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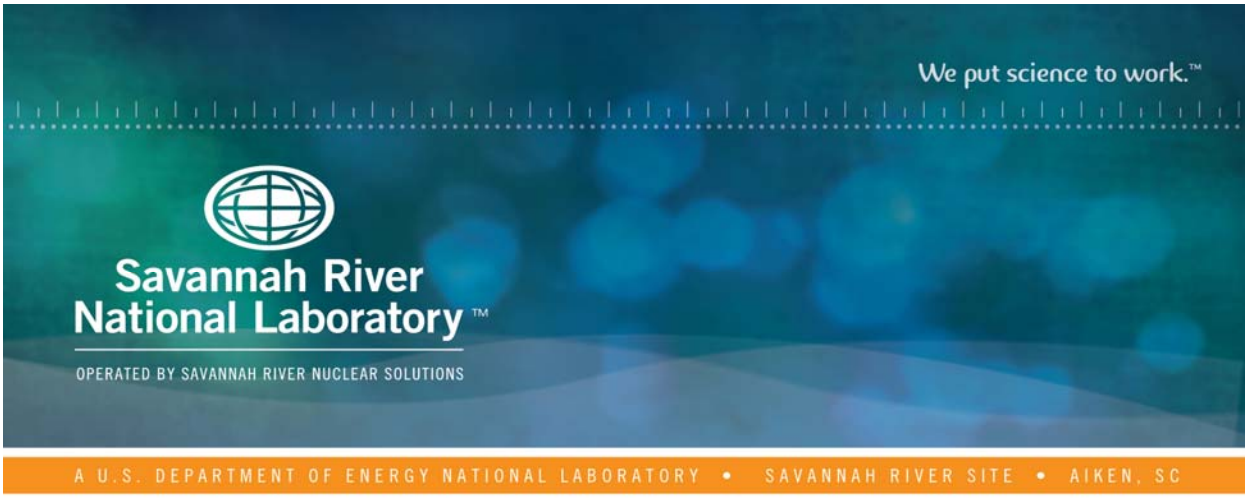

Scoping Studies to Determine Impact of a Low-Alkali Phase Separated Frit on the Behavior of the Frit Slurry and Slurry Mix Evaporator Rheology

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EXECUTIVE SUMMARY

The frits used in the vitrification process at the Defense Waste Processing Facility (DWPF) are alkali borosilicate glasses, which are composed mainly of B_2O_3, alkali (Li_2O and Na_2O) and SiO_2. As the total alkali concentration in a borosilicate glass is reduced, liquid-liquid immiscibility is exhibited by the glass-forming melt, which is analogous to the behavior of oil and water. Upon cooling, the resulting glass matrix is said to be phase separated. The immiscible region is controlled by both composition and temperature. Viscosity of the melt is also a factor as it impacts the reaction rate (kinetics) of phase separation. The reaction rate (kinetics) leading to phase separation is slow for higher viscosity melts, and if such a melt is cooled rapidly (e.g., quenched in water), the resulting glass could be homogeneous, or the scale of the phase separated microstructure could be of no practical significance. Phase separated alkali borosilicate glasses tend to form a more durable silica-rich phase and a less durable alkali borate-rich phase. The overall durability of the phase separated glass depends on the morphology (physical arrangements) of each of these phases. For example, droplets of the alkali borate-rich phase may form within a silicate rich matrix, which would be a more durable glass than a glass with an interconnected alkali borate-rich phase.

Based on the anticipated higher sodium concentration salt stream coming to DWPF from the Salt Waste Processing Facility (SWPF), there may be a future need to reduce the alkali concentration in the frit depending on the composition of the sludge in Tank 40. SWPF is projected to start operating in late 2019. Thus, it is possible that lower alkali, phase separated frits may become necessary for Sludge Batch 10 and later sludge batches to ensure that the composition of the material in the Slurry Mix Evaporator (SME) is acceptable relative to the Product Composition Control System models.

The presence of phase separation in a DWPF frit is not expected to impact the performance of the final glass waste form. However, the presence of a less durable alkali borate phase may influence the behavior of the frit during the aqueous feed preparation steps in the Chemical Process Cell (CPC). Therefore, the objective of this study was to perform experimental testing to determine whether the presence of phase separation in a lower alkali frit could have negative impacts on the following DWPF operations.

- Potential for gel formation in the frit slurry
- Rheological changes during SME processing

Based on the test conditions evaluated in this scoping study of lower alkali, visually phase separated frits, there do not appear to be negative impacts to either the frit slurry or the SME product rheological properties. The frit slurries remained free-flowing without a formic acid addition for the two-week test duration. This test duration, and the lack of formic acid addition, are conservative relative to normal operating conditions at DWPF. While the phase separated frits exhibited increased leaching of B and Li during SME testing with a reflux duration of approximately six hours, their impact on the rheological properties were minimal. In addition, the rapid cooling method used by the current frit supplier (Bekeson Glass LLC) during the manufacturing process is effective at mitigating phase separation, which was shown to decrease the concentrations of the frit components dissolved in the frit slurry and during the SME process.

The scoping studies described here demonstrate that lower alkali, phase separated frits should be considered an option for future frit development efforts. SME testing as part of future sludge batch qualification efforts will provide an opportunity to identify any unexpected rheological issues associated with a phase separated frit.

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LIST OF ABBREVIATIONS

CPC	Chemical Process Cell
DAC	Data Acquisition and Control
DWPF	Defense Waste Processing Facility
g	gram
HGR	hydrogen generation rate
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
L	liter
mL	milliliter
mm	millimeter
NG	nitric-glycolic
NIST	National Institute of Standards and Technology
Pa	Pascal
RPM	revolutions per minute
s	second
SB9	Sludge Batch 9
SEM	scanning electron microscopy
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
wt.%	weight percent

1.0 Introduction

The frits used in the vitrification process at the Defense Waste Processing Facility (DWPF) are alkali borosilicate glasses, which are composed mainly of B_2O_3, alkali (Li_2O and Na_2O) and SiO_2.[1] As the total alkali concentration in a borosilicate glass is reduced, liquid-liquid immiscibility is exhibited by the glass-forming melt,[2] which is analogous to the behavior of oil and water. Upon cooling, the resulting glass matrix is said to be phase separated. The immiscible region is controlled by both composition and temperature. Viscosity of the melt is also a factor as it impacts the reaction rate (kinetics) of phase separation. The kinetics are slow for higher viscosity melts, and if such a melt is cooled rapidly (e.g., quenched in water), the resulting glass could be homogeneous, or the scale of the phase separated microstructure could be of no practical significance. Phase separated alkali borosilicate glasses tend to form a more durable silica-rich phase and a less durable alkali borate-rich phase. The overall durability of the phase separated glass depends on the morphology (physical arrangements) of each of these phases. For example, droplets of the alkali borate-rich phase may form within a silicate rich matrix, which would be a more durable glass than a glass with an interconnected alkali borate-rich phase.

The ternary phase diagram for the lithium borosilicate system (Li_2O-B_2O_3-SiO_2) shows that compositions with less than approximately 20 weight percent (wt.%) Li_2O are phase separated, while the sodium borosilicate (Na_2O-B_2O_3-SiO_2) phase diagram shows that compositions with less than approximately 15 wt.% Na_2O are phase separated.[3] Typically, phase separated sodium borosilicate glasses appear homogeneous to the un-aided eye and electron microscopy would be needed to confirm the presence of two phases.[2] Phase separated lithium borosilicate glasses usually appear opalescent and may even be opaque as shown in Figure 1-1.

Figure 1-1. Examples of opalescent and opaque alkali borosilicate glasses that are phase separated.

To date, the frits used at DWPF[a] have had alkali concentrations of 14-20 weight percent (wt.%)[1] and none have shown any visual indicators of phase separation as in Figure 1-1. Frit 422[b] was previously identified as candidate frit for Sludge Batch 8; however, this frit was visually phase separated when fabricated in the laboratory.[4,5] Due to schedule constraints, an experimental program was not initiated to determine whether there would be any downstream impacts of using this phase separated frit. A higher alkali frit (Frit 803[c]) was ultimately recommended for processing.[6]

Based on the anticipated higher sodium concentration salt stream coming to DWPF from the Salt Waste Processing Facility (SWPF), there may be a future need to reduce the alkali concentration in the frit depending on the composition of the sludge in Tank 40. SWPF is projected to start operating in late 2019. Thus, it is possible that lower alkali, phase separated frits may become necessary for future Sludge Batch 10 and later sludge batches to ensure that the composition of the material in the Slurry Mix Evaporator (SME) is acceptable relative to the Product Composition Control System models.[7]

[a] Frits 200, 320, 418, 510, and 803.
[b] Frit 422 has the composition $8B_2O_3 – 8Li_2O – 3Na_2O – 81SiO_2$ (wt.%) with 11 wt.% alkali.
[c] Frit 803 has the composition $8B_2O_3 – 6Li_2O – 8Na_2O – 78SiO_2$ (wt.%) with 14 wt.% alkali.

Considering the regions of immiscibility for the lithium borosilicate and sodium borosilicate systems (< 20 wt.% Li_2O and <15 wt.% Na_2O), it is possible that most, if not all the frits previous used in DWPF are compositions that will exhibit phase separation under certain temperature conditions during fabrication. The presence of phase separation in a DWPF frit is not expected to impact the performance of the final glass waste form. However, the presence of a less durable alkali borate phase may influence the behavior of the frit during the aqueous feed preparation steps in the Chemical Process Cell (CPC). Therefore, the objective of this study was to perform experimental testing to determine whether the presence of phase separation in a lower alkali frit could have negative impacts on the following DWPF operations.

- Potential for gel formation in the frit slurry
- Rheological changes during SME processing

2.0 Glass Selection

The target compositions of the frits used in this study are shown in Table 2-1. A brief description of each composition follows.

1. Frit 131 was a higher alkali frit (23.4 wt.%) used during DWPF pilot testing that exhibited gel formation[8] in the frit slurry. It was included as a control.
2. DOPT4 (D-Optimal 4) was a lower alkali (9 wt.%), visually phase separated frit developed by SRNL[9] and previously tested by the Vitreous State Laboratory to evaluate the potential for gel formation in the frit slurry.[10] The presence of phase separation in this frit was confirmed with SEM by the Vitreous State Laboratory.
3. SB9PS-Na2 was a lower alkali (10 wt.%), visually phase separated frit that was fabricated by the current DWPF frit supplier (Bekeson Glass LLC) for a previous manufacturability scoping test.[5] Material fabricated by the supplier was available for testing, which allowed for a comparison to frit fabricated at SRNL.
4. Frit 803 is currently being used by DWPF for Sludge Batch 8 and Sludge Batch 9 processing and is not visually phase separated. It was included as a control as there have been no issues indicated for the frit slurry and rheology in the SME. Material fabricated by the DWPF frit supplier was available for testing (Lot B080).[11]

Table 2-1. Target Frit Compositions (wt.%)

	B_2O_3	Li_2O	Na_2O	SiO_2
Frit 131*	14.7	5.7	17.7	57.9
DOPT4 (D-Optimal 4)	17	8	1	74
SB9PS-Na2	8	8	2	82
Frit 803	8	6	8	78

*Frit 131 also contains 0.5 La_2O_3, 2 MgO, 1 TiO_2, and 0.5 ZrO_2 (wt.%)

3.0 Experimental Procedure

3.1 Frit Fabrication

Each batch (except Frit 803) was prepared from the proper proportions of reagent-grade chemicals.[12] The raw materials were blended in a shaker-mixer for 10 minutes with zirconia ball media and then placed into a uniquely identified platinum alloy crucible. Each crucible was covered with a loose-fitting lid and placed into a pre-heated high-temperature furnace at the desired melt temperature for one hour.[13] SRNL SB9PS-Na2 was melted at 1450°C, while SRNL Frit 131 and SRNL DOPT4 were melted at 1200°C. At the end of the isothermal hold, the crucibles were removed, and the molten glass was poured onto a clean, stainless steel plate. The melt was allowed to cool to ambient temperature. Each glass was crushed with a hammer

and then ground with an analytical mill. Two melts per composition were fabricated and then combined during the grinding step. The ground glasses were sieved to the DWPF size specification (80-200 mesh).[1] A sample of each sieved frit was submitted for digestion and chemical composition analysis via Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

3.2 Frit Slurry Mixing Test

The methods used for the mixing test followed those used in previous testing at SRNL in which 50 grams (g) of frit was combined with 50 g of de-ionized water.[8] The slurry was mixed with a Teflon stir bar on a magnetic stir plate at 500 revolutions per minute (RPM) for two weeks during working hours. In this testing configuration, 500 RPM was selected as it was the slowest speed that could maintain suspension of the particles during mixing. Testing was conducted at room temperature. pH measurements were taken for the first six working days.[14] At the end of test, the slurries were centrifuged, and the leachate was collected and passed through a 0.45 micrometer syringe filter. A sample of the filtered leachate was submitted for chemical composition analysis via ICP-AES.

3.3 SME Testing

The apparatus used for SME testing was based on the simulant testing flow system used for hydrogen generation rate (HGR) testing[15] and combined design elements from equipment used for previous one liter and four liter sludge batch qualification CPC testing.[16,17]

Heating was provided by two 0.375-inch diameter Alloy 800 heating rods powered by an automated direct current power supply (TDK-Lambda Genesys, GEN150-10). Mixing was controlled using a mixer system consisting of a Servodyne mixing head coupled to a 1-inch diameter, 4-blade, 45° pitched turbine Teflon® impeller agitator shaft via a Parr high torque magnetic drive. The slurry was continually stirred over the course of the testing. Purge gas was controlled using an MKS Model 647 Multi Gas Controller and MKS Model 1179 Flow Controller. An offgas condenser allowed condensate to reflux back into the vessel containing the sample material and be removed for slurry concentration. Non-condensable gas exiting the condenser was vented to the fume hood.

3.3.1 Data Acquisition and Control

A Data Acquisition and Control (DAC) application was programmed using National Instruments LabVIEW software. The software that controlled the process parameters for the experiments was the control software used for the other recent HGR measurement testing that was originally developed for DWPF CPC flowsheet and qualification testing. The DAC logged process data and controlled mixing speed, purge gas flow rate, and heating rod temperature. A proportional-integral-derivative control algorithm governed the amount of power supplied to the heating rods by comparing the bulk process temperature to the process temperature setpoint. Consistent with previous sludge batch qualification testing, efforts were made to eliminate localized hot regions in the process vessel by minimizing the differential temperature between the heating rods and the process temperature and by insulating the process vessel. A control limit was defined to prevent the rods from overheating, which inhibited the heating rods from exceeding the bulk temperature by more than 30°C.

3.3.2 Test Protocol

Simulated Sludge Receipt and Adjustment Tank (SRAT) product generated during SB9 nitric-glycolic (NG) flowsheet testing[18] was used for this testing.[19] The starting pH was 5.6. Approximately 700 g of SB9 NG SRAT product was loaded into the SRAT vessel. Antifoam 747 was added, and the vessel contents were heated to 93°C. Heat to the vessel was turned off, and a 50 wt.% frit slurry was added to target a waste loading of 36 wt.%. The frit slurry was composed of 153.3 g of frit and 153.3 g of deionized water. Each slurry was mixed with a Teflon stir bar on a magnetic stir plate for approximately 24 hours prior to the addition to the SRAT vessel.

After the frit addition, antifoam 747 was added prior to boiling. The slurry was concentrated to a target of 48 wt.% total solids and refluxed[20] over a period of approximately six hours. SME testing parameters were as follows:

- Measurement apparatus: nominally 1 liter (L) flow system, Teflon® vessel and lid. Total volume (liquid and gas) of approximately 1.2 L.
- SRAT product total dried solids: 22.4 wt.%
- Sample density: 1.16 g/mL
- Sample volume: 602 mL
- Sample mass: 700 g
- Target purge rate: 100 standard cubic centimeters per minute
- Condenser cooling water setpoint: 10°C
- Mixing rate: 200 RPM
- Antifoam addition mass (total): 0.10 g
- Mass of frit addition: 154 g
- Mass of frit water: 154 g
- Mass of dewater[d]: 366 g

3.4 Analytical Methods

3.4.1 Weight Percent Total Solids

Slurry samples were placed in a convection oven at 110°C for least 12 hours to determine weight percent total solids by change in mass.[21]

3.4.2 Sample Preparation for ICP-AES Measurements

The frit samples were mechanically ground in an agate mixer mill, then sieved to -100 mesh. The ground samples were then prepared via two different fusion techniques; a lithium metaborate fusion[22] and a sodium peroxide/sodium hydroxide fusion.[23] The DWPF Waste Compliance Plan Batch 1 glass was also included in the analyses as a reference.[24]

Slurry samples were first calcined at 1100°C, and then mechanically ground in an agate mixer mill and sieved to -100 mesh. The ground samples were then prepared via two different fusion techniques; a lithium tetraborate/lithium nitrate fusion[25] and sodium peroxide/sodium hydroxide fusion.[23]

3.4.3 ICP-AES Measurements

All of the prepared solutions were analyzed with ICP-AES.[26] The ICP-AES was calibrated before each run, verified after every ten samples, and at the end of the sample series with National Institute of Standards and Technology (NIST) traceable standards to ensure that the calibration did not drift throughout the sample measurements. Each sample was analyzed in duplicate.

3.4.4 Rheological Measurements

Flow curve measurements were obtained using a Haake RS6000 rheometer with a Z38 cylindrical rotor and Z43 cup.[27] A cooling/heating bath was used to control the temperature of the rotor, sample, and cup at 25°C. Based on the frit size, the Z38 rotor has been determined to be suitable for the measurement of SME product rheology by reducing the impact spiking (jamming) of the frit particle between the rotor and cup.

[d] The amount of dewater is dependent upon the volumes of rinse water used during the experiments and was not constant.

A NIST traceable Newtonian oil standard was used to verify the operability of the rheometer daily at 25°C. Each SME sample was vigorously shaken, tapped to removed entrained air prior to measurement, and poured into the cup. The cup was loaded onto the rheometer and the bob was slowly inserted. Excess fluid was removed, and the flow curve measurement was initiated.

For each SME product, only the up-flow curves were fitted to the Bingham Plastic rheological model (Equation 1) due to the non-linear response that can occur during the down-curve. Two flow curve analyses were performed per SME sample.

$$\tau = \tau_{BP} + \eta_{BP} \cdot \gamma \qquad \text{(Equation 1)}$$

where: τ = shear stress (Pascal [Pa])
τ_{BP} = Bingham Plastic yield stress (Pa)
η_{BP} = Bingham Plastic Viscosity (Pa·second[s])
γ = shear rate (1/s)

3.5 Quality Assurance

This work was requested via a Technical Task Request[28] and directed by a Task Technical and Quality Assurance Plan.[29] The functional classification of this task is Production Support. This task is not waste form affecting and does not need to follow the quality assurance requirements of RW-0333P.[30] Microsoft Excel was used to support this work. Data are recorded in the PerkinElmer E-Notebook under Experiment IDs C7592-00311-25, C7605-00021-17, and C9827-00219-03. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60.[31] This document, including all calculations, was reviewed by a Design Check. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[32]

4.0 Results and Discussion

Sample results from this testing based on frits fabricated at SRNL are designated by "SRNL" in the sample identifications, while those results based on frits fabricated at Bekeson Glass LLC are designated by "Supplier."

4.1 Frit Fabrication and Analysis

Photographs of the three glasses fabricated at SRNL are shown in Figure 4-1. The milky white appearances of SRNL SB9PS-Na2 and SRNL DOPT4 are a primary indicator of the presence of phase separation in these glasses. The wave-like appearance of SRNL Frit 131 is not indicative of phase separation, but is a result of pouring the molten glass onto a stainless-steel plate.

Figure 4-2 shows the Supplier SB9PS-Na2 glass prior to grinding.[5] The formation of a thin glass ribbon is a result of the molten glass pour stream being forced between water cooled rollers as it exited the melter. Dimensions of the ribbon are approximately 3.5 centimeters wide with a nominal thickness of 0.65-0.80 millimeter (mm). Based on feedback from the supplier, the white marks shown by the arrow are typically observed on all the frits produced for DWPF and are a result of mechanical scuffing by the rollers on the surface of the glass. Isolated areas of phase separation were observed on the ribbons where the thickness (0.9-1.2 mm) exceeded the nominal thickness, and were located at the outer edges of the ribbon as shown by the circled region in Figure 4-2. Based on the appearance of the ribbon, phase separation was significantly reduced due to the higher cooling rate from the water-cooled rollers. Additional examples of the impact of rapidly quenching other lower alkali compositions are shown in SRNL-STI-2015-00025.[5]

SRNL Frit 131	SRNL SB9PS-Na2	SRNL DOPT4

Figure 4-1. Images of as-poured glasses that were fabricated at SRNL.

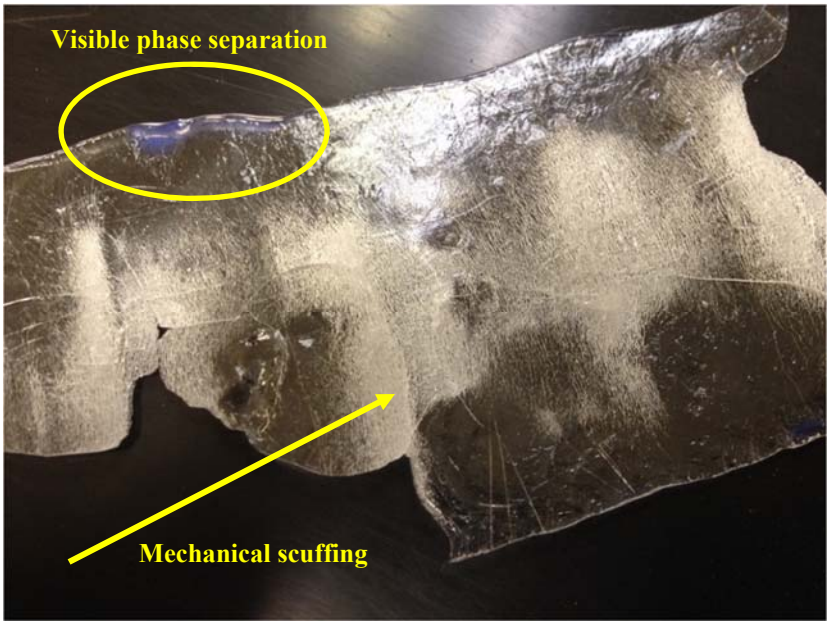

Figure 4-2. Example of an as-manufactured SB9PS-Na2 glass ribbon by the current DWPF frit supplier using a roller quenching process.

The target and measured compositions of all glasses, including those fabricated by the DWPF frit supplier, are shown in Table 4-1. The WCP Batch 1 standard glass[24] is also shown. Except for SiO_2, the measured concentrations of the major oxides (target concentrations greater than 0.5 wt.%) are less than 1 wt.% different from the target values. The higher deviations for SiO_2 are likely due to analytical errors rather than batching errors since the Batch 1 standard glass is over 2 wt.% high and there is no trend in the deviation of the measured values for the frit samples. These variations in SiO_2 are not expected to impact the conclusions of this study.

Table 4-1. Target and Measured Frit Compositions (wt.%)

	SRNL Frit 131		SRNL DOPT4		SRNL SB9PS-Na2	
Oxide	**Target**	**Measured**	**Target**	**Measured**	**Target**	**Measured**
B_2O_3	14.7	14.8	17	16.3	8	7.98
La_2O_3	0.5	0.41	---	<0.06	---	<0.06
Li_2O	5.7	5.26	8	7.14	8	7.13
MgO	2	1.61	---	<0.08	---	<0.08
Na_2O	17.7	17.8	1	0.92	2	1.93
SiO_2	57.9	55.9	74	71.8	82	83.3
TiO_2	1	0.94	---	<0.08	---	<0.08
ZrO_2	0.5	0.46	---	<0.07	---	<0.07

	Supplier SB9PS-Na2		Supplier Frit 803		Batch 1 Glass Standard	
Oxide	**Target**	**Measured**	**Target**	**Measured**	**Target[24]**	**Measured**
B_2O_3	8	7.11	8	7.94	7.78	7.99
La_2O_3	---	<0.06	---	<0.06	---	<0.06
Li_2O	8	7.18	6	5.48	4.43	4.27
MgO	---	<0.08	---	<0.08	1.42	1.34
Na_2O	2	2.18	8	7.89	9.00	8.95
SiO_2	82	88.6	78	78.8	50.20	52.37
TiO_2	---	<0.08	---	<0.08	0.68	0.64
ZrO_2	---	<0.07	---	<0.07	0.10	0.09

4.2 Frit Slurry Mixing Test

The pH measurements taken during the first six working days are shown in Table 4-2 as a function of elapsed time. Generally, the values were within pH 10-11 and exhibited a slight increase over time. Since the trend was consistent with the results from previous mixing tests with Frits 200, 320, and 131 in water,[8] measurements were not continued for the remainder of the testing period.

Table 4-2. pH Measurements

Elapsed Time (hour/minute)	SRNL Frit 131	SRNL DOPT4	SRNL SB9PS-Na2	Supplier SB9PS-Na2	Supplier Frit 803
0	10.64	10.24	10.52	10.58	10.54
20:45	11.06	10.61	10.80	10.61	10.12
44:40	11.11	10.59	10.51	10.27	10.11
68:25	11.20	10.36	10.91	10.64	10.20
140:30	11.14	10.55	10.92	10.82	10.08
164:30	11.30	10.69	11.04	10.84	10.15

After each night or weekend of settling, the stir bars could be restarted. The frit slurries remained free flowing for the two-week test duration. As testing progressed, the SRNL Frit 131 sample had the smallest

volume of free liquid remaining after settling and seemed to be more gel-like as was previously observed.[8] The SRNL Frit 131 slurry also appeared to flow more slowly in the bottle when gradually rotated by hand as compared to the other frit slurries.

The percentage of dissolved frit components for each of the compositions shown in Table 4-3 was determined using the initial measured compositions of each frit prior to the start of the mixing tests (Table 4-1) and the aqueous sample results after the mixing tests were completed (Appendix Table A-1). Generally, less than 10% of the glass-forming components (B and Si) and alkali (Li and Na) were dissolved from the frit. The longer duration of this mixing test should be conservative relative to normal operating conditions at DWPF, which would therefore result in significantly lower percentages of dissolved frit components.

The SB9PS-Na2 frit fabricated by the supplier exhibited a lower leach rate than the same frit made at SRNL, which demonstrates that the leach behavior over the two-week test duration is impacted by the fabrication method. Phase separation was observed throughout the sample fabricated at SRNL (Figure 4-1), while only isolated areas of phase separation were observed in the ribbons produced by the supplier (Figure 4-2).

During pilot scale testing of the DWPF flow sheet, the frit slurry with Frit 131 and water gelled in the make-up vessel due to the high leach rate. To decrease the tendency for gel formation, a small amount of formic acid was added to the frit slurry to lower the pH. While DWPF ultimately used a frit with less alkali for processing Sludge Batch 1a (Frit 200[e]), the addition of 1.5 weight percent formic acid to the frit slurry was retained as standard practice in the facility. Based on melting rate testing, Frit 320[f] was recommended for Sludge Batch 2, which had an alkali concentration that was greater than Frit 200, but less than Frit 131.[33] Leach testing was performed to determine whether Frit 320 would exhibit gel formation as previously observed for Frit 131. Using the data provided in WSRC-TR-2001-00404,[8] the percentage of dissolved frit components was calculated for the Frit 131 and Frit 320 frit slurries with water and 1.5 wt.% formic acid solution (Table 4-4). The percentage of dissolved frit components in the Frit 320 frit slurry with water is comparable to both SRNL Frit 131 and the phase separated SRNL fabricated SB9PS-Na2 shown in Table 4-3 for similar testing conditions. These calculations show that, as demonstrated previously,[8] the addition of 1.5 wt.% formic acid to the frit slurry significantly reduced the concentration of dissolved frit components[g] and Frit 320 was used successfully during SB2 processing. It is assumed that a similar trend would be observed for the phase separated frits evaluated in the current study. Thus, the formic acid addition could be a mitigation strategy for a future sludge batch if a frit that exhibits a higher percentage of dissolved frit components is considered.

[e] Frit 200 has the composition $12B_2O_3 – 5Li_2O – 2MgO – 11Na_2O – 70SiO_2$ (wt.%) with 16 wt.% alkali.
[f] Frit 320 has the composition $8B_2O_3 – 8Li_2O – 12Na_2O – 72SiO_2$ (wt.%) with 20 wt.% alkali.
[g] The pH of the Frit 320 frit slurry with water and 1.5 wt.% formic acid solution was 4.3 as compared to 11.2 for the water only frit slurry.

Table 4-3. Post Mixing Test Percentage of Dissolved Frit Components

Component	SRNL Frit 131	SRNL DOPT4	SRNL SB9PS-Na2	Supplier SB9PS-Na2	Supplier Frit 803
B	10	11	10	3	0
Li	8	13	9	4	1
Na	7	11	7	3	0
Si	5	3	3	2	0

Table 4-4. Post Mixing Test Percentage of Dissolved Frit Components Calculated from WSRC-TR-2001-00404

	Frit 131		Frit 320	
Component	**Water**	**1.5 wt.% Formic Acid Solution**	**Water**	**1.5 wt.% Formic Acid Solution**
B	10	3	9	2
Li	8	4	7	3
Na	8	3	8	2
Si	6	0	8	0

4.3 SME Testing

The percentage of dissolved frit components for each of the compositions after the SME cycles was determined using the initial concentrations of B and Li in the SB9 NG SRAT product (Appendix Table A-2), the final concentrations of B and Li in the SME products (Appendix Table A-3) and the measured compositions of each frit (Table 4-1). These results are shown in Table 4-5. Only B and Li were evaluated since these are frit components that were present at low concentrations in the SB9 NG SRAT product (<55 mg/L). Except for SRNL DOPT4, less than 10% of B and Li were dissolved from the frit during 24 hours of frit slurry mixing and the subsequent SME cycle. There are slight differences (if any) between the values calculated using the target and measured frit compositions. While SRNL DOPT4 does exhibit a higher percentage of dissolved frit components, the composition of this frit is not representative of typical compositions used by DWPF, which have lower B_2O_3 concentrations. As discussed in the previous section, the formic acid addition could be a mitigation strategy for a future sludge batch if a frit that exhibits a higher percentage of dissolved frit components is considered. Similar to the frit slurry mixing tests, the SME product based on the Supplier SB9PS-Na2 frit exhibited a lower percentage of dissolved B and Li.

Table 4-5. Post SME Cycle Percentage of Dissolved Frit Components

Component	SRNL Frit 131	SRNL DOPT4	SRNL SB9PS-Na2	Supplier SB9PS-Na2	Supplier Frit 803
B	5	21	2	1	0
Li	8	30	4	2	1

4.3.1 Rheology

The rheological results for the SME samples are provided in Table 6-1. This table provides the Bingham plastic yield stress and plastic viscosity for each sample and the average for each sample. The shear rate range in which the data was fitted to the Bingham plastic model and the coefficient of determination for each sample are also provided. Weight percent total solids data and pH are included for reference. Rheological measurements were conducted 12-14 days after the completion of the SME cycle testing. Flow

curves, from which the Bingham plastic yield stress and plastic viscosity were calculated, are provided in Appendix B.

For many of these samples, the complete shear rate range was not used for fitting the Bingham plastic model due to the generation of Taylor vortices[34] (secondary flow), which generate higher stresses and occur earlier in the shear rate for thinner SME product. After completion of the flow curve measurement, a bed of frit particles that settled at the bottom of the cup, under the region of shear, was observed for the two thinner SME products (those produced with SRNL Frit 131 and SRNL DOPT4). The other SME product samples produced with the other frit compositions did not have this noticeable buildup.

Lower yield stress and plastic viscosity were observed for the SME products produced with SRNL Frit 131 and SRNL DOPT4, which exhibited the highest percentages of dissolved frit components during the SME testing as shown in Table 4-5. Higher pH was also observed in these two samples due to increased leaching of alkali. The mechanism for the decrease in rheological properties was not investigated but could possibly be influenced by differing particle size distributions in the frits or increased ionic strength of the supernate.

5.0 Conclusions

Based on the test conditions evaluated in this scoping study of lower alkali, visually phase separated frits, there do not appear to be negative impacts to either the frit slurry or the SME product rheological properties. The frit slurries remained free-flowing without a formic acid addition for the two-week test duration. This test duration, and the lack of formic acid addition, are conservative relative to normal operating conditions at DWPF. While the phase separated frits exhibited increased leaching of B and Li during SME testing, their impact on the rheological properties were minimal. In addition, the rapid cooling method used by the current frit supplier during the manufacturing process is effective at mitigating phase separation, which was shown to decrease the concentrations of the frit components dissolved in the frit slurry and during the SME process. Thus, lower alkali, visually phase separated frits should be considered a viable option for future frit development efforts.

6.0 Future Work

Based on the anticipated higher sodium concentration salt stream coming to DWPF from SWPF, there may be a future need to reduce the alkali concentration in the frit depending on the composition of the sludge in Tank 40. SWPF is projected to start operating in late 2019. Thus, it is possible that lower alkali, phase separated frits may become necessary for future sludge batches to ensure that the composition of the material in the SME is acceptable relative to the Product Composition Control System models. The scoping studies described here demonstrate that lower alkali, phase separated frits should not be excluded from the frit optimization process for future sludge batch processing at DWPF. SME testing as part of future sludge batch qualification efforts will provide an opportunity to identify any unexpected rheological issues associated with a phase separated frit.

It was shown that the current supplier's manufacturing process mitigates phase separation in lower alkali frit compositions. Should either the DWPF frit supplier or the supplier's manufacturing method change in the future, additional study would be warranted to determine whether the tendency for phase separation in the frit has increased.

Lower alkali frit compositions are more refractory, requiring higher melting temperatures for manufacturing. Future frit optimization efforts should include viscosity measurements for lower alkali compositions, to determine whether they fall within the range of the supplier's manufacturing capability. Additional studies may also need to be performed to determine the impact of lower alkali frit compositions on the melting behavior of the melter feed.

Table 6-1. Bingham Plastic Rheological Results

SME Product ID	SME Cycle Date	Rheological Measurement Date	pH	Total Solids (wt.%)	Run	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Shear Rate Range (1/s)
SRNL Frit 131	9/5/18	9/17/18	6.5	49	1	14.2	1.20	0.9879	0 - 200
					2	13.8	1.18	0.9864	
					Average	**14.0**	**1.19**	----	----
SRNL DOPT4	9/5/18	9/18/18	7.0	48	1	10.6	0.64	0.9876	0 - 150
					2	10.8	0.64	0.9896	
					Average	**10.7**	**0.64**	----	----
SRNL SB9PS-Na2	9/6/18	9/18/18	5.9	48	1	23.5	3.06	0.9913	0 - 290
					2	24.0	2.99	0.9883	0 - 270
					Average	**23.7**	**3.03**	----	----
Supplier SB9PS-Na2	9/4/18	9/18/18	5.7	49	1	25.1	3.14	0.9815	0 – 300
					2	25.8	3.02	0.9896	
					Average	**25.5**	**3.08**	----	----
Supplier Frit 803	9/4/18	9/18/18	5.7	49	1	34.2	4.52	0.9835	0 - 300
					2	34.5	4.55	0.9830	
					Average	**34.4**	**4.53**	----	----

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Appendix A. Raw Analytical Data

Table A-1. Average Post Frit Slurry Mixing Study Aqueous Results (mg/L)

Component	SRNL Frit 131	SRNL DOPT4	SRNL SB9PS-Na2	Supplier SB9PS-Na2	Supplier Frit 803
B	4495	5795	2520	755	87.7
Li	2035	4155	2915	1290	133
Na	9575	731	1055	516	143
Si	12,950	9540	13,100	7120	348

Table A-2. Average Concentrations of B and Li in the SB9 NG SRAT Product

Component	Concentration (mg/L)
B	52.4
Li	23.4

Table A-3. Average Concentrations of B and Li in the SME Products (mg/L)

Component	SRNL Frit 131	SRNL DOPT4	SRNL SB9PS-Na2	Supplier SB9PS-Na2	Supplier Frit 803
B	839	3575	272	167	106
Li	671	3295	466	311	98.5

Appendix B. Flow Curves

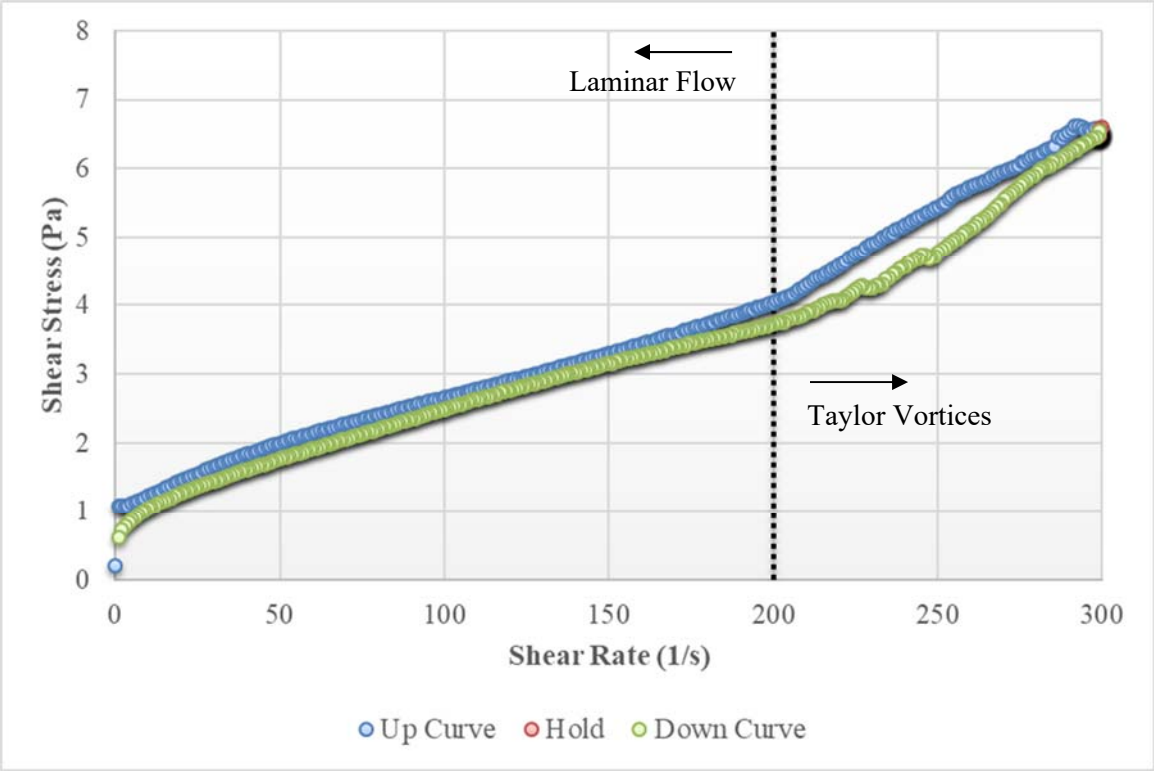

Figure B-1. Flow curve for SRNL Frit 131 Run 1.

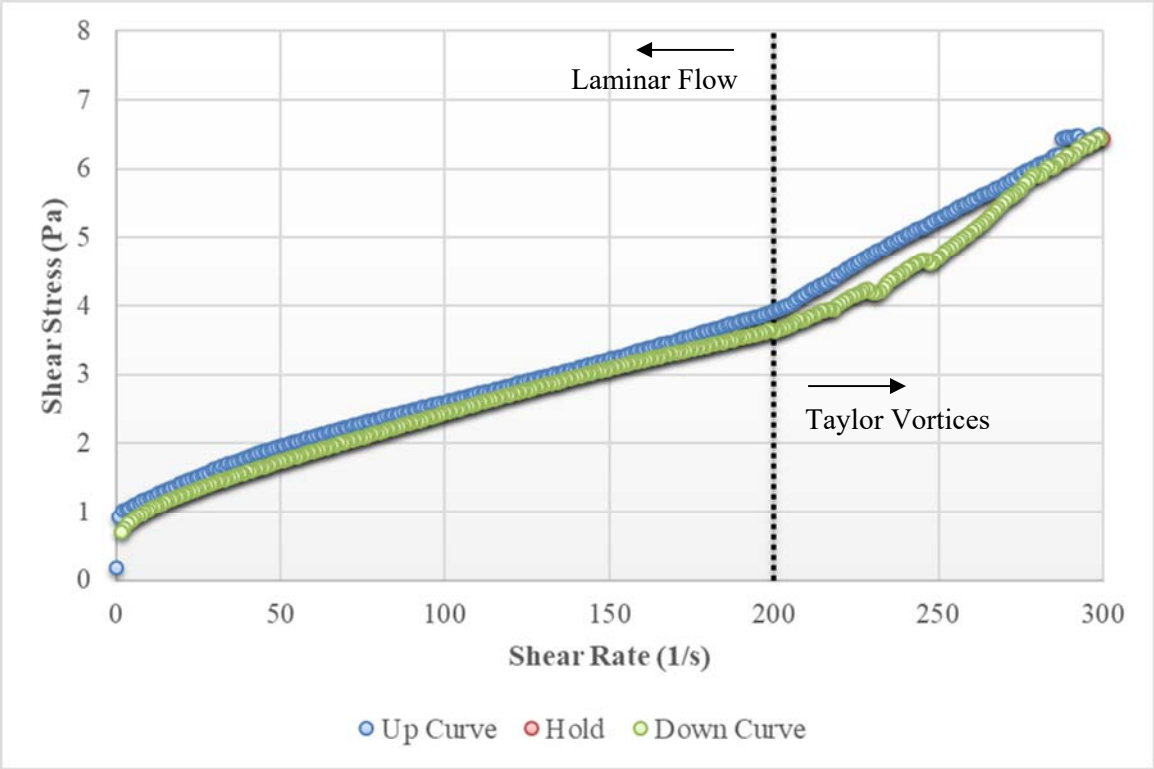

Figure B-2. Flow curve for SRNL Frit 131 Run 2.

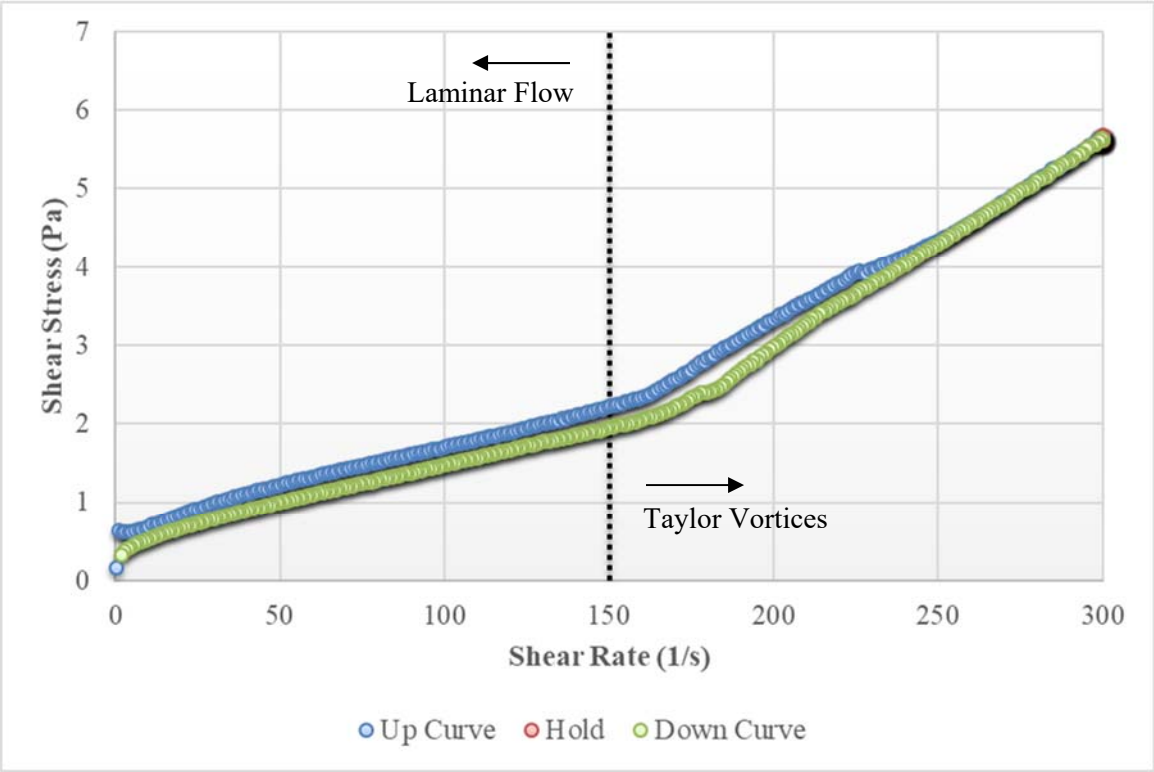

Figure B-3. Flow curve for SRNL DOPT4 Run 1.

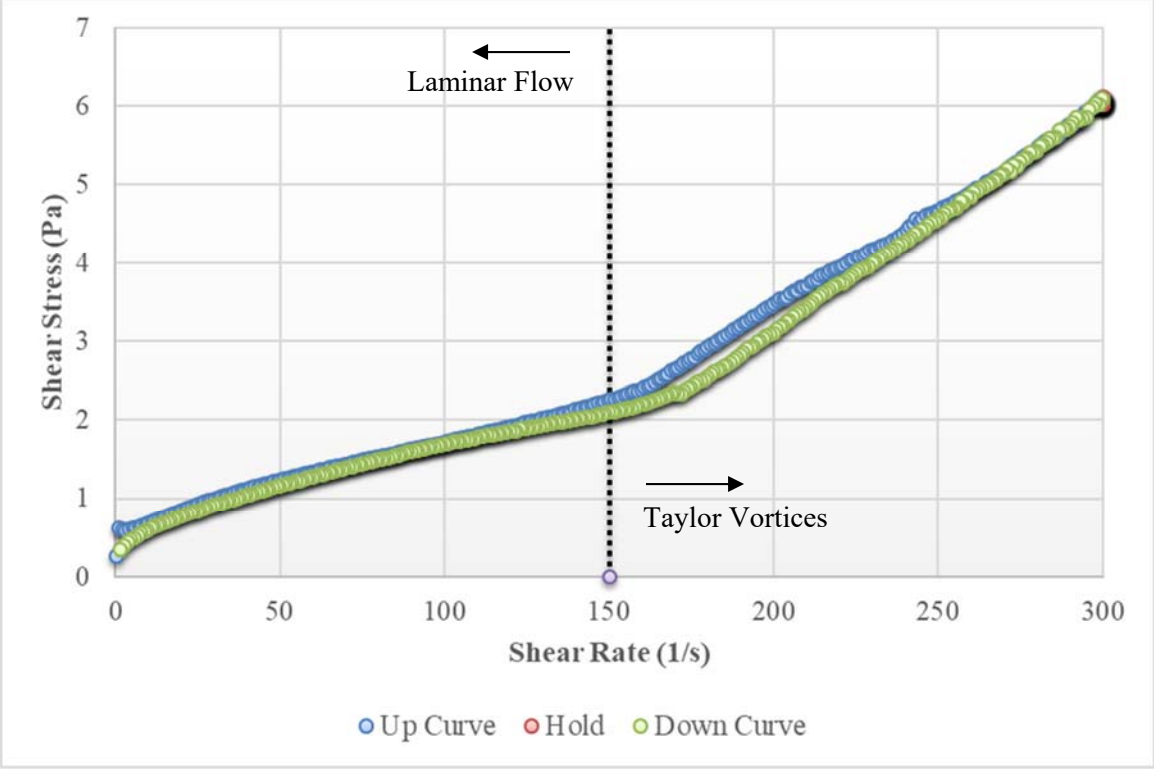

Figure B-4. Flow curve for SRNL DOPT4 Run 2.

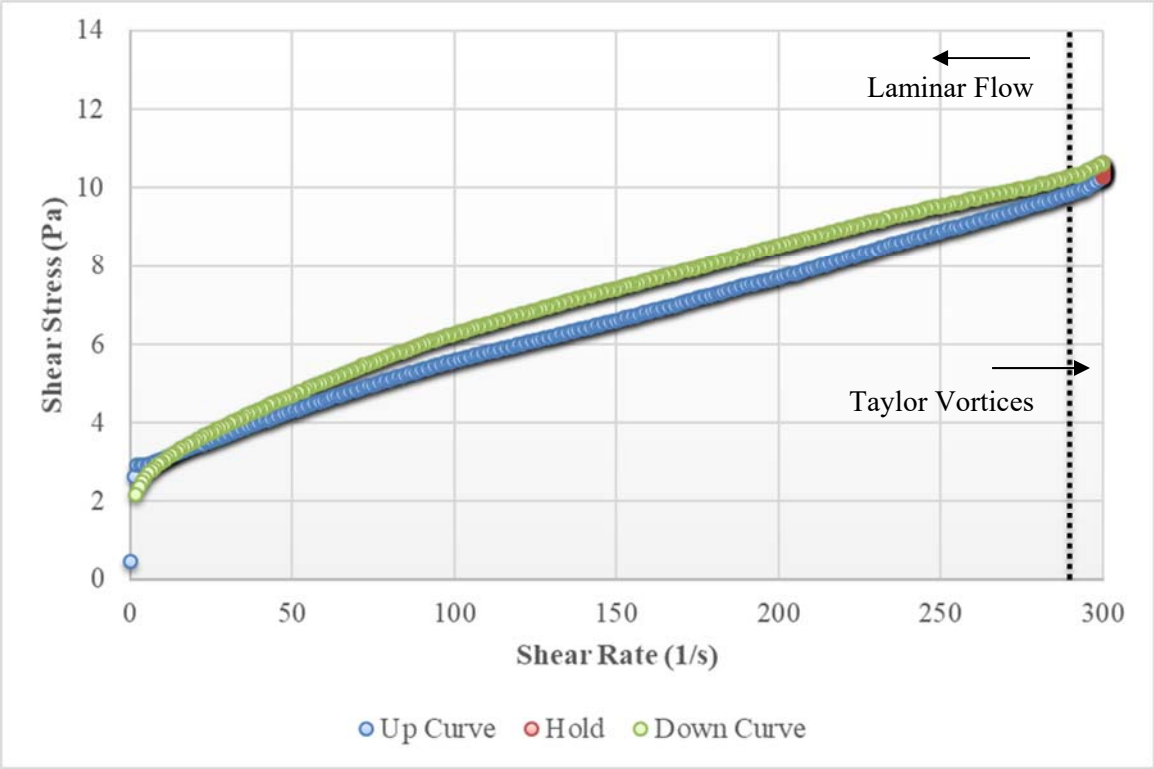

Figure B-5. Flow curve for SRNL SB9PS-Na2 Run 1.

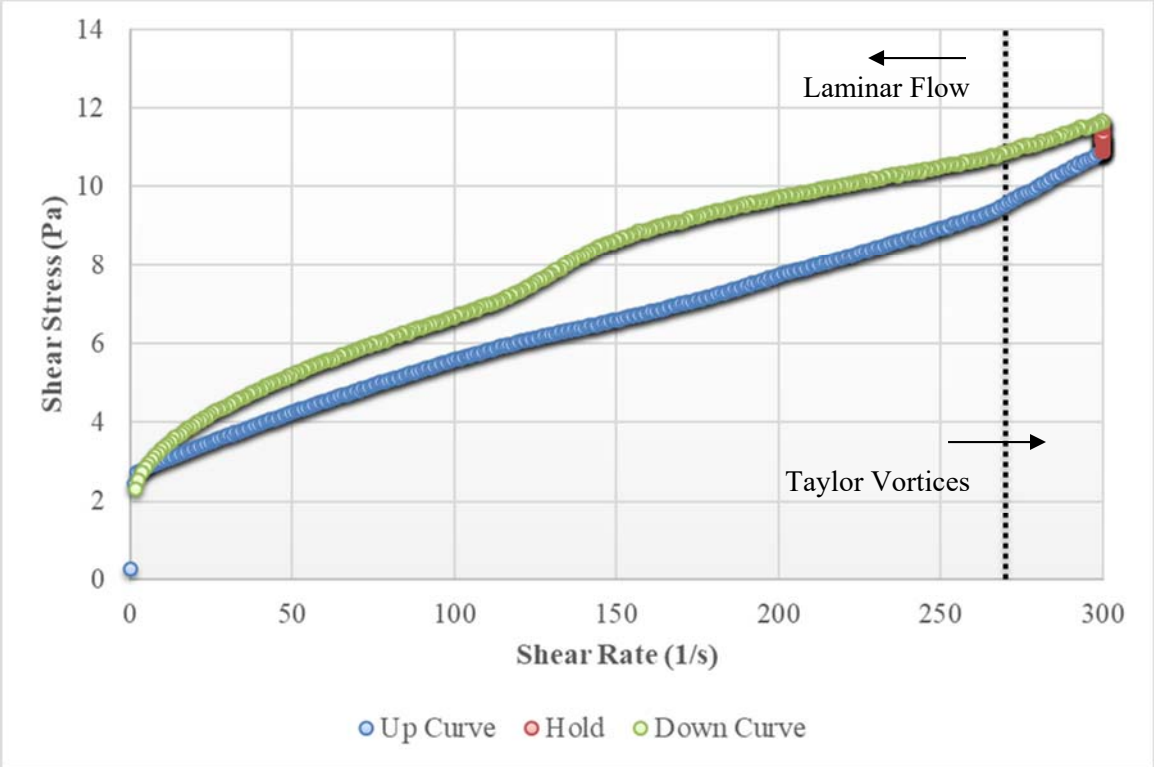

Figure B-6. Flow curve for SRNL SB9PS-Na2 Run 2.

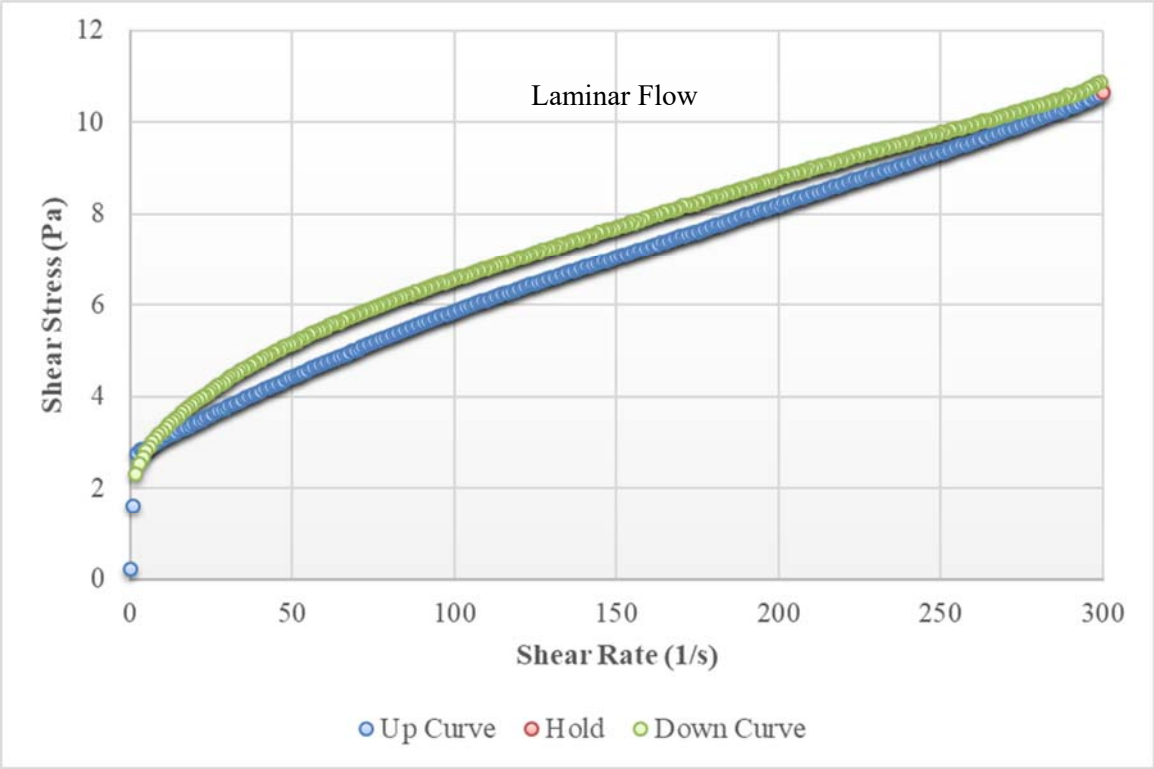

Figure B-7. Flow curve for Supplier SB9PS-Na2 Run 1.

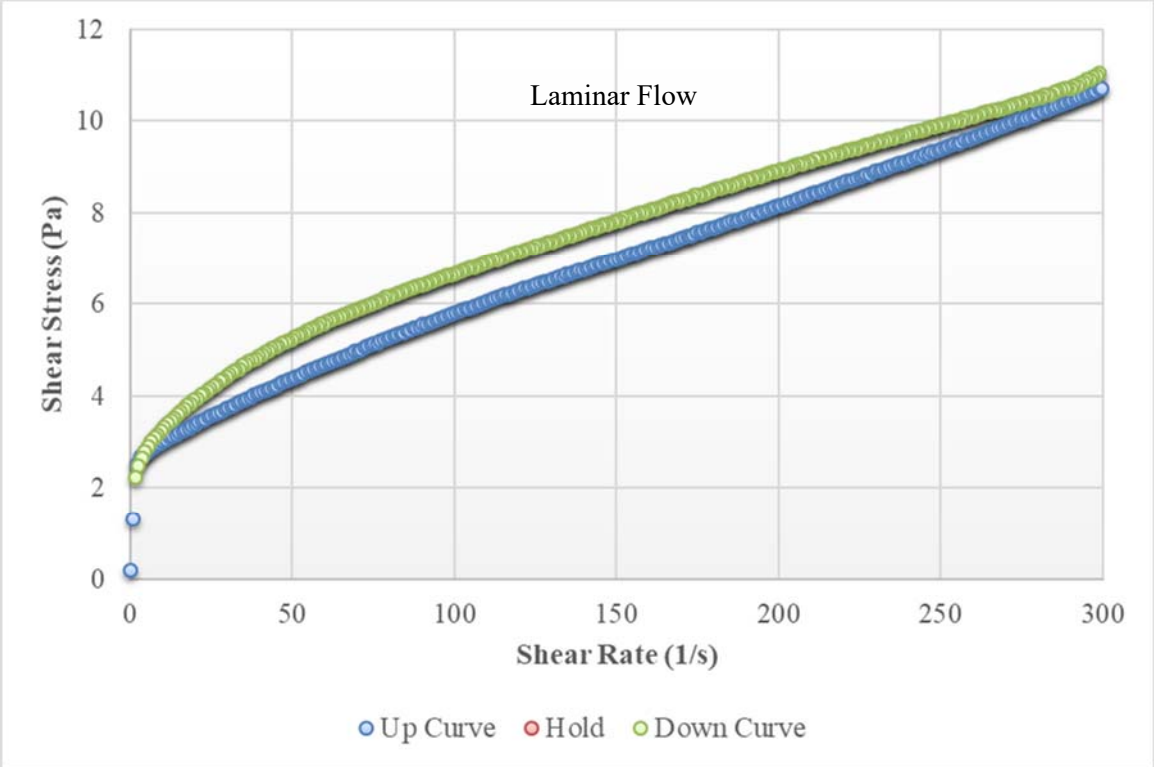

Figure B-8. Flow curve for Supplier SB9PS-Na2 Run 2.

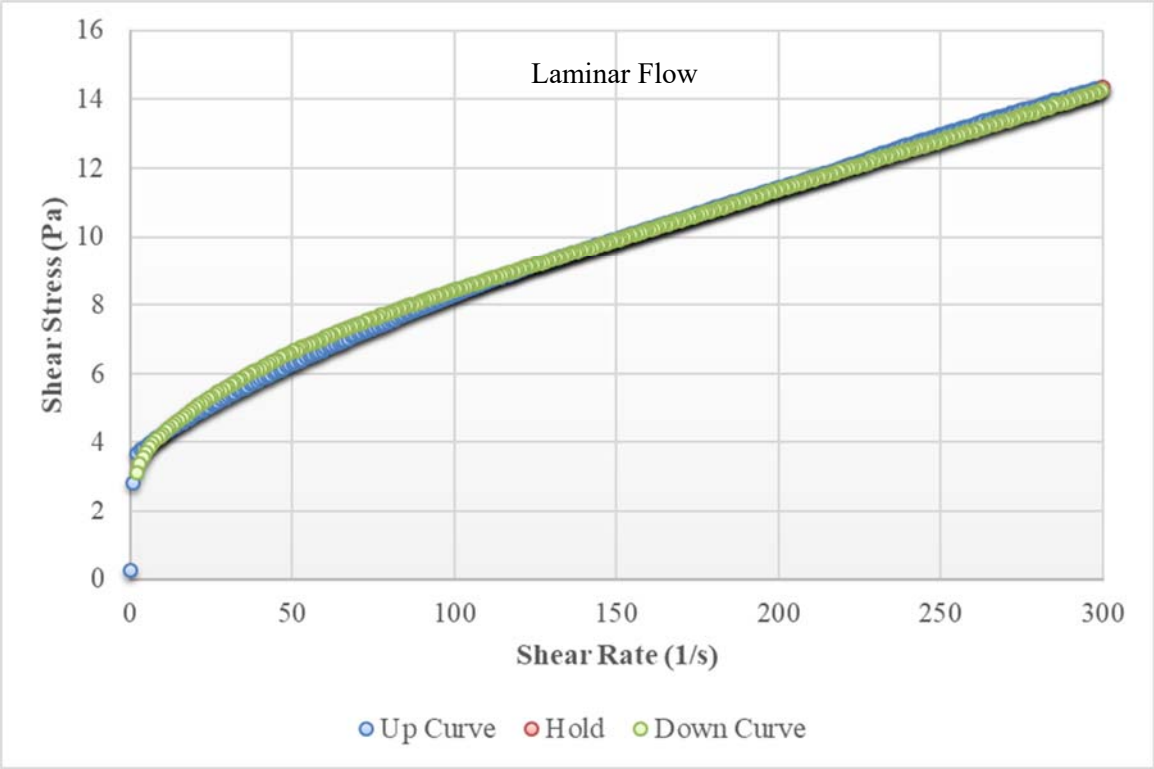

Figure B-9. Flow curve for Frit 803 Run 1.

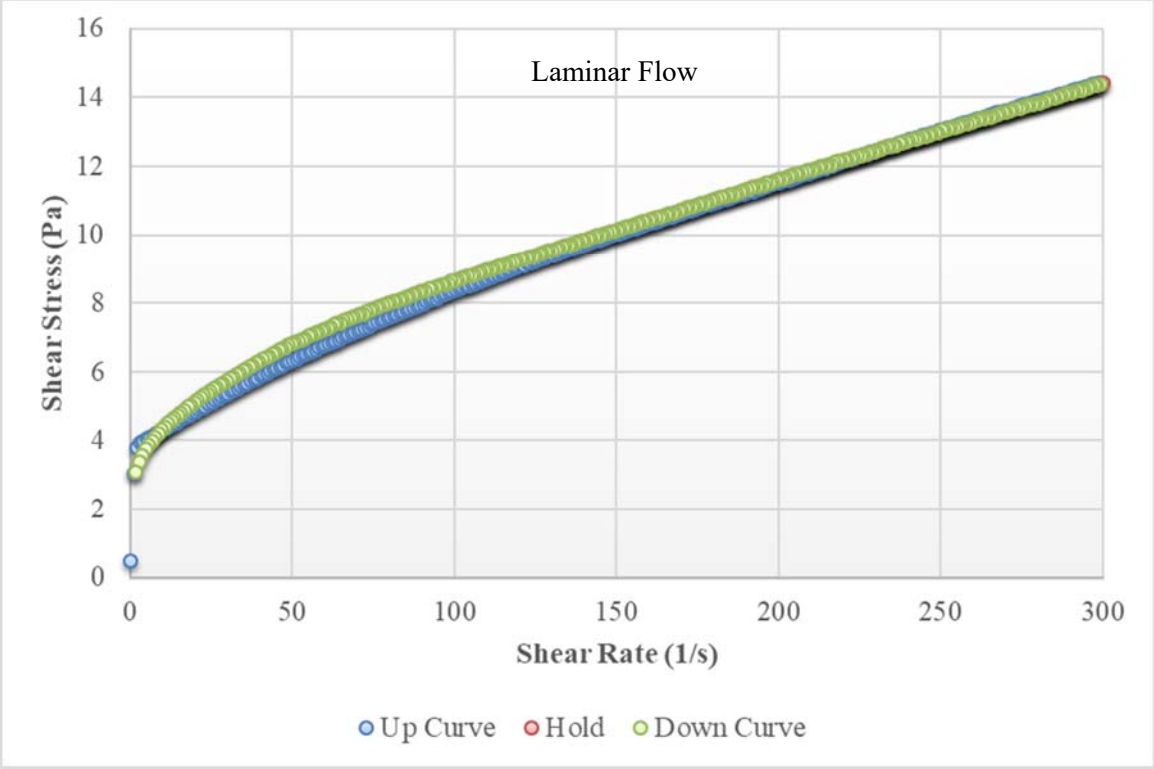

Figure B-10. Flow curve for Frit 803 Run 2.