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Rheology

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RHEOLOGICAL AND ELEMENTAL ANALYSES OF SIMULANT SB5 SLURRY MIX EVAPORATOR-MELTER FEED TANK SLURRIES

A. I. Fernandez

FEBRUARY 2010

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under
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DISCLAIMER

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LIST OF ACRONYMS

ACTL	Aiken County Technology Laboratory
DWPF	Defense Waste Processing Facility
HIP	High pH (pH ~ 10)
LOP	Low pH (pH ~ 7.5)
MFT	Melter Feed Tank
PSAL	Process Science Analytical Laboratory
SB5	Sludge Batch 5
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TTR	Technical Task Request
XRD	X-ray Diffraction

1.0 EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) will complete Sludge Batch 5 (SB5) processing in fiscal year 2010. DWPF has experienced multiple feed stoppages for the SB5 Melter Feed Tank (MFT) due to clogs. Melter throughput is decreased not only due to the feed stoppage, but also because dilution of the feed by addition of prime water (about 60 gallons), which is required to restart the MFT pump. SB5 conditions are different from previous batches in one respect: pH of the Slurry Mix Evaporator (SME) product (9 for SB5 vs. 7 for SB4). Since a higher pH could cause gel formation, due in part to greater leaching from the glass frit into the supernate, SRNL studies were undertaken to check this hypothesis.

The clogging issue is addressed by this simulant work, requested via a technical task request from DWPF. The experiments were conducted at Aiken County Technology Laboratory (ACTL) wherein a non-radioactive simulant consisting of SB5 Sludge Receipt and Adjustment Tank (SRAT) product simulant and frit was subjected to a 30 hour SME cycle at two different pH levels, 7.5 and 10; the boiling was completed over a period of six days. Rheology and supernate elemental composition measurements were conducted.

The caustic run exhibited foaming once, after 30 minutes of boiling. It was expected that caustic boiling would exhibit a greater leaching rate, which could cause formation of sodium aluminosilicate and would allow gel formation to increase the thickness of the simulant. X-ray Diffraction (XRD) measurements of the simulant did not detect crystalline sodium aluminosilicate, a possible gel formation species. Instead, it was observed that caustic conditions, but not necessarily boiling time, induced greater thickness, but lowered the leach rate. Leaching consists of the formation of metal hydroxides from the oxides, formation of boric acid from the boron oxide, and dissolution of SiO_2, the major frit component. It is likely that the observed precipitation of $Mg(OH)_2$ and $Mn(OH)_2$ caused the increase in yield stress. The low pH run exhibited as much as an order of magnitude greater B and Li (frit components) leachate concentrations in the supernate. At high pH a decrease of B leaching was found and this was attributed to adsorption onto $Mg(OH)_2$. A second leaching experiment was performed without any sludge to deconvolute the leach rate behavior of Frit 418 from those of the SB5 sludge-Frit 418 system. At high pH, the sludgeless system demonstrated very fast leaching of all the frit components, primarily due to fast dissolution of the main component, silica, by hydroxide anion; various semiconductor studies have established this reactivity. Overall, the frit-water system exhibited greater leaching from a factor two to almost three orders of magnitude (varying by conditions and species). The slower leaching of the sludge system is possibly due to a greater ionic strength or smaller driving force. Another possible reason is a physical effect, coating of the frit particles with sludge; this would increase the mass transfer resistance to leaching.

Based on this study, the cause of clogs in the melter feed loop is still unknown. A possible explanation is that the SME product, like the simulant, is too thin and could contribute to a loss of two-phase flow which could cause plugging of a restricted and poorly mixed zone like the melter feed loop. This is feasible since a previous study of a slurry showed an increase in resistance to flow at lower flow rates. Testing with a radioactive SME sample is underway and should help understand this potential mechanism.

2.0 INTRODUCTION

The Defense Waste Processing Facility (DWPF) will complete Sludge Batch 5 (SB5) processing in fiscal year 2010. Recently, DWPF has noted a loss of feed to the melter feed loop due to clogs, which in turn has resulted in multiple feed stoppages to the melter. Moreover, addition of prime water (about 60 gallons) is required to restart the melter feed pump and further dilutes the feed. The stoppages and the remedial measures both cause a decrease in overall melter throughput.

In order to discover the cause of this problem, a review of available data was performed by DWPF Engineering and potential trends were examined. One difference noted was the SB5 Slurry Mix Evaporator (SME) product pH, which is rather high (9 for SB5 vs. 7 for SB4). The pH of the SME slurry product can greatly influence the rheological properties, which depend in part on the partitioning of soluble and insoluble solids. Previous observations indicated that a higher pH can lead to gel formation[1] which could in turn lead to clogging of transfer lines. A reason given for these undesirable physical and chemical changes was the greater amount of leaching from the frit at higher pH. Thus, chemical methods used to decrease pH could make the pumping and transferring of SB5 SME product more efficient.

The aim of the experiment was to compare the rheological and leaching behavior of a SB5 slurry simulant (including frit) at low and high pH (7 and 10) during a 30 hour, boiling SME cycle. This work is based on the task plan SRNL-RP-2009-01199, which was requested via technical task request HLW-DWPF-TTR-2009-0030.[2,3] The work involved the use of two one-liter rigs to perform SME cycles on two SB5 simulant (non-radioactive) slurries with differing pH levels, 7.5 and 10; otherwise the simulants and the procedures were identical. Rheological and composition measurements were used to determine the effect of pH on the likelihood of gel formation in SB5 sample slurry and to determine whether a positive correlation was observed with leach rate.

To better understand the results, a blank experiment was run to deconvolute the effects of the sludge simulant from those of leaching from the glass frit. This experiment was performed with a frit-water mixture only; no sludge simulant was used.

3.0 EXPERIMENTAL

The R&D Directions are given in documents SRNL-L3100-2009-00247[4] and SRNL-L3100-2009-302[5]. Details were recorded in notebook WSRC-NB-2005-00143. The experiments were carried out at Aiken County Technology Laboratory (ACTL).

3.1 SIMULANT PREPARATION

SRAT product from a previous study,[6] SB5-6, containing no mercury was selected due to a concern that high pH levels might contribute to formation of dimethylmercury, an extremely toxic substance.[7,8] Offgas composition was not monitored since noble metals, known to generate hydrogen, were not present. Properties of the SB5-6 are summarized in Table 1.

Table 1. Properties of SB5-6 SRAT Product Simulant

pH	density	Total solids %	calcined %
4.4	1.23	25.3	14.9

3.2 APPARATUS

Due to the limited amount of SB5-6, two 500 g samples were used and these were placed in one liter vessels. A thermocouple, mechanical mixer, anti-foam addition funnel, air purge input, Friedrich condenser, and a heating mantle were installed. The air purge flow rates, both in and out, were measured with MKS flow controllers. Figure 1 shows a picture of the rigs for the low pH ("LOP") and high pH ("HIP") runs; the runs were performed concurrently.

Figure 1. **Picture of low and high pH apparatuses**.

3.3 PROCEDURE

A 276 g mixture of 50 wt% Frit 418 in water was added to the SRAT products to produce the SME slurry simulants and to achieve a waste loading of 35 wt%. The original SRAT product had a pH of 4.4; addition of the frit-water mixture increased the pH somewhat and the slurry pH was adjusted to the desired levels of 7.5 and 10 by addition of 50 wt% NaOH. The temperature at boiling was 102°C, air purge flow rate was 100 mL/min, the cooling water temperature was 10°C, and the boil-up rate was 0.7 g/min.

The mixing speed was originally set at 260 rpm for both tests to obtain a slight vortex, which indicated adequate mixing; however, the HIP slurry thickened immediately after addition of NaOH and visual inspection of this mixing vortex required a speed of 360 rpm. After 30 minutes of boiling, 500 ppm antifoam was added to the HIP rig due to the presence of about 10 cm of foam. This was the only foaming observed during the course of this work. At about the halfway point, 15 hours, a rheology sample was withdrawn and then pH measurements were performed on each run. The pH values decreased to 6.15 and 7.84 for the LOP and HIP runs, respectively; this is significantly lower than the initial values, 7.5 and 10, respectively. This change could have occurred due to precipitation of Mg, Mn, or other species, which can consume hydroxide anion and thus decrease pH (see section 4.2.1). This dependence of the supernate concentrations of some metal species with pH has been observed before in real waste.[9] A 50% solution of NaOH was added again to obtain the desired pH values. Some pH drift, albeit less, was also observed after 20 hours of boiling; no further pH observations were done.

On average, five hours of boiling was performed per day for six days so that the 30 hour cumulative time was satisfied for each. The degree of leaching in the supernate was monitored by using the Process Science Analytical Laboratory (PSAL) Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) to determine the elemental supernate concentrations of B, Li, and Si which are the principal elements that exist in Frit 418 but are not present in the sludge. With one exception, a sample was withdrawn at the end of each day and later subjected to elemental analysis. The experiments were run under conditions of reflux for the first 25 of the total 30 hours and the remaining time was used to remove water to obtain a target of 45% total solids content. The rheology was measured after 15 hours and after 30 hours of boiling with a RS-600 rheometer using a concentric cylinder geometry. The flow elements consisted of a 5 minute ramp up to 300 s^{-1} shear rate, a 1 minute hold, and a 5 minute ramp down to zero shear rate.

XRD measurements were performed with a Bruker D8 X-ray diffractometer (Cu Kα, 1.54 Å). Step scanning was performed over the 2Θ ranges of 5-70° with a step size of 0.02° and a dwell time of 1 s. A NaI scintillation detector was used. Search-match identification was performed with Jade software version 8.5 from Materials Data Inc. Samples were prepared by using a filter to remove the supernate.

In addition to the sludge experiments, a blank test was run without the presence of SB5-6; i.e., only Frit 418 and water were used. A mixture of 2000 g of water and 1077 g of Frit 418 was added to the apparatus and two runs, at the same pHs, were performed separately. The apparatus was the same as that used for the sludge experiments except that a high temperature pH probe was used to perform the measurements *in situ*. Boiling was performed for only seven hours and hot samples were withdrawn every hour for elemental analysis. Rheology measurements were not possible because of the lower viscosity of the frit-water mixture. It is important to note that immediately upon the addition of frit to water, the pH increased to about 10. This is due to the well known reactions of metal oxides with water to form hydroxides.[10] Thus, the LOP frit-water run required the addition of acid (HNO_3 was used) to lower the pH down to 7.5.

4.0 RESULTS

4.1 RHEOLOGY MEASUREMENTS

Rheology measurements were performed at the halfway point and at the end of the experiments, see Figures 2 and 3. Water was removed from both runs in the last five hours of boiling to ensure the 45% total solids content target was achieved; these were measured with a moisture analyzer. Thus, comparisons can be made between LOP and HIP runs at each time, but comparisons cannot be made between the 15 hour and 30 hour measurements since the total solids compositions were different. Because of the irregularity and uncertainties exhibited by the rheograms, calculations of the consistencies and yield stresses are not very meaningful. The reason for the irregularities of the low pH rheograms is uncertain. While the spike in Figure 2 can be explained as a frit particle being stuck for a short time between the concentric cylinders of the rheometer, the unusual, overall shapes of the rheograms indicate a separation of particles due to the thinness of the slurry in an accelerated system (centrifugal force due to the rotation of the inner cylinder).

Nonetheless, it is clear that the high pH slurry is thicker and has a greater yield stress (y-intercept). This is consistent with the need to operate at a higher mixing speed, as noted above. Moreover, it seems that boiling time did not contribute to the thickening since there is little variation between the 15 hour and 30 hour samples in the caustic run. It is more likely that the pH has a greater influence on the rheology than the boiling time.

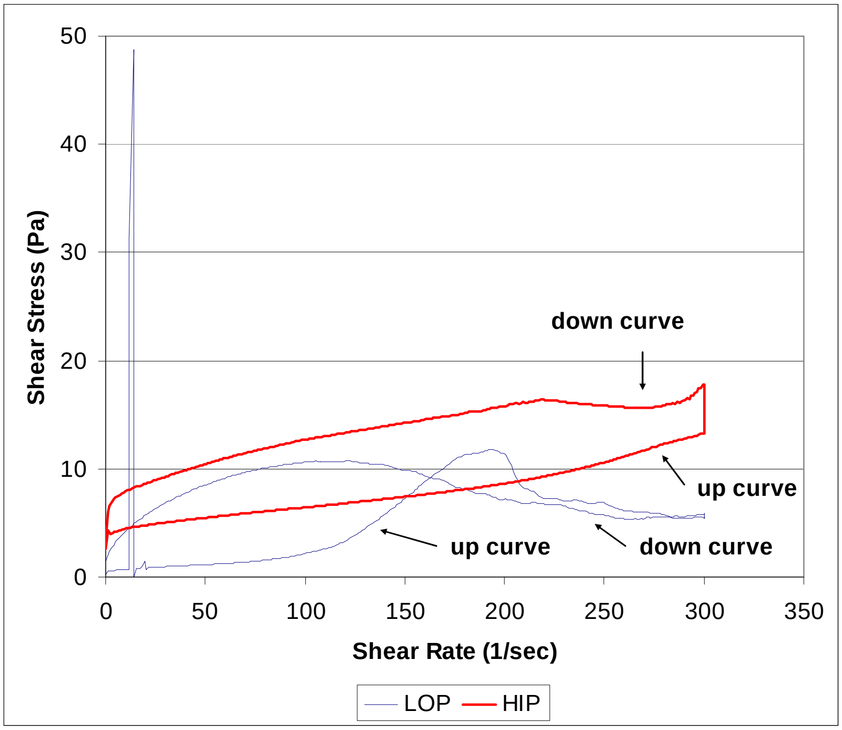

Figure 2. Rheograms of both low and high pH slurries after 15 hours of boiling.

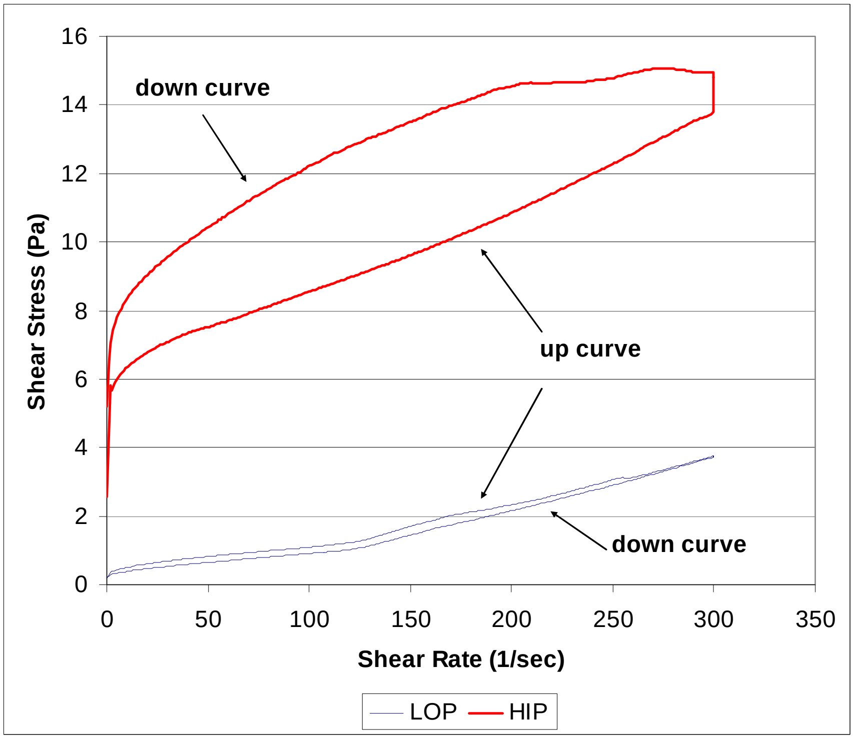

Figure 3. Rheograms of both low and high pH slurries after 30 hours of boiling.

4.2 ELEMENTAL ANALYSES

4.2.1 SB5-Frit 418 Study

ICP-AES was used to determine the amount of leaching by measuring the supernate concentrations of B, Li, and Si which are the principal elements that exist in Frit 418 but are not present in the sludge. The composition[11,12] of Frit 418 is shown in Table 2. Supernate samples were withdrawn and measured on five of the six separate days of boiling, including the final result. Using the composition of Frit 418, the concentrations of the contaminants (from leaching) in the supernate, and assuming that all of the B and Li partitioned into the supernate (since we do not know how much could have partitioned into the non-frit, solid phase), lower limit leaching percentages were calculated for the final sample after 30 hours of boiling, see Table 3. These percentages refer to the fraction of the mass of each leached element in the supernate divided by the total mass of the element in the added frit. The Si percentages are not included because a significant amount of Si, about 2% on a calcined solids basis, was added as part of the original SB5-6 recipe.

Table 2. Composition of Frit 418, wt%.

B_2O_3	Li_2O	Na_2O	SiO_2
8	8	8	76

Table 3. Calculated lower limit of leaching percentages (mass) of B and Li.

pH	B	Li
LOP	2.3%	4.7%
HIP	0.13%	1.1%

Figure 4 shows a semi-log plot of the lower limit leaching percentages of these elements as a function of time. As expected, the low and high pH runs exhibit an increase of leachate concentrations with time, especially for B and Li. However, it is the lower pH run that shows a significantly greater amount of leaching, about an order of magnitude greater by the end of the experiments; i.e., there is an inverse proportion between pH and leaching in the sludge runs. Overall, the results indicate that leaching increased as a function of time, is greatest for Li, and has an inverse proportion with pH.

As indicated in the Procedure section, when frit is brought into contact with water, alkali hydroxides are formed,[9]

$$M_2O + H_2O \rightarrow 2\,MOH \qquad (1)$$

This accounts for the leaching of Li and Na. Boron oxide reacts to produce boric acid,[13,14]

$$B_2O_3 + H_2O \rightarrow H_3BO_3 \text{ (or } B(OH)_3\text{) + products} \qquad (2a)$$

$$B(OH)_3 + 2\,H_2O \rightarrow [B(OH)_4]^- + H_3O^+ \qquad (2b)$$

SiO_2, the major component of the frit, reacts in caustic medium and exhibits a strong dependence on hydroxide anion concentration,[15-17]

$$SiO_2 + 4\,OH^- \rightarrow \text{products} \qquad (3)$$

From Figure 4, it is clear that Li leaching, equation (1), is faster than that of B, equation (2). At low pH, the difference is fairly small and may be due to either a preferential attack by water on the Li or due to a difference in products—Li becomes quickly solvated while the boron oxide undergoes various steps to produce a weak acid. At high pH the B concentration is considerably lower. A likely explanation is that B_2O_3 can undergo adsorption[18] onto $Mg(OH)_2$ particles; at high pH levels, this insoluble precipitate is likely to be present as discussed below.

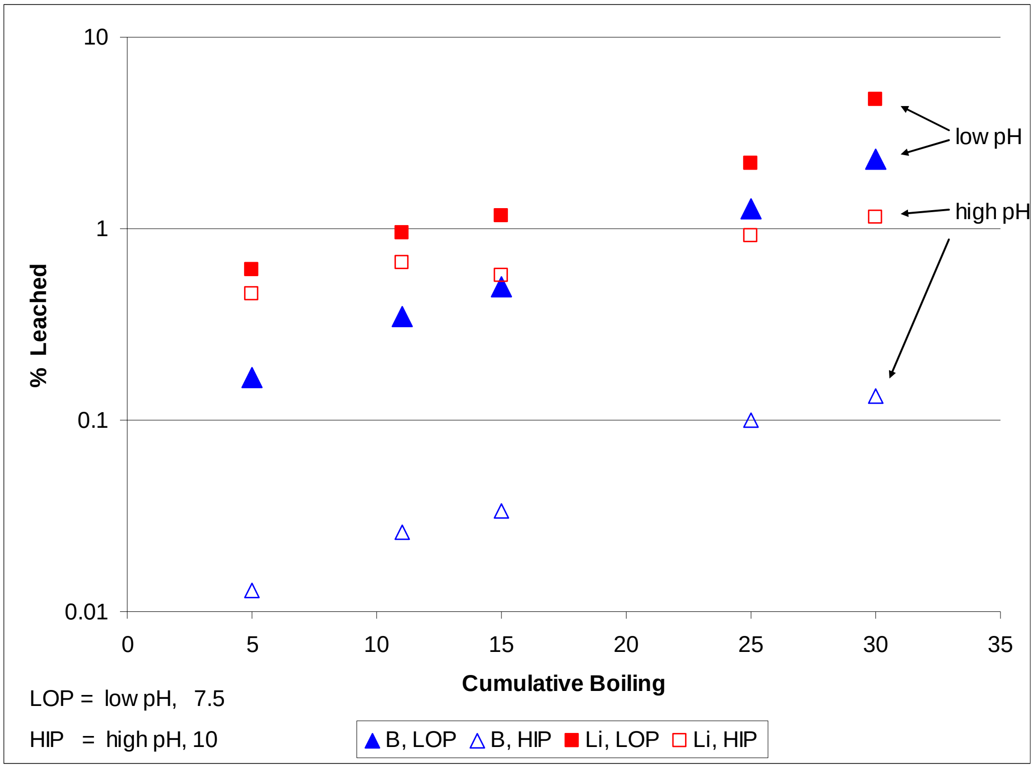

Figure 4. Lower limit leaching % of B, Li, and Si as a function of time and pH.

The supernate concentrations of sludge (not from frit) elements Mg and Mn decreased by about 1.5 and 3 orders of magnitude, respectively, in the high pH run, see Figure 5; the low pH run exhibited little variation. The reason for the increase of elemental concentrations at the end of boiling in the low pH run is not understood since a concentration correction was already applied; the target solids content, 45 wt%, was accomplished by removing water in the last five hours of the experiment.

The initial Mg and Mn concentrations are plotted, Figure 5, at -2 hours; this negative time value is used because no sample was withdrawn at the beginning of boiling. Instead these are dilution-corrected (addition of water and frit) supernate concentrations of Mg and Mn in the original SB5-6 SRAT product. By plotting these initial values, two effects can be deconvoluted: preparation and boiling time. The former refers to the steps used to prepare the slurry: a) addition of water, b) addition of frit, c) heating to boil, and d) adjustment of pH (addition of NaOH) at the beginning of boiling. The plot shows that the precipitation occurred only in the high pH run during two occasions, sometime near the beginning of the run and after the 15 hour sample. These three constraints correspond to adjustment of pH to caustic levels, once at the beginning of boiling and once after 15 hours of boiling. Thus, it can be concluded that these drops in concentration are likely due to the adjustment of pH (addition of NaOH) and not boiling time. Unfortunately, no samples were withdrawn just before and just after the adjustment of pH at the beginning of boiling.

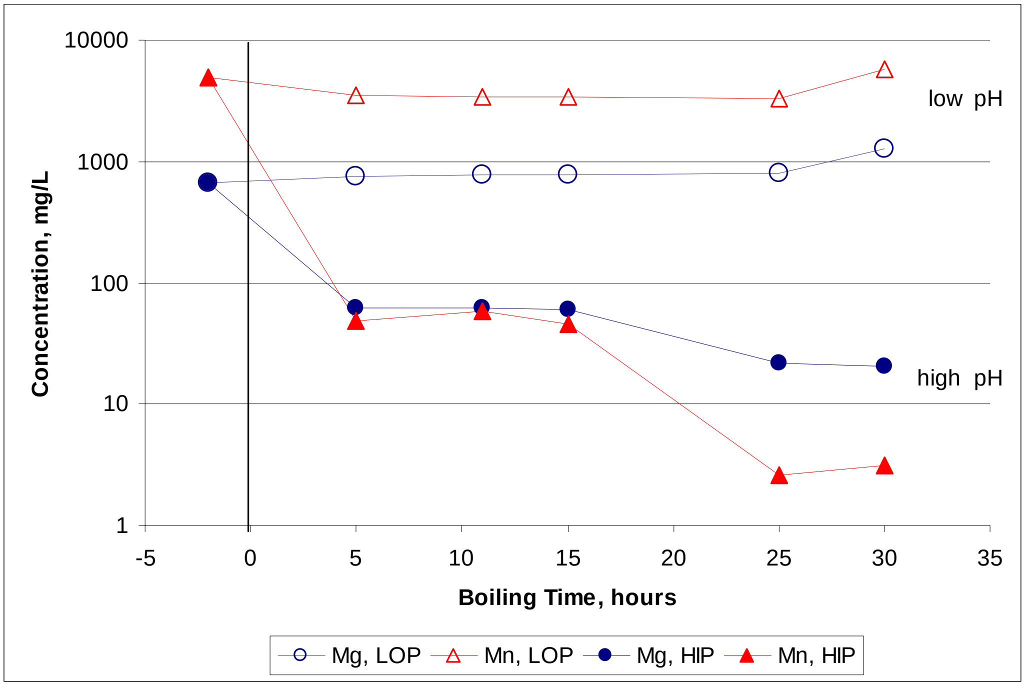

Figure 5. Concentration of several elements as a function of time.

The identities of the precipitates are most likely insoluble $Mg(OH)_2$ and $Mn(OH)_2$. Using the literature values of the solubility product constants at 25°C of $Mg(OH)_2$ and $Mn(OH)_2$, 5.61×10^{-12} and 1.60×10^{-13}, respectively,[19,20] and adjusting the values for the temperature, yields a ratio[21] of the equilibrium concentrations of Mg to Mn of 19, while the observed ratio in this high pH run after 25 hours of boiling is 17. This agreement indicates that caustic conditions effect the precipitation of hydroxides of Mg and Mn. Finally, since these metals account for about five weight percent of the original sludge composition (most of Mg and Mn were in supernate, 74% and 94%, respectively) and because these underwent a considerable amount of precipitation, it is likely that this increase in insoluble solids could be sufficient to explain the increase in thickness at high pH. Note the lack of precipitation in the low pH run and the corresponding lack of thickening. Thus, it appears that precipitation or increase of insoluble solids is correlated with thickening.

The measurements also demonstrate that the concentrations of the following elements, also not present in the frit, Ba, Ca, K, and S, did not vary with time as much as the Mg and Mn for both runs; these are tabulated in Appendix A. Of these elements, Ca precipitated to an appreciable degree, possibly due to formation of calcium carbonate.

4.2.2 Frit 418-Water Blank Study

To separate the effects of the frit from that of the sludge, a blank test was run without sludge. Figure 6 shows the lower limit percent leaching in the frit-water experiment. Note that Na is not included in the analysis because of its presence in the sludge. Again, as expected, the leaching increases with time and Li is leached more quickly than B. Unlike the sludge system, here we observe that high pH leads to greater leaching. This is not surprising since semiconductor studies show that SiO_2 is etched more quickly under caustic conditions, such as in aqueous solutions of KOH.[15-17] And since SiO_2 quickly reacts and since it is the major component at 71 mole%, the leaching rates of the B and Li should also be greater and should be similar to the former. This is confirmed by inspection of Figure 6 where the leaching levels of Si, B, and Li at high pH are indistinguishable after about 2 hours of boiling.

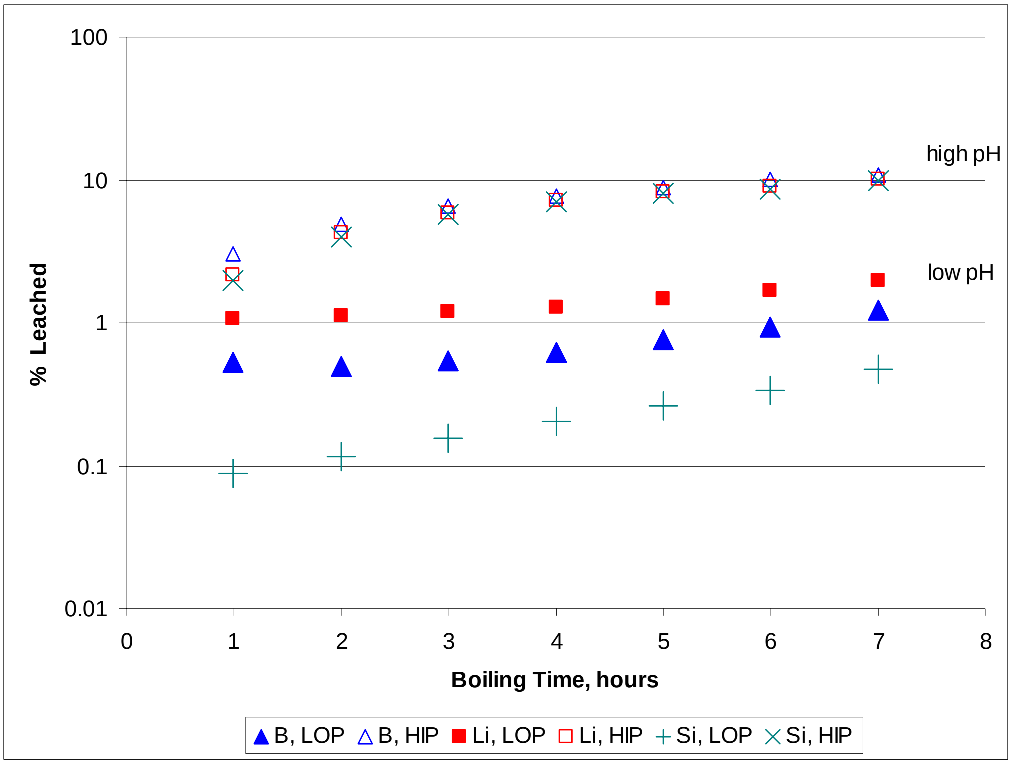

Figure 6. Lower limit leaching % as a function of time and pH in Frit-water system.

4.2.3 Comparison of Both Systems

In order to compare the sludge and frit-water leaching % results, a combined plot, including the Si concentrations, is shown in Figure 7 and the calculated values are tabulated in Appendix B. The concentrations, used to calculate leaching %, are tabulated in Appendix C. The time axis is limited to 15 hours for clarity. The leaching in the frit-water system varies from a factor of two to almost three orders of magnitude greater (depending on conditions and species) than the sludge system even though the boiling time of the former is less than a fourth. A possible reason is a smaller driving force or greater ionic strength in the sludge system. Another possibility for the greater leaching in the frit-water system is the absence of a physical effect, coating of frit particles by sludge; i.e., the sludge coating could inhibit mass transfer and thus slow the leaching processes, equations (1) – (3). This effect could account for the observed lower leach rate of Si in the sludge system at high pH, despite the high concentration of OH^- which, according to equation (3), would increase the leach rate.

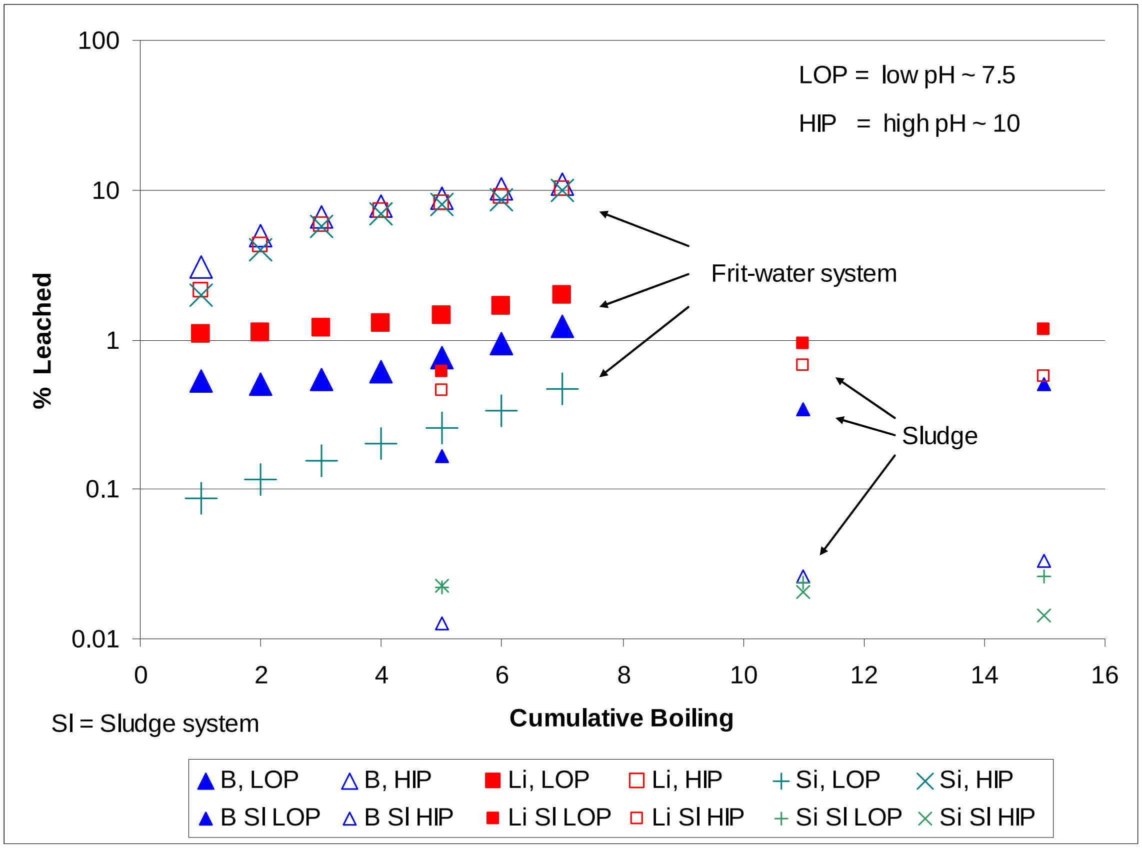

Figure 7. Lower limit leaching % of sludge (smaller symbols) and Frit-water systems.

The greatest differences between the two systems, Figure 7, are the amounts of Si and B leached at high pH, almost three orders of magnitude variation. The frit water system is simpler and its behavior is easier to explain. At low pH, this system exhibits considerable leaching of the elements with Li being dominant. The B leaching is somewhat slower, perhaps for the same reasons as in the sludge system, possibly due to preferential attack of water on alkali oxide or, since boric acid is a weak acid, the final reaction may be a reversible equilibrium step. Leaching of silica is much slower because of the relatively low hydroxide anion concentration, equation (3). At high pH, the OH^- concentration is high and leaching of silica dominates. And since SiO_2 is the main component of the frit at 71 mole%, the other components closely match the silica leaching rate.

The sludge system behaves differently. Like the frit-water system, at low pH the dominant leaching mechanism is via hydration of the metal oxide, such as Li. Again, the B is leached somewhat more slowly, possibly for reasons given above. The silica leaching is very low due to the low OH^- concentration. At high pH, however, the sludge system shows a considerable decrease in B leaching and, surprisingly, the silica leaching remains essentially the same at low values; the silica leaching is not increased dramatically at higher OH^- concentrations in the sludge system. As stated above, the decrease of B concentration in the supernate is likely due to adsorption onto particles of $Mg(OH)_2$, which were precipitated under caustic conditions. The low supernate concentration of Si may be due to a similar effect, adsorption of sludge particles onto the frit, which could increase the mass transfer resistance to transport of OH^- to the silica on the frit surface. That is, in the sludge system a coating could form to slow the OH^- reaction with the silica but the water, which is neutral and at much higher concentration, likely encounters less mass transfer resistance and thus allows for a faster leaching of Li.

4.3 XRD MEASUREMENTS

Finally, X-ray Diffraction (XRD) analyses were performed to determine whether sodium aluminosilicate crystals were present in the solid phase. Inspection of the XRD spectra in Figures 8 and 9 indicate the presence of SiO_2 crystals (quartz) and $Al(OH)_3$ crystals (bayerite, quartz, gibbsite, and nordstrandite) in both runs, but no sodium aluminosilicate was observed. Thus, while there is no evidence that crystalline sodium aluminosilicate is present, the observation of the broad continua in the XRD spectrum indicates a considerable amount of amorphous solid which could contain undetectable sodium aluminosilicate;[22,23] thus, its contribution to thickening cannot be ruled out.

XRD does not reveal the presence of $Mg(OH)_2$ or $Mn(OH)_2$ in the solid phase even though the PSAL measurements of the supernate indicated considerable precipitation, on the order of several weight percent, which is just above the XRD detection limit. There are several possible reasons for this discrepancy. The precipitate could have been formed in the amorphous state. It is also possible that the stronger Al and Si signals could obscure weak hydroxide peaks. Thirdly, B_2O_3 could block detection by coating the $Mg(OH)_2$ (and possibly $Mn(OH)_2$) particles, see section 4.2.1. A fourth possibility is that the hydroxide particle sizes could be smaller than the detection limit of XRD; for example, nanoscale crystallites of magnesium hydroxide have been produced hydrothermally.[24]

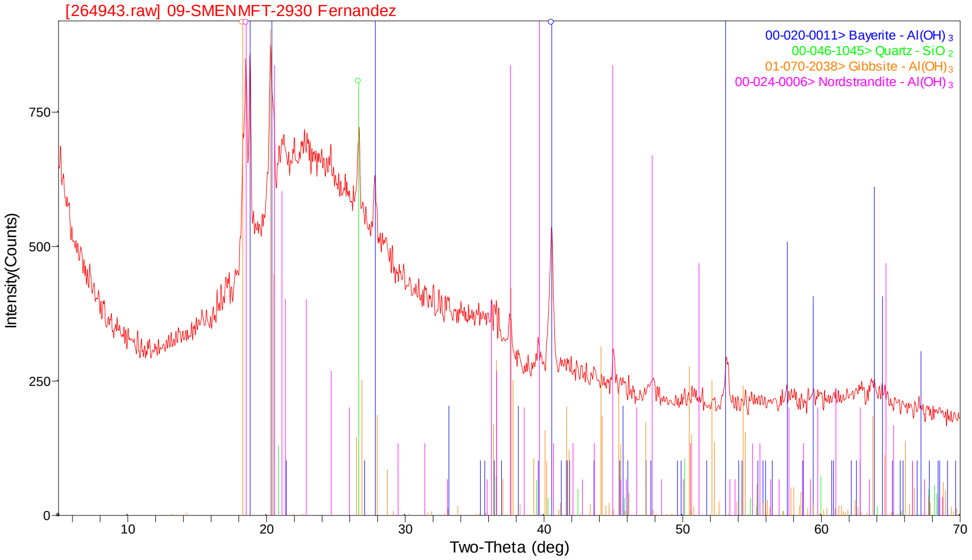

Figure 8. XRD measurements of the low pH solids.

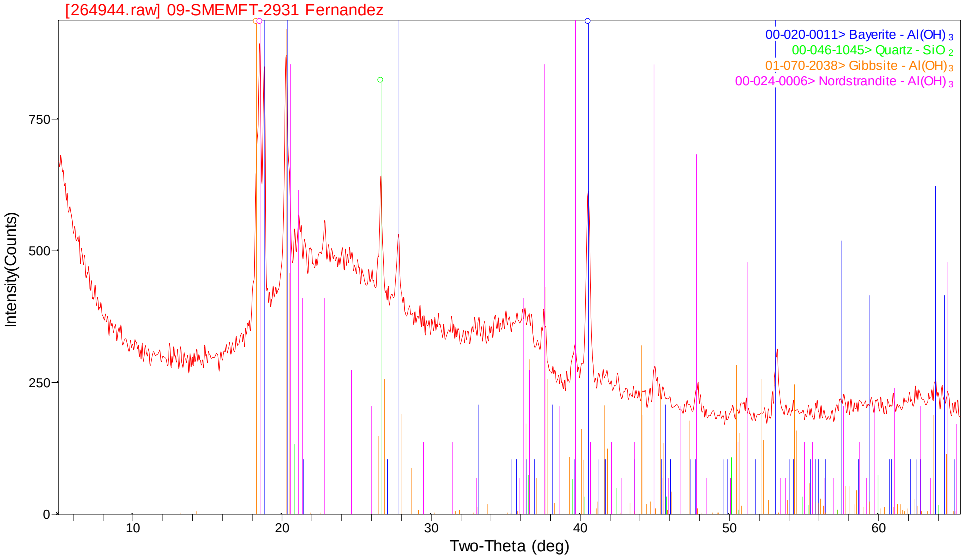

Figure 9. XRD measurements of the high pH solids.

5.0 CONCLUSIONS

It was expected that thickening and gel formation could occur when non-acidic or alkaline conditions are encountered in a) glass frit-water mixtures and b) the MFT feed loop. Since the XRD measurements did not detect sodium aluminosilicate in crystal form in both low and high pH slurries, it is unlikely that gel formation via this crystal occurs in SB5 simulant SME processes over a wide range of pH values.

The observations imply that subjecting SB5 simulant sludge to caustic conditions, such as those found in a SB5 SME cycle (reflux boiling), will cause a measurable increase in thickness (relative to neutral or acidic conditions) but that this is not due to crystalline sodium aluminosilicate-mediated gel formation since none was detected by XRD in both the low and high pH runs. However, amorphous sodium aluminosilicate could have been present. Because of the absence of sodium aluminosilicate and in light of the elemental composition, rheology, and thermochemistry, it is likely that the precipitation of the insoluble hydroxides of Mg and Mn, observed under caustic conditions, contributes to the thickening of the SB5-6 slurry.

Leaching consists of the formation of metal hydroxides from the oxides, the formation of boric acid from the boron oxide, and dissolution of silica. It was not expected that an increase in pH would lead to a decrease in leaching in the SB5 simulant system. Thus, a blank study, consisting of only Frit 418 and water was conducted to gain further insight. The opposite behavior was seen in the frit-water system, an increase in pH leads to an increase in leaching; this behavior is not surprising as silica dissolution by hydroxide anion has been well established in the semiconductor literature. The measurements also revealed greater leaching of B, Li, and Si elements from a factor of two to almost three orders of magnitude relative to the sludge runs. Two possible reasons why the sludge system exhibits less leaching are: a) a higher ionic strength would provide a smaller driving force to leach and b) the presence of sludge coating on the frit particles would increase mass transfer resistance. More specific comparisons of both systems show that the B leaching shows a negative correlation with pH level in the sludge, unlike the frit-water system. This is likely due to the removal of B by adsorption onto $Mg(OH)_2$.

Because the increase in thickness was modest in the caustic case, likely due to precipitation of the insoluble hydroxides of Mg and Mn, the cause of the clogs in the DWPF melter feed loop is still unknown. An alternative explanation is that the SB5 waste, like the simulant used in this study, is too thin and that this could contribute to a loss of two-phase flow which could cause plugging of a restricted and poorly mixed zone like the melter feed loop.[25] This is feasible: a slurry can exhibit increasing flow resistance at lower flow rates.[26]

Future work could include a study of a SB5 SME product's flow behavior as a function of pH level and flow rate. The observations could help determine whether a thin slurry could separate into liquid and solid phases and cause a clog in a constricted and poorly-mixed zone such as in a pipe or near a valve.

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APPENDIX A. ELEMENTAL CONCENTRATIONS VERSUS TIME

LOP, pH = 7.5

Boil time, hr*	[Ba], mg/L	[Ca], mg/L	[K], mg/L	[S], mg/L
-2**	0.25	1723	255	237
5	0.98	1860	231	177
11	0.86	1830	233	241
15	1.25	1830	236	257
25	0.42	2050	250	251

HIP, pH = 10

Boil time, hr*	[Ba], mg/L	[Ca], mg/L	[K], mg/L	[S], mg/L
-2**	0.25	1723	255	237
5	0.98	1055	249	176
11	0.87	990	247	188
15	1.08	747	160	116
25	0.3	647	174	122

* The values after 30 hours of boiling are misleading, abnormally high due to removal of water.

** The negative time indicates that these supernate concentrations of components are of the original SB5-6 SRAT product sludge at room temperature before the addition of frit and water, and well before the beginning of boiling.

APPENDIX B. LEACHING % VERSUS TIME (FIGURE 7)

SB5-Frit 418 System LOP, pH ~ 7.5

Boiling time, hr	B	Li	Si
5	0.167	0.609	0.022
11	0.346	0.942	0.024
15	0.500	1.167	0.026
25	1.270	2.175	0.029
30	2.321	4.682	0.047

SB5-Frit 418 System HIP, pH ~ 10

Boiling time, hr	B	Li	Si
5	0.013	0.459	0.022
11	0.026	0.666	0.020
15	0.034	0.570	0.015
25	0.099	0.921	0.014
30	0.134	1.139	0.016

Frit 418-Water System LOP, pH ~ 7.5

Boiling time, hr	B	Li	Si
1	0.528	1.082	0.087
2	0.499	1.109	0.115
3	0.541	1.194	0.156
4	0.616	1.297	0.204
5	0.759	1.469	0.260
6	0.938	1.676	0.335
7	1.230	1.976	0.474

Frit 418-Water System HIP, pH ~ 10

Boiling time, hr	B	Li	Si
1	3.071	2.144	1.992
2	4.891	4.272	4.012
3	6.573	5.871	5.672
4	7.784	7.245	7.005
5	8.815	8.294	7.998
6	10.101	9.069	8.651
7	10.823	10.218	9.827

APPENDIX C. SUPERNATE CONCENTRATION VERSUS TIME

Concentration in units of mg/L

SB5-Frit 418 System LOP, pH ~ 7.5

Boiling time, hr	B	Li	Si
5	18.7	102	35.2
11	38.5	157	38.1
15	55.7	195	42.2
25	142	363	45.6
30	282	851	82.4

SB5-Frit 418 System HIP, pH ~ 10

Boiling time, hr	B	Li	Si
5	1.43	76.5	35.7
11	2.90	111	32.5
15	3.74	95.0	23.1
25	11.1	154	22.9
30	16.3	207	28.0

Frit 418-Water System LOP, pH ~ 7.5

Boiling time, hr	B	Li	Si
1	70.6	217	167
2	66.8	222	220
3	72.4	239	298
4	82.5	260	391
5	102	294	497
6	126	336	642
7	165	396	907

Frit 418-Water System HIP, pH ~ 10

Boiling time, hr	B	Li	Si
1	411	429	3810
2	654	855	7680
3	879	1180	10850
4	1040	1450	13400
5	1180	1660	15300
6	1350	1820	16600
7	1450	2050	18800

Distribution:

S. L. Marra, 773-A
A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
F. M. Pennebaker, 773-42A

J. E. Occhipinti, 704-S
D. C. Sherburne, 704-S
R. T. McNew, 704-27S
J. F. Iaukea, 704-30S
J. W. Ray, 704-S
H. B. Shah, 766-H
J. M. Gillam, 766-H
B. A. Hamm, 766-H
D. D. Larsen, 766-H
C. J. Bannochie, 773-42A
D. K. Peeler, 999-W
M. E. Stone, 999-W
A.I. Fernandez, 999-W
D.C. Koopman, 999-W
D.P. Lambert, 999-W
J.D. Newell, 999-W
J.M. Pareizs, 777-42A
B.R. Pickenheim, 999-W
S.H. Reboul, 773-42A

J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
E. W. Holtzscheiter, 704-15S
M. T. Keefer, 766-H