

4.0 DISCUSSION

4.1 FEED PREPARATION (22-L GLASS SRAT/SME RUNS)

Each SRAT/SME run at ACTL began with ~16,000 grams of SB3 (Decant #5) sludge simulant (Lorier 2003). An air purge and helium purge, as appropriate, were added to the kettles at flowrates of ~3372 sccm and 16.9 sccm, respectively. Nominal amounts of sieved coal, sand, and trim chemicals – silver nitrate, gadolinium nitrate, palladium nitrate hydrate, rhodium nitrate dihydrate, and ruthenium chloride, were then added. The addition of 33 ml of antifoam (IIT 747, 10%) was also performed prior to heating the vessels to 93°C for acid addition. Once 93°C was achieved, nitric acid was first added to the vessel, followed by formic acid. Upon completion of the acid addition, the mantle temperature setpoint was increased to 110°C for boiling, and 66 ml of antifoam were added. The batch was then dewatered (concentrated to original volume), and then refluxed for 12 hours after dewatering was completed. The SRAT cycles were complete after this point, and the SME cycles were immediately begun.

At the beginning of the SME cycles, the air purge of each kettle was lowered to ~1184 sccm, the helium purge lowered to 6.0 sccm as appropriate, and 16.5 ml of antifoam were added to each kettle. The temperature was lowered to ~93°C for the first frit addition. The first frit addition was performed by adding the amounts of Frit 202, formic acid, and deionized water, specified in the run plan. The contents of the kettle were heated again to boiling for dewatering / concentration. The second frit addition proceeded in the same manner as the first. With both frit additions, the target final feed material waste loading was 35%. Upon completion of the final concentration addition, the contents of the kettle were cooled and then transferred into a carboy – all final SME products were transferred into the same carboy for batch consistency.

The pH was monitored throughout the runs. Figure 4-1 displays the measured pH for the four runs. All runs were similar in behavior. Some offset of pH is seen during the SME cycles depending on the length of time required to complete the dewatering / concentration with each frit addition. All of the SRAT and SME products had a measured pH of >7 at the elevated temperatures.

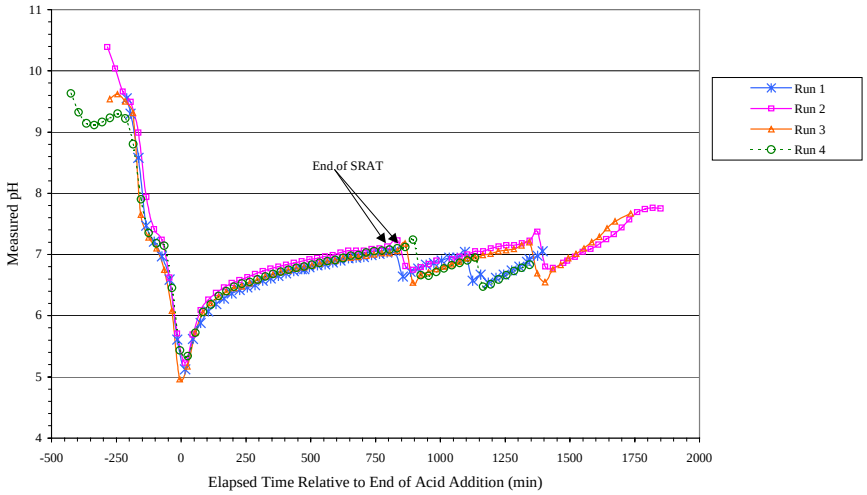

Figure 4-1. Measured pH during the SRAT/SME Runs

In two of the runs, four ~10 ml samples of the slurry were taken to track the anion concentrations. Only the first set of samples from Run #1 was analyzed. The analytical results for the in-process samples are given in Table A1 of Appendix A. Nitrite, nitrate, formate, and oxalate are reported. The in-process data shows a gradual decrease in nitrite concentration through the run, with the DWPF nitrite limit (<1000 mg/kg) obtained five hours into boiling. Oxalate concentration also showed a very small decrease through the run. Nitrate concentration slightly increased as nitrite was being destroyed, and formate concentration remained relatively the same.

Analytical samples were pulled from each kettle at the completion of each SRAT and SME cycle. Characterization included chemical constituents and physical properties. The average measured compositions of the SRAT and SME products are listed in Table 4-1. This table also gives the target SRAT and SME values. The individual run product analyses are given in Table A2 of Appendix A.

The average composition of the four SRAT products closely matched the target SRAT composition. Iron oxide and sodium oxide, which are the two largest components, least closely matched their target compositions. However, the sum of oxides for the average composition was lower than for the target, possibly indicating incomplete digestion of the insoluble components. These oxides, along with manganese oxide and silica, have consistently shown problems with meeting the target in other SB3 simulant SRAT runs with the Decant 5 composition (Herman et al. 2003a). Possible explanations rendered included the presence of sodium oxalate complicates the analyses; obtaining completely representative samples of the slurry and products is difficult; and that the presence of different particle size species like sand contributes to both of these problems. Based on the results presented in Table A1 of Appendix A, the individual product analyses showed reasonable agreement from run to run. Measured silica displayed wide variation from run to run, which can be attributed to obtaining representative amounts of the added sand.

Table 4-1. Measured Compositions of the SB3 Decant #5 SRAT and SME Products (calcined oxide basis, wt. %).

Species	Target SRAT	Average SRAT Product	Target SME	Average SME Product
Al_2O_3	16.0	16.1	5.60	4.72
B_2O_3	N/A	0.334	5.20	5.63
BaO	0.216	0.210	0.076	0.048
CaO	3.17	3.40	1.11	0.934
CuO	0.181	0.125	0.06	0.061
Fe_2O_3	35.3	32.2	12.4	9.17
K_2O	0.277	0.305	0.097	0.104
Li_2O	N/A	0.215	4.60	4.77
MgO	0.320	0.188	1.41	1.51
MnO	5.93	3.75	2.07	1.46
Na_2O	38.6	31.5	17.4	14.4
NiO	1.31	0.911	0.457	0.252
SiO_2 (total)	3.10	3.68	51.1	56.3
ZnO	0.359	0.331	0.126	0.091
ZrO_2	0.672	0.586	0.235	0.178
Sum	105.44	93.84	101.94	99.63

The average SME product composition was slightly off target for several of the primary components. The primary sludge components, Al_2O_3 and Fe_2O_3, were lower than targeted, whereas the primary frit components, B_2O_3 and SiO_2, were higher than targeted. The individual SME product analyses showed similar trends. The product from Run #4, however, was the closest to the target. This data could indicate that too much frit was added or that incorrect predictions for the SME calcined solids were made. This will be explored later in this section of the report in the calcined solids results. Based on the available data, the SME composition appears to most closely match ~32 weight percent waste loading (based on Li_2O). Although the composition was slightly different than targeted, it still provided a representative feed to meet the objectives of the SMRF testing.

The average SME product oxide weight percents from Table 4-1 were entered into a spreadsheet that uses the same equations as those in DWPF Product Compositional Control System (PCCS). The PCCS is used by DWPF to determine if a SME product will make an acceptable glass product. The average SME product (or melter feed) met the durability and homogeneity requirements. The predicted glass liquidus temperature of 940°C (new model used) and the glass viscosity (67 poise) at 1150°C were both acceptable as well.

As mentioned above, noble metals were added to the feed at the quantities anticipated in SB3. When the chemical composition analyses were performed, Pd, Rh, and Ru were measured. Both Pd and Rh were close to their targets of 0.0275 and 0.0511 weigh percent, respectively. The

measured Ru was ~10% of the anticipated value of 0.183 weight percent. Since a known amount of Ru was added to the SRAT, it is possible that the analytical technique was not completely identifying the amount of Ru present in the samples. Historically, ICP – Mass Spectrometry has been used to analyze the noble metals in radioactive slurry and products, but ICP – Atomic Emission Spectrometry was utilized for these non-radioactive runs.

The anions in the SRAT and SME products from each run were measured in duplicate. The individual analyses are provided in Table A3 of Appendix A. The average results for the SRAT and SME are given in Table 4-2.

Table 4-2. SRAT and SME Product Anion Results

Anion	SRAT Product Average (mg/kg)	SME Product Average (mg/kg)
Nitrite	479	<100
Nitrate	29750	26775
Formate	25075	23875
Oxalate	32075	32300

The anion data indicates that the SRAT product nitrite met the DWPF specification of <1000 mg/kg. By the end of the SME cycle, the nitrite was less than the detection limit. The measurable nitrite in the SRAT products was unanticipated based on the earlier Phase I runs with 10% noble metals. An investigation of the possible causes was performed. An error was found in the determination of the amount of acid to add for this set of runs. The error occurred because the initial slurry weight when scaling the acid addition was used from the Phase I runs. Samples were removed at the start of processing in the Phase I runs, but they were not removed during this set of SRAT/SME runs. Therefore, the moles of acid required per liter of slurry was under-predicted for this set of SRAT/SME runs. The difference was about 7% acid. While the specific acid amount was not repeated, this set of runs provided a more refined prediction of the minimum amount of acid that would be required to process Decant #5 with nominal noble metals to produce an acceptable SRAT product nitrite concentration.

Table 4-2 indicates that the concentration of the nitrate and formate decreased by the end of the SME cycle, while the oxalate concentration appeared to remain roughly the same or within analytical error. Based on the assumed starting composition, the known acid addition amounts, and the measured SRAT and SME product results, destruction of the anions was calculated. The individual destructions are given in Table A4 of Appendix A. In general, formate and oxalate destruction was similar for all of the SRAT runs, where formate was minimal and oxalate was around 20%. However, different destruction behavior was evident in the SME runs. Runs #1 and #4 had minimal formate destruction, whereas Runs #2 and #3 had formate destruction of around 23% during the SME. When both formate destruction percentages are considered, total destruction was around 21% for Run #2 and #3, while the other runs showed negligible destruction or formation. The largest change in oxalate percentage occurred during SME Runs #2 and #3. Negligible change was seen for the other two runs. The total oxalate destruction ranged from approximately 6 to 22% depending on the particular run. No obvious explanation for the differences was found other than the slight changes in anion concentrations from run to run.

The physical properties of the SRAT and SME products were characterized by the ITS-Mobile Lab on duplicate samples. The total and dissolved solids were measured, and then the insoluble

and soluble solids were calculated. The calcined solids were measured at 1100˚C. The average results are given in Table 4-3, while the individual run measurements are given in Table A5 of Appendix A.

Table 4-3. Average Physical Property Measurements for SRAT and SME Products

Parameter	Total Solids	Insoluble Solids	Soluble Solids	Calcined Solids	Density (g/ml)
SRAT Average	19.16%	8.94%	10.23%	11.99%	1.10
SME Average	46.27%	37.99%	8.28%	38.92%	1.31

The target SRAT total solids were 18.55%, therefore the overall average total solids were close to the target. The target SME total solids were 45%, so the overall average was slightly higher than targeted. The calcine factor based on the average SME results would be 0.84, which matches the target sludge calcine factor in the input calculations. The target SME density was 1.45 g/ml, so the density was a little less than targeted. Overall, the reported values in Table 4-3 are consistent with previous SB3 simulant runs [Herman et al. (2003) and Herman et al. (2003a)]. As shown in Table A5, slight variation in the measured properties was seen from run to run.

When the redox calculation was performed before the runs to determine the formic/nitric acid split, destruction for formate and oxalate due to processing had to be estimated. The analyzed SME product anion data was used to recalculate the predicted redox. Based on the data in Tables 4-1 through 4-3 and the redox equation given in Section 3.1, the predicted $Fe^{2+}/\Sigma Fe$ was recalculated and was determined to be 0.26. As mentioned earlier, the redox equation for SB3 has subsequently been revised. This new equation would give a predicted redox of 0.31.

The generated gases from Runs #1 and #3 were monitored using a GC. Plots of the data are given in Figures A2 and A3 of Appendix A. Typical gas behavior was seen. Peaks of carbon dioxide were generated starting during acid addition. A drop in the carbon dioxide peak was seen during change out of the acid titrator pump. Additional peaks of carbon dioxide were seen at the start of boiling in the SRAT and at the start of boiling with each frit addition in the SME. Nitrous oxide peaks occurred simultaneously with the carbon dioxide peaks at the start of boiling; however, the peak width was bigger than that seen for carbon dioxide. The peak carbon dioxide was ~29 volume percent and the peak nitrous oxide was ~1.2 volume percent. Hydrogen was not detected during the SRAT cycle or during the first frit addition cycle. Hydrogen began to be generated during the second frit boiling cycle and reached a maximum of ~0.2 volume percent or 0.067 lbs/hr on a DWPF scale for Run #1 and 0.086 lbs/hr for Run #3. Total hydrogen generation was 0.159 pounds for Run #1 and 0.306 pounds for Run #3 on a DWPF scale. Based on the hydrogen data, it is suspected that nitrite was not completely destroyed until late in the first frit concentration cycle or at the beginning of the second frit addition cycle. This hypothesis is based on previous SRAT processing experience that indicated hydrogen evolution after nitrite destruction. This could have been a consequence of under predicting the acid by about 7% as previously discussed in this section.

4.2 SMRF TESTS

4.2.1 SMRF Operational Strategy

It was intended to run the SMRF as closely as possible to previous SMRF tests perfomed in 2002 as documented by Lorier et al. (2002) in order for a "direct comparison" of melt rate and cold cap behavior to be made. These tests included Purex/Frit 200, SB2/Frit 200, and SB2/Frit 320. Smith (2003) documented the run plan for this SB3/Frit 202 test. The targeted melt pool and vapor space (plenum) temperatures were 1125°C and 750°C, respectively.

When a cycle of feed is sent to the SMRF, the vapor space temperature drops below 750°C and then recovers as the cold cap melts away and the vapor space heater calls for more power. Once the vapor space temperature recovers to 750°C and is still rising, a feed sequence is triggered by the control system. Each feed sequence trigger started the feed pump which then operated for a preset amount of time (20 seconds unless otherwise noted) at a preset speed (nominally 200 to 300 rpm). Details of the actual operation of the SMRF for this test are documented in notebook WSRC-NB-2002-00135 (starting on page 136). The SMRF was operated per SRTC procedure ITS-0076, Rev 0, *Slurry Fed Melt Rate Furnace Operating Procedure*.

The basic premise for determining melt rate in the SMRF is that the thickness and distribution of the cold cap should control the overall feed and glass production rates for any particular melter feed. In other words, the cold cap for a faster melting feed should more quickly dissipate, thereby allowing more heat from the exposed melt pool to aid in the reheating of the vapor space and therefore more frequent feed cycles. A slower melting feed should result in less frequent feed cycles. If a shorter amount of time is used for the feed pulse, then the cold cap should disappear sooner and therefore more feed cycles should then be initiated. To a degree, the system should come to some equilibrium over time as to the amount of feed delivered and the rate of glass that is melted.

However, it has been observed in past tests (Lorier et al. 2002) that slower melting feeds have resulted in several overfeeding situations in the SMRF. It is postulated that this is due to the ability of the vapor space heaters to allow the vapor space temperature to recover fairly quickly to 750°C (feed initiation temperature) even with a melt pool that is fully covered with a thick cold cap. Another observation that has been made is that the vapor space temperature at times does not go below 750°C during a feed cycle. This results in additional feed cycle(s) when the vapor space temperature begins to rise and therefore contributes to the overfeeding of the SMRF. Under this condition, the rate of glass production should give a better measure of melt rate, but over time the measured melt rate would be falsely low due to the insulation of the melt zone in the glass/cold cap contact area from heat supplied by the vapor space heaters. Therefore, inspection of the cold cap was performed throughout the SB3/Frit 202 test. It was also understood that this SMRF had not been fed in the past for the length of time planned in the test. Therefore, the chance of overfeeding was felt to be somewhat higher than the previous short term melt rate tests. It had been recognized that changes to the way the SMRF was operated may be necessary to complete this longer-term (several days) test.

4.2.2 Initial Feeding for Melter Glass Turnover

The SMRF was first charged with 1.15 kg of beaded DWPF startup glass. This is the same beaded startup glass that was charged into the DWPF Melter 2 for startup. The use of this startup

glass would therefore mimic as closely as possible what would happen in the DWPF Melter 2 startup if SB3 sludge was fed to the DWPF Melter immediately after startup. The composition of this beaded DWPF startup glass is given in Table 4-4 as determined by Corning Engineering Laboratory Services (CELS). The calculated liquidus (new model used) and viscosity of this glass are 897°C and 71 poise (at 1150°C), respectively.

Table 4-4. Beaded DWPF Startup Glass Composition

Oxide	Weight Percent*
Li_2O	5.11
Na_2O	11.1
Al_2O_3	4.18
B_2O_3	7.33
CaO	1.44
Fe_2O_3	10.7
MgO	0.70
MnO_2	3.02
NiO	0.74
SiO_2	55.0
ZrO_2	0.68
Sum	100.00

* Normalized average of two samples

After heatup on the morning of 1/28/03 for several hours to operating temperature, an additional 8.05 kg of this glass was charged to the SMRF. This would result in a glass level of about 4 inches or ½ inch above the top of the overflow pour tube (normal glass level is 3.5 inches). The pour tip induction heater was then turned on and, after some difficulty with a fault error, the pour tip heater was energized. Glass flow through the pour tip did not occur for several hours even after several power increases to the pour tip (up to 145V). Therefore, the glass pool setpoint was increased from 1125°C to 1150°C to help the pouring problem. At 1525 on 1/28/03 the first reasonable pour stream was observed. The glass temperature was maintained at 1150°C in order to achieve one melter turnover of glass (8 kg) to the SMRF on day 1 before actual melt rate tests were to be conducted.

During feeding, the vapor space/glass pool heater power ratio remained fairly constant at approximately 2.4. The cold cap was periodically observed and there was always some exposed melt pool glass between the SMRF wall and the cold cap or this portion of the cold cap had vent holes. Changing the feed pump speed from 250 to 300 rpm did not result in an overall higher feed rate as the number of feed pulses was reduced to compensate for the higher amount of feed delivered per feed pulse. At 1920 the cold cap was inspected and a ¼ inch wide ring of glass with some bubbles at the SMRF wall still remained. At 2100 on 1/28/03 the cold cap was inspected just after feeding was stopped for the evening. The cold cap was very dark and no vent holes were observed. The feed rate had dropped in the final half-hour but the rate was still about 32 g/min (feed rate until this time had been about 47 g/min). The cold cap was fairly thick (~ ½" thick) and somewhat hard. This overfeeding, as discussed previously, had occurred in some previous SMRF runs. An inspection of the cold cap about 30 minutes later showed that the cold cap was being melted. This would indicate that the cold cap did not have an insulating layer like that

observed in the SMRF during the feeding of SB2/Frit 200 (25% WL) material that resulted in an interface layer being present in the SMRF three days after slurry feeding had been stopped. This interface layer may have negatively impacted melt rate for SB2/Frit 200 feed in these previous SMRF tests. At this time, the amount of glass poured was 7.65 kg. After subtracting the extra 1.2 kg of DWPF startup glass charged to the SMRF, the amount of glass poured due to feeding was then 6.45 kg (average pour rate 20.5 g/min). The total amount of feed that had been fed to the SMRF was 16,687 g (average feed rate 53 g/min). This would be the equivalent of 6.68 kg of glass, which agreed quite well with the amount of glass actually poured due to feeding.

4.2.3 Feeding at "Standard" SMRF Operating Conditions

The main purpose of the first day's SMRF feeding was to try and achieve close to one SMRF glass turnover before beginning the actual melting tests and so a glass pool temperature of 1150°C was used. Before the restart of feeding on 1/29/03, the glass pool was reduced to 1125°C. In addition, the insulation around the pour tip was replaced to help in glass pouring. An inspection of the melt pool showed no signs of an interface layer or unmelted cold cap from the previous day's feeding. At 0836 feeding was restarted with a pulse time of 20 seconds, a feed pump speed of 300 rpm, and the vapor space temperature and feed initiation setpoints both at 750°C. These setpoints were the same as used in previous SMRF tests (338 rpm for the feed pump speed had been used before). At 0855 the cold cap appeared to be normal. At 0940 the cold cap was getting darker (indicating a thick cold cap) and at 1015 feeding was stopped due to overfeeding of the SMRF. Figure 4-2 shows the cumulative amounts of feed delivered to the SMRF and the amount of glass poured.

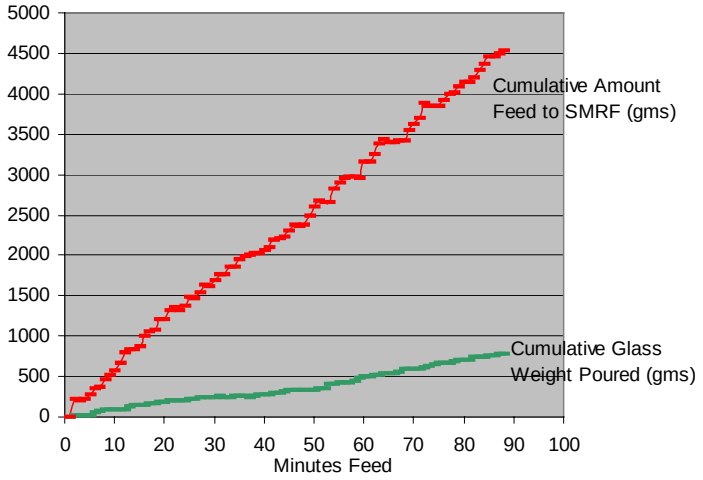

Figure 4-2. Cumulative SB3/Frit 202 Feed Fed and Glass Poured – 1/29/03 AM Run

The overall feed rate was 51.5 g/min or 20.6 g/min of equivalent glass over this time frame. The overall pour rate was 9.0 g/min but there are two distinct slopes in the cumulative weight plot. The first portion of the plot up to approximately 50 minutes has a pour rate of 7.7 g/min while the second half of the plot shows a pour rate of 11.1 g/min. At this time, the total amount of glass poured from the SMRF was 7.2 kg (very close to one melter turnover). Due to overfeeding and the short period of time, it was difficult to determine an actual melt rate for this feeding period.

The assumption was made that the overall pour rate (and therefore melt rate) was 9.0 g/min. This is fairly close to the SMRF melt rate for SB2/Frit 200 of 9.6 g/min per the 8/7/02 test (Lorier et

al. 2002) which resulted in overfeeding of the SMRF as well. The melt rate for SB2/Frit 320 (25% WL) tested on the SMRF was about 13.7 g/min (Lorier et al. 2002). It should be noted that all attempts to feed the SB3/Frit 202 while running the SMRF in standard conditions resulted in overfeeding, including a subsequent test on the same day (1/29/03) that resulted in overfeeding after only 30 minutes. Therefore the results of this portion of the test are the best available data for comparing SB3 (Decant #5)/Frit 202 with other feeds previously tested in the ACTL SMRF. It appears that this feed has a melt rate slightly lower than SB2/Frit 200 (25% waste loading) feed. However, waste throughput, not melt rate, is the key to faster treatment of the SRS HLW. The "simulated waste" throughput for the SB3/Frit 202 at 35% WL is somewhat less than 2.8 g/min (assuming melt rate of 9.0 g/min). The waste throughput for SB2/Frit 320 at 25% WL is 3.4 g/min (based on 7/30/02 SMRF test). For SB2/Frit 200, the waste throughput is somewhat less than 2.4 g/min (based on 8/7/02 SMRF test). These melt rates and waste throughput values are summarized in Table 4-5.

Table 4-5. Comparison of SMRF Melt Rates/Waste Throughputs for Various Simulated Feeds

Run Date	Feed Type (Sludge/Frit)	Waste Loading	Glass Pour Rate (g/min)	Waste Throughput (g/min)
1/29/03	*SB3/Frit 202	32%	9.0	2.8
7/30/02	*SB2/Frit 200	25%	9.6	2.4
8/07/02	SB2/Frit 320	25%	13.7	3.4

* SMRF overfed during test

4.2.4 Feeding with Clamped Vapor Space Output

At this time, it was decided that long-term feeding of the SMRF with this material could not be attained with the existing feeding strategy. It was determined that the amount of power that the vapor space heaters could deliver was too high. The recovery of the vapor space was being achieved to a great degree by the vapor space heaters and not the melting of the cold cap. In an ideal SMRF test, the additional heat supplied by the exposure of the glass pool to the vapor space as the cold cap is melted away should control how much feed is delivered (rate of feed pulses). Unfortunately for relatively slower melting feeds, the vapor space can quickly recover to the feed initiation temperature even with full cold cap coverage.

As the purpose of this test was to develop a workable flowsheet (in other words from a glass melting perspective no major foaming, no interface layer, no biscuit formation, acceptable glass, etc), a limit on the vapor space heater output of 75% (was 100%) was programmed in the vapor space controller. This was done to try and limit the ability of the vapor space temperature to recover after feed pulses and therefore allow the amount of the exposed glass pool to have a greater impact on the overall feed rate (and hopefully melt rate). In addition, the glass pool temperature was increased to 1150°C (the normal upper glass pool temperature of the DWPF Melter) to allow better uninterrupted feeding of the SMRF. None of the testing perfomed after these changes can be used to compare melt rates to previous SMRF runs, but the work can be used to determine if long term feeding can be achieved without incident as well as glass redox and noble metals deposition information.

After this change, the SMRF poured glass at an average of 12.1g/min for 13 hours of continuous feeding from 1800 1/29/03 to 0700 1/30/03. In retrospect, it may have been better to not increase

the glass temperature from 1125°C to 1150°C so that a better comparison of melt rate to previous tests could have been made since the only difference would have been the clamped vapor space controller output.

Because it appeared that the SMRF was actually being underfed, the vapor space output limit was increased to 87% at 0700 on 1/30/03 and the SMRF was fed for another three hours until the feed supply was exhausted. The glass pour rate was 15.2g/min for this time. No problems with the appearance of the cold cap were observed throughout this feeding period of 16 hours with a clamped vapor space output. The next morning the melt pool was inspected and there was no sign of an interface layer.

A total of 23.85 kwh and 23.57 kwh were used respectively by the vapor space and glass pool heaters during the 13 hour 75% clamping test. This resulted in a vapor space/glass pool heater power ratio of about 1.8. This ratio is much lower than the ratio of about 2.4 observed when feeding SB3/Frit 202 feed to the SMRF without this output clamp. This indicates that the melt pool then had a greater impact on the recovery of the vapor space temperature back to the feed initiation setpoint, thereby preventing overfeeding of the SMRF. For future long term SMRF tests, the clamping of the vapor space power output should be considered.

4.2.5 SMRF Glass Turnover

Pour samples were taken at various times during slurry feeding. By looking at the weight percent of various oxides in these samples, a good estimate of how much glass was poured before the glass in the SMRF had changed from the DWPF startup glass composition to that of the SB3/Frit 202 material being fed to the SMRF can be made. This information could be used in future SMRF tests when the startup frit is not the same composition as the feed being tested. One SMRF glass turnover is 8 kg. Gd_2O_3 would have been a good choice because it is not in the DWPF startup glass. Due to analytical problems, however, the analytical results for Gd_2O_3 in the SMRF glass samples were almost one order of magnitude greater than what should have been in the feed. Therefore K_2O and Na_2O were chosen because they are not in the DWPF startup glass. Table 4-6 summarizes the results and indicates that at least by 1.21 melter turnovers the composition of the glass in the SMRF had been changed from that of the DWPF startup glass to that of the SB3/Frit 202 material being fed to the melter. The amounts of total glass produced shown in Table 4-6 are all reduced by 1.2 kg from the actual total glass poured at the time when glass samples were taken. This was done to compensate for charging the SMRF with 9.2 kg of DWPF startup glass versus 8 kg.

Table 4-6. SMRF Glass Composition for K_2O and Na_2O at Various Melter Turnovers

Glass Produced (kg)	SMRF Glass Turnovers	*Weight % K_2O	*Weight % Na_2O
6.2	0.65	0.017	11.9
10.7	1.21	0.381	14.0
13.3	1.54	0.373	14.4
16.9	1.99	0.396	14.4
22.1	2.63	0.368	14.5

*Note: Average weight %'s of K_2O and Na_2O in SB3/Frit 202 Feed were 0.371 and 14.35 respectively (feed samples SB3/202-08 feed and SB3/202-12 feed).

4.2.6 Glass Redox

The targeted redox for the feed produced using a revised acid addition strategy was 0.2 ($Fe^{2+}/\sum Fe$). Redox values for glass pour samples taken during the run are summarized in Table 4-7. The values cited are the average of two values determined for each sample. The glass changed from a fairly oxidized glass (0.12) at 0.65 turnovers (basically the DWPF startup glass) to a more reduced glass (0.26) at the end of the run (2.63 turnovers).

Table 4-7. Glass Redox Values for SMRF Glass Samples at Various Melter Turnovers

SMRF Glass Turnovers	Redox – $Fe^{2+}/\sum Fe$
0.65	0.12
1.21	0.14
1.54	0.12
1.99	0.18
2.63	0.26

Redox measurements were also taken on the glass drain samples and the values range from 0.22 to 0.25. These numbers agree quite well with the redox of the final glass poured during day 1 at 2.63 melter turnovers (see Table 4-7). Therefore the "final" redox for the SB3/Frit 202 glass is in the range 0.22 to 0.26 and is fairly close to the targeted redox of 0.2. A revised redox model that was completed after the run was used to predict the redox from the analyzed feed composition and a value of 0.31 was obtained. A discussion of the differences of these two redox models is not in the scope of this task and will therefore be given in a future report.

4.2.7 SMRF Draining

On 1/30 the SMRF was drained via the induction heated drain tube. A total of 6.9 kg of glass was drained. Glass drain samples were taken at the start of the drain and at every one kg of glass drained. The main purpose of these glass samples was to determine if noble metals in the feed had settled to the bottom of the SMRF during feeding. A highly reduced feed would possibly result in more of the noble metals settling as they could be reduced to their denser metallic forms. Table 4-8 gives the weight percents of the noble metals in the glass from the start of draining up to 3 kg of glass drained.

Table 4-8. Weight Percents of Noble Metals at Various Amounts of SMRF Glass Drained

Glass Drained (kg)	Wt % PdO	Wt % RhO_2	Wt % RuO_2
0	0.015	0.017	0.017
1	0.008	0.019	0.016
2	0.007	0.020	0.020
3	0.007	0.019	0.016

NOTE: Weight %'s of PdO, RhO_2, and RuO_2 in SB3/Frit 202 feed were 0.005, 0.023, and 0.013 respectively.

The weight percents show that neither ruthenium nor rhodium settled to the bottom of the SMRF in this run. The weight percent palladium in the glass at the start of drain is higher than the amount of palladium in the feed (0.015 versus 0.005), but the absolute amounts are so small that it would be difficult to say whether or not palladium has indeed settled. In addition, previous work by Bickford and Smith (1997) showed that the percents of ruthenium and rhodium retained in the pilot scale Integrated DWPF Melter System (IDMS) Melter were much higher (35.1 and 21.2 percent respectively) than palladium (less than 1 percent). Therefore it can be concluded that there was no detectable settling of palladium as well in the SMRF. This data, however, only proves that there was no evidence of noble metals settling in this short (several days) test. It cannot be used to conclude that the settling of noble metals will not be a problem during long term feeding of the DWPF Melter with SB3 material. If, however, noble metals had been found to settle to the bottom of the SMRF in this short test, it would have raised a major concern for the processing of this SB3/Frit 202 feed. Longer term testing on a more prototypic melter would be needed to determine whether the settling of noble metals would be a problem for SB3 with the more reduced feed.

4.2.8 Glass Composition/Durability

As discussed before, glass pour samples were taken throughout the test. The oxide weight percents for the samples, along with two feed samples, are given in Appendix B. The targeted SME oxide weight percents were previously given in Table 4-1. With regards to the major constituents, SiO_2 was high (measured about 56% versus a target of 51%) while Na_2O and Fe_2O_3 were both low by about 3 weight percent.

Some of the glass samples were subjected to the Product Consistency Test (PCT) to determine chemical durability of the glass. PCT was performed on the glass samples using technical procedure "Nuclear Waste Glass Product Consistency Test (PCT) Method – GTOP-3-025" (ASTM 2002). The PCT was conducted in triplicate for each SB3/Frit 202 glass. Also included in this matrix were the Environmental Assessment (EA) glass and the Approved Reference Material (ARM-1) glass. Leach rates for the standard EA glass and the SB3/Frit 202 samples are reported in g element leached/L of leachant and are summarized in Table 4-9. The resultant leach rates for B, Li, Na, and Si are all approximately one order of magnitude less than the EA glass analyzed at the same time and therefore indicate that all of the glass analyzed was much more durable than the EA glass.

Table 4-9. PCT Release Rates (g element/L leachant) for SMRF SB3/Frit 202 Glass Samples

Sample ID	B	Li	Na	Si
EA	15.91 (16.7)*	8.68 (9.6)*	11.80 (13.3)*	3.74 (3.9)*
SB3-202-04	1.04	1.04	1.02	0.62
SB3-202-07	1.02	1.02	0.80	0.61
SB3-202-11	1.10	1.09	1.09	0.66
SB3-202-14	1.15	1.11	1.10	0.66
SB3-202-16	1.28	1.20	1.25	0.71

*NOTE: Values in ( )'s are the averages of 42 replicate EA glass durability analyses as reported in WSRC-TR-92-346. These are considered baseline EA glass release rates for B, Li, Na, and Si.

5.0 CONCLUSIONS/SUMMARY

A "workable flowsheet" for a nominal SB3 (Decant #5)/Frit 202 has been demonstrated on a small-scale basis for the DWPF feed preparation and vitrification processes. This workable flowsheet includes an acid addition strategy for the feed processing steps at DWPF in the DWPF Chemical Process Cell. Frit 202, a candidate frit per previous SB3 frit development work, was chosen in part due to its availability for the timing of this work. The targeted WL for this run was 35% (32% was the actual calculated WL from the final SME product) to try and ensure that the glass produced was within the Property Acceptability Region (PAR) limits of the DWPF Product Composition Control System (PCCS). This test was the first that treated SB3 simulant material via a small scale SRAT/SME and then vitrified the resultant material via slurry feeding in a small-scale melter (SMRF). The results of the test did not indicate any major processing issues associated with the SRAT/SME. Nitrite was destroyed to below the DWPF specification and hydrogen generation was below the SRAT and SME process limits. The SMRF (melter) portion of the test was successful as well (with regards to cold cap behavior, waste throughput, glass quality) for this particular material.

An acid addition strategy with a modified (preliminary) correlation to predict glass redox was successfully used in the small scale SRAT/SME for this test. The correlation was revised to account for various new components in the waste such as coal and sodium oxalate. Both the acid and redox correlations used for these runs were preliminary and revised to account for the coal and sodium oxalate that could potentially be in SB3.

During the SMRF testing, there was no evidence that the slightly reduced glass caused settling of noble metals to the bottom of the glass pool. However, due to the short length of this test and the configuration of the SMRF, one cannot conclude that this will not be a problem in the DWPF Melter.

Melt rate as defined by SMRF pour rate was somewhat lower for this feed than for SB2/Frit 200 and SB2/Frit 320 (both previously tested in the SMRF at 25% WL). However, the overall waste throughput (2.8 g/min at 32% WL) was less than SB2/Frit 320 (3.4 g/min) but greater than SB2/Frit 200 (2.4 g/min). Overall waste throughput in the DWPF Melter, not melt rate, will help determine the success of SRS's accelerated cleanup efforts for HLW. Further development is needed to optimize the process with regards to melt rate, waste loading, and most importantly waste throughput. This development includes the slurry feed testing of other frits that have been documented elsewhere to possibly enhance the waste throughput of SB3 in the DWPF. This work may be required after a more definite SB3 composition is obtained. There are still some uncertainties around the amount of coal and sodium oxalate in SB3. Additional work may be required on acid addition, redox, and frit selection, among others. This will be determined at a later date.

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APPENDIX A

SRAT/SME Processing

List of Assumptions for SRAT/SME Calculations : The following list of assumptions were made or used when performing the acid addition calculations for the SRAT/SME runs. The assumptions used to prepare the sludge for the runs are also included. In most cases, previous runs with the Decant 5 composition were factored into the assumptions. The term "Melt Rate" refers to the 22-L SRAT runs performed to prepare Decant 5 feed for the melt rate testing, while the term "Phase I" refers to the 4-L Phase 1 simulant flowsheet run with the Decant 5 composition.

1. Measured total solids for the CETL starting sludge – 17.51%
2. Sludge composition was similar to the "Phase 1" composition based on the measured equivalent total solids.
3. After addition of sodium and potassium compounds, total and insoluble solids were similar to "Melt Rate" measurements – 18.6% and 14.4%, respectively
4. Initial batch size was 16 kg before trimming for noble metals, sand, coal, and Gd.
5. Density equivalent to "Phase I" - 1.15 g/ml
6. Initial nitrite equivalent to "Melt Rate" measurement – 9150 mg/kg
7. Initial nitrate equivalent to " Melt Rate" measurement – 2460 mg/kg
8. Initial Mn equivalent to "Melt Rate" calcined solids analyses – 2.82 wt%
9. Total inorganic carbon equivalent to "Melt Rate" measurement on trimmed sludge – 920 ug/ml or 800 mg/kg
10. Base equivalents from "Phase I" SRAT receipt analyses – 0.380 eq/L (actual measurement on non-trimmed feed for this run was 0.374 eq/L)
11. Initial oxalate equivalent to "Melt Rate" measurement – 51600 mg/kg
12. Supernate density equivalent to a measurement made for the scoping SB3 Run SB3-20 (75% sodium oxalate with 10% noble metals) - 1.07 mg/l
13. Mn in supernate based on "Phase I" measurement – 0 mg/L
14. Coal and sand targets are based on dilution of dried sludge solids with sodium oxalate from "Phase I" calculation – 0.485 and 0.757 wt%, respectively
15. Noble metals and Gd based on nominal amounts anticipated for SB3 in the dried solids -

Ag	0.00054 wt%	Gd	0.037 wt%	Pd	0.0276 wt%
Rh	0.0511 wt%	Ru	0.1830 wt%		

16. Rinse water would be added in an equivalent amount to "Phase I" to ensure thorough rinsing of all containers used for weighing trim chemicals and sludge – 250.45 g
17. Post trim mass of slurry – 16.34 kg
18. Target nitrite destruction - 100%
19. Destruction of formate based on actual destruction from "Phase I" and the effect of noble metals and the SME process were based on scoping SB3 Runs SB3-20 and SB3-21 (75% sodium oxalate at 10% and nominal noble metals, respectively) – 37%
20. Oxalate destruction used similar methodology to formate destruction assumption – 21.7%
21. Total acid amount calculated from "Phase I" starting feed of 2.998 kg (2.607 L) and actual acid of 2.914 moles - 1.118 moles/L or 15.555 moles total acid
22. DWPF existing acid addition equation used with an added term for oxalate (coefficient of 0.5) to calculate acid and then percent of stoichiometry was adjusted to match target total acid – 97.1%
23. Ratio of formic to nitric acid – 0.568
24. DWPF SRAT Scale Factor – 1571
25. SME density target - 1.45 g/ml
26. Calcine factor for the sludge to the SME equivalent to scoping SB3 Run SB3-21 – 0.84
27. Frit slurry weight percent solids - 45wt%
28. Frit slurry formic acid ratio - 1.5 g formic/100 g frit
29. SME solids target total weight percent - 45%

Table A1. SRAT In Process Slurry Sample Anion Results (mg/kg)

Sample ID	Sample Time (min)*	Nitrite	Nitrate	Formate	Oxalate
-0	21	1617	27137	26594	37666
-2	115	1151	29758	27477	33016
-5	295	952	30270	27124	29728
-8	475	828	29866	26378	28776

*Relative to End of Acid Addition

Table A2. SRAT and SME Product Calcined Oxide Compositions

Oxide	SRAT Run #1	SME Run #1	SRAT Run #2	SME Run #2	SRAT Run #3	SME Run #3	SRAT Run #4	SME Run #4
Al_2O_3	16.4	4.43	16.9	4.63	15.3	4.59	15.6	5.23
B_2O_3	0.324	5.76	0.180	5.67	0.468	5.72	0.366	5.37
BaO	0.211	0.045	0.214	0.046	0.207	0.045	0.209	0.057
CaO	3.42	0.863	3.41	0.925	3.36	0.881	3.42	1.06
CuO	0.121	0.056	0.109	0.052	0.145	0.059	0.127	0.076
Fe_2O_3	33.18	8.66	32.68	8.89	31.60	8.78	31.46	10.4
Gd_2O_3	0.064	0.015	0.063	0.016	0.061	0.016	0.059	0.019
K_2O	0.281	0.096	0.301	0.100	0.333	0.102	0.303	0.117
Li_2O	0.109	4.85	0.110	4.81	0.358	4.88	0.282	4.56
MgO	0.170	1.57	0.164	1.51	0.222	1.53	0.198	1.44
MnO	4.01	1.74	4.18	1.48	3.57	1.48	3.25	1.15
Na_2O	31.4	14.2	31.0	14.4	30.6	13.6	32.9	15.5
NiO	0.956	0.242	0.912	0.241	0.898	0.239	0.879	0.286
SiO_2	2.50	57.4	2.44	56.7	5.02	57.5	4.75	53.6
ZnO	0.322	0.095	0.329	0.086	0.350	0.089	0.322	0.096
ZrO_2	0.588	0.177	0.596	0.168	0.575	0.163	0.584	0.203
Sum	94.04	100.13	93.56	99.72	93.13	99.60	94.73	99.15

Table A3. SRAT and SME Product Anion Results (mg/kg)

Sample ID	Nitrite	Nitrate	Formate	Oxalate
SRAT Run #1	466	30400	25700	32200
SRAT Run #2	436	30600	26000	31800
SRAT Run #3	462	30000	25000	31500
SRAT Run #4	551	28000	23600	32800
SME Run #1	<100	27100	25700	32000
SME Run #2	<100	25700	21000	34100
SME Run #3	<100	25400	21000	33100
SME Run #4	<100	28900	27800	30000

Table A4. Calculated Formate and Oxalate Destructions

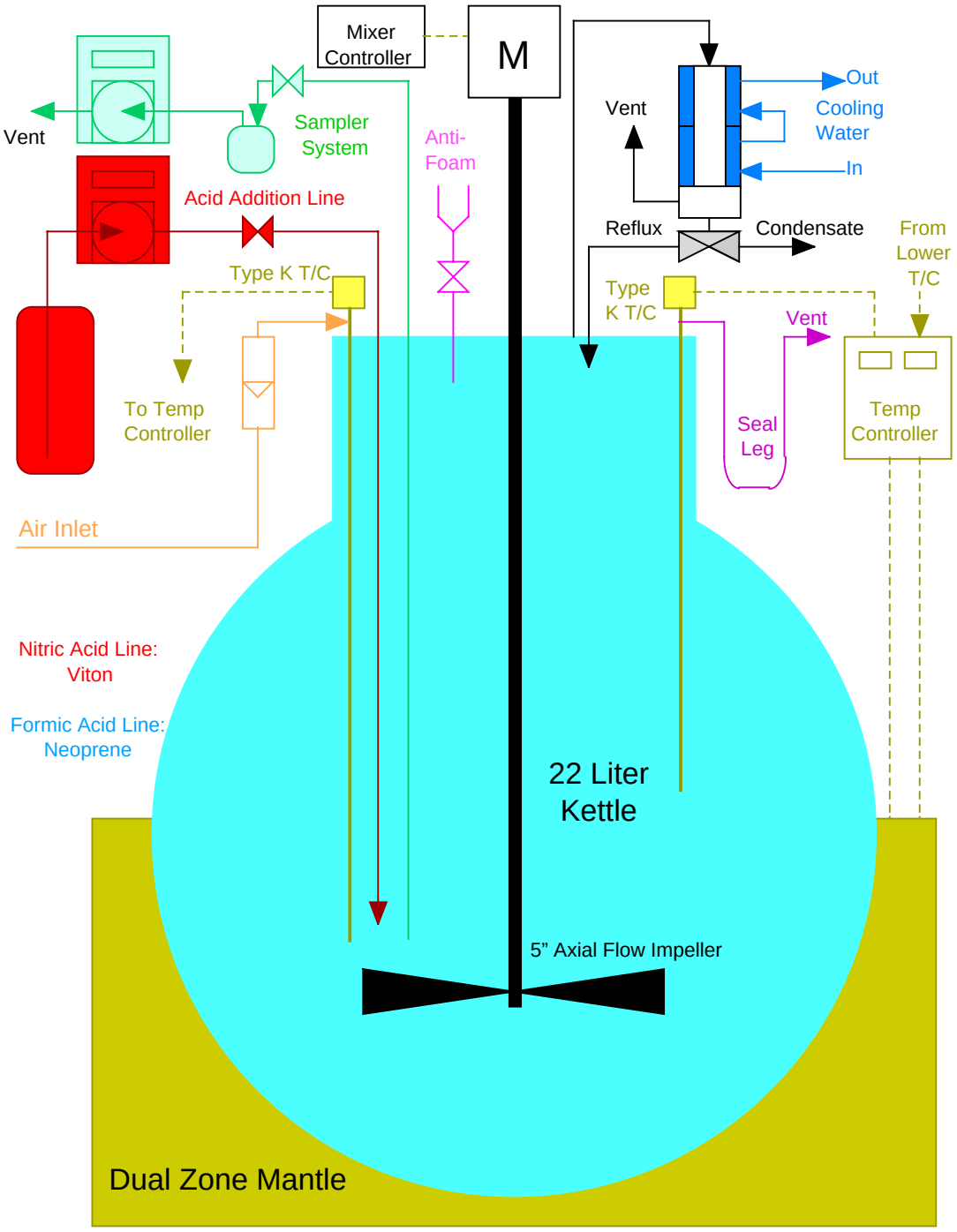
Parameter	Run #1^	**Run #2^**	Run #3^	Run #4^
Formate Added in SRAT (g)	397.6	397.6	397.6	397.6
SRAT Product Formate Mass (g)	408.4	413.7	397.2	370.2
Formate Removed in Samples (g)	1.15	0	1.15[#]	0
% Formate Destruction in SRAT	**-3.01%**	**-4.19%**	**-0.19%**	**6.88%**
Additional Formate Added (g)	62.33	63.04	63.04	63.04
Formate Removed with SME Samples (g)*	5.49	3.12	2.44	2.66
SME Product Formate Mass (g)	426.8	356.5	356.4	465.8
% Formate Destruction in SME	**8.26%**	**24.7%**	**22.2%**	**-8.16%**
% Total Formate Destruction	**5.25%**	**20.5%**	**22.0%**	**-1.28%**
Oxalate Added (g)	642.7	642.7	642.7	642.7
SRAT Product Oxalate Mass (g)	511.6	506.0	500.5	514.6
Oxalate Removed in Samples (g)	1.38	0	1.38[#]	0
% Oxalate Destruction in SRAT	**20.2%**	**21.3%**	**22.0%**	**19.9%**
Oxalate Removed with SME Samples (g)*	6.87	3.81	3.08	3.70
SME Product Oxalate Mass (g)	531.4	578.9	561.7	502.6
% Oxalate Destruction in SME	**-5.28%**	**-15.3%**	**-12.9%**	**1.62%**
% Total Oxalate Destruction	**15.0%**	**6.00%**	**9.04%**	**21.6%**

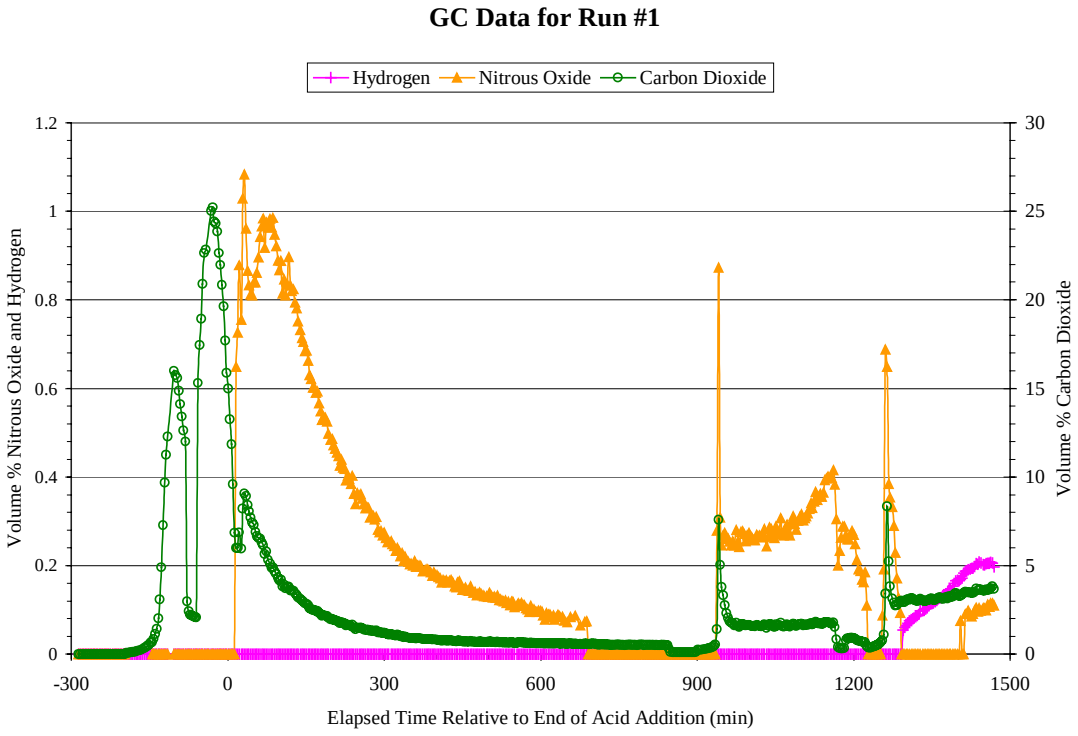
^ The SRAT product masses were not recorded during processing; therefore, final masses were estimated based on the input amounts.
*Total includes the formate or oxalate removed with the SRAT product sample.
[#]Samples were not analyzed so equivalent removal to Run #1 was assumed.

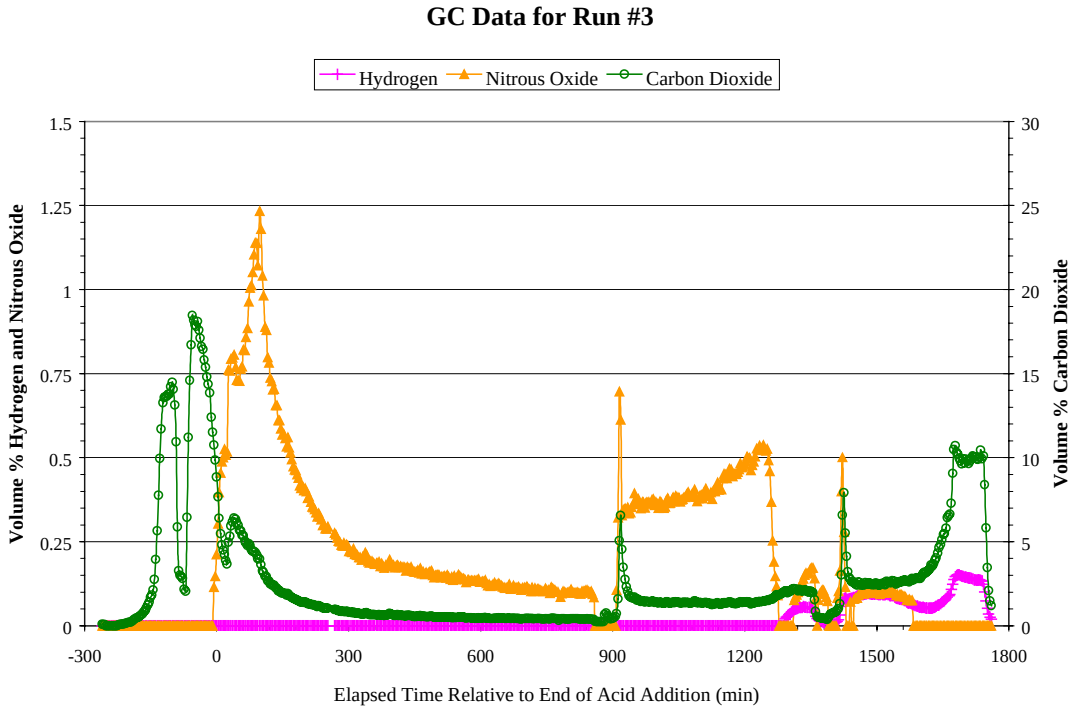
Table A5. Physical Property Data of the SRAT and SME Products

Sample ID	Total Solids	Insoluble Solids	Soluble Solids	Calcined Solids	Density (mg/l)	pH
SRAT Run #1	19.05%	8.67%	10.38%	11.92%	1.08	8.07
SRAT Run #2	19.14%	8.76%	10.39%	11.76%	1.13	8.01
SRAT Run #3	19.27%	9.31%	9.96%	12.19%	1.09	8.05
SRAT Run #4	19.20%	9.01%	10.18%	12.08%	1.09	7.98
SME Run #1	47.5%	39.0%	8.54%	39.97%	1.37	7.68
SME Run #2	47.1%	39.5%	7.69%	39.79%	1.22	8.33
SME Run #3	46.6%	38.8%	7.79%	39.56%	1.31	8.32
SME Run #4	43.8%	34.7%	9.11%	36.4%	1.33	7.44

Figure A1. 22L Glass SRAT/SME Vessel







Figures A2 and A3. GC Plots for Runs 1 and 3

APPENDIX B

Glass and Feed Samples – Analytical Composition Results

Table B1. Glass and Feed Samples – Analytical Composition Results

Oxide wt%	Al_2O_3	B_2O_3	BaO	CaO	Cr_2O_3	CuO	Fe_2O_3	Gd_2O_3	K_2O	Li_2O	MgO	MnO	Na_2O	NiO	PdO	RhO_2	RuO_2	SiO_2	TiO_2	ZnO	ZrO_2
SB3/202-01	4.27	6.75	0.006	1.40	0.093	0.011	10.7	0.019	0.017	4.69	0.945	2.35	11.9	0.691	0.011	0.008	0.013	54.1	0.009	0.000	0.284
SB3/202-06	4.77	5.52	0.043	1.06	0.195	0.039	9.48	0.066	0.381	4.69	1.43	1.72	14.0	0.382	0.007	0.023	0.023	54.7	0.022	0.047	0.116
SB3/202-09	4.78	5.30	0.047	1.03	0.194	0.042	9.19	0.073	0.373	4.64	1.50	1.73	14.4	0.373	0.018	0.025	0.021	53.4	0.023	0.056	0.107
SB3/202-13	4.81	5.37	0.047	1.01	0.174	0.043	9.28	0.075	0.396	4.71	1.50	1.63	14.4	0.328	0.005	0.019	0.017	56.0	0.023	0.055	0.091
SB3/202-16	4.69	5.19	0.051	0.940	0.208	0.041	9.07	0.079	0.368	4.65	1.61	1.72	14.5	0.331	0.008	0.018	0.016	56.8	0.025	0.061	0.087
SB3/202-17	4.64	5.38	0.049	0.903	0.220	0.054	9.21	0.075	0.359	4.76	1.62	1.67	13.6	0.334	0.015	0.017	0.017	57.6	0.026	0.056	0.082
SB3/202-18	4.68	5.32	0.049	0.917	0.199	0.045	8.91	0.076	0.385	4.79	1.61	1.65	14.2	0.321	0.008	0.019	0.016	56.4	0.025	0.057	0.079
SB3/202-19	4.73	5.40	0.047	0.933	0.182	0.045	9.11	0.074	0.433	4.83	1.55	1.58	14.2	0.298	0.007	0.020	0.020	58.0	0.023	0.055	0.076
SB3/202-20	4.78	5.47	0.052	0.912	0.195	0.043	9.17	0.077	0.393	4.84	1.71	1.72	13.9	0.336	0.007	0.019	0.016	57.4	0.026	0.062	0.083
SB3/202-08 feed	4.82	5.16	0.052	0.966	0.157	0.049	9.49	0.081	0.392	4.73	1.56	1.62	14.6	0.302	0.002	0.020	0.027	55.1	0.024	0.062	0.081
SB3/202-12 feed	4.43	5.26	0.046	0.846	0.145	0.047	8.26	0.072	0.350	4.77	1.62	1.61	14.1	0.282	0.002	0.015	0.025	58.5	0.024	0.056	0.073

NOTE: Samples 01 through 16 are from glass pouring. Samples 17 through 20 are from glass draining. Samples 08 and 12 are feed samples.