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Rheological and Physical Properties of AZ-101 LAW Pretreated Waste and Melter Feed

A.P. Poloski
P. R. Bredt
R. G. Swoboda
D. E. Wallace

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Test specification: 24590-LAW-TSP-RT-02-009 Rev 0
Test plan: TP-RPP-WTP-188 Rev 0
Test exceptions: none
R&T focus area: Pretreatment & Vitrification
Test Scoping Statement(s): B-17

Battelle—Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by Test Specification 24590-LAW-TSP-RT-02-009 Rev. 0 and Test Plan TP-RPP-WTP-188 Rev. 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager WTP R&T Support Project	Date

Summary

Objectives

This document describes work performed under Battelle—Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-188 Rev 0 "AZ-101 (Envelope B) Melter Feed Rheology Testing." The objective of this report is to present physical and rheological properties of AZ-101 waste that is in a state similar to two streams anticipated in the Waste Treatment Plant (WTP). The first stream considered was the pretreated low-activity waste (LAW) stream that consists of the effluent from the cesium ion exchange column. The second stream is the LAW melter feed material. This material consists of the pretreated LAW waste stream mixed with a formulation of glass-former chemicals.

Conduct of Testing

The measurements of physical properties described in this document were performed in accordance with *Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements* (24590-WTP-GPG-RTD-001 Rev 0). Pretreated AZ-101 material at a Na concentration of 4.3 M was the source material for all these measurements. Initially, the 4.3 M Na pretreated material was diluted to three other Na concentrations (1.75 M, 2.75 M, and 3.75 M). It was observed that the material at 4.3 M Na did not contain visible solids. Physical properties were determined for the 1.75 M, 2.75 M, and 3.75 M Na samples at 25°C and 40°C. Lastly, a Haake RS300 rheometer was used to measure the rheological properties of the 1.75 M, 2.75 M, and 3.75 M Na samples at 25°C and 40°C.

The 1.75 M, 2.75 M, and 3.75 M Na pretreated waste samples were then mixed with project-approved glass-former chemicals (GFC) in a formulation consistent with "LAWB-83."[a] This material should be considered representative of the LAW melter feed stream in the WTP. The melter feeds were agitated to suspend the solids, and aliquots were drawn from all three homogenized samples at room temperature. The settling behavior of these 1.75 M, 2.75 M, and 3.75 M Na melter-feed aliquots were measured at 25°C and 40°C. The physical properties of these aliquots were then measured at 25°C and 40°C. Next, the samples were allowed to remain undisturbed for a 48-h period at a temperature of 40°C. A shear vane was used with a Haake RS300 rheometer to determine the 1.75 M, 2.75 M, and 3.75 M Na LAW melter-feed settled-solids shear strength at 40°C. The rheological properties of the 1.75 M, 2.75 M, and 3.75 M Na LAW melter feeds were measured with a Haake RS300 rheometer at 25°C and 40°C. Rheological measurements were performed on the 2.75 M Na melter feed sample based on mixing/aging times of 1 hour, 2 days, and 1 week. Particle-sizes were also measured on the 1.75 M Na melter feed sample.

Results and Performance Against Objectives

A sample of AZ-101 pretreated LAW sample was received at an initial sodium concentration of 4.3 M. The sample was diluted to 1.75, 2.75, and 3.75 M Na concentrations. The results from the testing of the AZ-101 pretreated waste at 1.75 M, 2.75 M, and 3.75 M Na concentrations are summarized in Table S.1 and Table S.2. Physical-properties analysis on these samples indicates a density ranging from 1.10 to 1.20 g/mL with dissolved-solids contents ranging from 12% to 23%, and pH ranging from 13.2 to

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[a] LAWB-83 is a glass formulation developed by Vitreous State Laboratory (VSL) at the Catholic University of America.

13.6 as concentration increases from 1.75 to 3.75 M Na. No precipitated solids were measured or observed in these samples. Flow curves from these samples indicate that the fluid should be characterized as a low-viscosity Newtonian fluid with the maximum measured viscosity of 2.4 cP.

Table S.1. Summary of AZ-101 Pretreated LAW Measurements at 25°C

Physical Property [a]	Units	1.75 M	2.75 M	3.75 M
pH	n/a	13.2	13.4	13.6
Viscosity (Newtonian)	cP	1.4	1.8	2.4
Bulk Density	g/mL	1.095	1.150	1.203
Vol% Settled Solids	%	a	a	a
Density of Centrifuged Solids	g/mL	a	a	a
Vol% Centrifuged Solids	%	a	a	a
Wt% Centrifuged Solids	%	a	a	a
Supernatant Density	g/mL	1.095	1.150	1.203
Density of Settled Solids	g/mL	a	a	a
Wt% Settled Supernatant	%	a	a	a
Wt% dissolved solids in supernatant	%	12.1%	17.9%	23.1%
Wt% total solids in Centrifuged Sludge	%	a	a	a
Wt% Total Solids	%	12.1%	17.9%	23.1%
Wt% Undissolved Solids (UDS)	%	a	a	a
Wt% UDS in Settled Sludge	%	a	a	a
wt% UDS in Centrifuged Sludge	%	a	a	a
Average Particle Density	g/mL	a	a	a
Settled solids Density	g/mL	a	a	a
Centrifuged Solids Density	g/mL	a	a	a
Wt% centrifuged solids	%	a	a	a
Wt% settled solids	%	a	a	a
Vol% UDS	%	a	a	a
Vol% UDS in settled solids	%	a	a	a
Vol% UDS in centrifuged solids	%	a	a	a
a—too little solids to quantify.				

Table S.2. Summary of AZ-101 Pretreated LAW Measurements at 40°C

Physical Property [a]	Units	1.75 M	2.75 M	3.75 M
Viscosity (Newtonian)	cP	1.1	1.4	1.7
Bulk Density	g/mL	1.086	1.137	1.187
Vol% Settled Solids	%	a	a	a
Density of Centrifuged Solids	g/mL	a	a	a
Vol% Centrifuged Solids	%	a	a	a
Wt% Centrifuged Solids	%	a	a	a
Supernatant Density	g/mL	1.086	1.137	1.187
Density of Settled Solids	g/mL	a	a	a
Wt% Settled Supernatant	%	a	a	a
Wt% dissolved solids in supernatant	%	12.1%	17.9%	23.1%
Wt% total solids in Centrifuged Sludge	%	a	a	a
Wt% Total Solids	%	12.1%	17.9%	23.1%
Wt% UDS	%	a	a	a
Wt% UDS in Settled Sludge	%	a	a	a
Wt% UDS in Centrifuged Sludge	%	a	a	a
Average Particle Density	g/mL	a	a	a
Settled solids Density	g/mL	a	a	a
Centrifuged Solids Density	g/mL	a	a	a
Wt% centrifuged solids	%	a	a	a
Wt% settled solids	%	a	a	a
Vol% UDS	%	a	a	a
Vol% UDS in settled solids	%	a	a	a
Vol% UDS in centrifuged solids	%	a	a	a
a—too little solids to quantify.				

The results from the tests performed on the melter-feed material are summarized in Table S.3 and Table S.4. When glass-former chemicals were added to the AZ-101 pretreated LAW, the pH of the solution dropped from the 13.2 to 13.6 range to a 7.9 to 7.1 range as Na concentration increases from 1.75 to 3.75 M. This is most likely due to the relatively large quantity of boric acid in the LAWB-83 melter-feed formulation. Such a large change in pH can result in significant solids precipitation. This solids precipitation was observed in decanted AZ-101 supernate that was separated from the settled-solids layer for shear-strength analysis. It is hypothesized that these precipitated solids bridge the insoluble glass-former chemicals, resulting in extremely high measured shear strengths exceeding 18,000 Pa. Materials with shear strengths of this magnitude will be extremely difficult to mobilize in the WTP. To avoid this situation during WTP operation, the melter-feed solids must constantly be suspended and not allowed to settle. If loss of agitation occurs in the WTP, operational controls must be in place to transfer this material to an actively mixed tank before the solids can settle.

Table S.3. Summary of AZ-101 Melter-Feed Measurements at 25°C

Physical Property[a]	Units	1.75 M	2.75 M	3.75 M
pH	n/a	7.9	7.5	7.1
Viscosity (Newtonian)	cP	18.9	80.0	118.7
Bulk Density	g/mL	1.534	1.736	1.890
Vol% Settled Solids	%	50.2%	73.8%	93.0%
Density of Centrifuged Solids	g/mL	1.934	1.939	1.953
Vol% Centrifuged Solids	%	50.2%	73.7%	93.2%
Wt% Centrifuged Solids	%	63.4%	82.4%	96.5%
Supernatant Density	g/mL	1.151	1.171	1.092
Density of Settled Solids	g/mL	1.91	1.93	1.94
Wt% Settled Supernatant	%	36.6%	17.6%	3.5%
Wt% dissolved solids in supernatant	%	16.0%	18.8%	20.5%
Wt% total solids in Centrifuged Sludge	%	71.8%	72.0%	70.9%
Wt% Total Solids	%	51.4%	62.7%	69.1%
Wt % UDS	%	42.1%	54.0%	61.1%
Wt% UDS in Settled Sludge	%	67.2%	65.4%	63.6%
Wt% UDS in Centrifuged Sludge	%	67.2%	65.6%	63.6%
Average Particle Density	g/mL	2.84	2.95	3.54
Settled solids Density	g/mL	1.92	1.93	1.95
Centrifuged Solids Density	g/mL	1.92	1.94	1.95
Wt% centrifuged solids	%	62.7%	82.3%	96.1%
Wt% settled solids	%	62.7%	82.5%	96.1%
Vol% UDS	%	22.8%	31.8%	32.7%
Vol% UDS in settled solids	%	45.4%	42.9%	35.1%
Vol% UDS in centrifuged solids	%	45.4%	43.1%	35.1%

Table S.4. Summary of AZ-101 Melter-Feed Measurements at 40°C

Physical Property [a]	Units	1.75 M	2.75 M	3.75 M
Maximum Settled Solids Shear Strength	Pa	>18,600	>11,600	>11,600
Viscosity (Newtonian)	cP	13.5	32.6	72.2
Bulk Density	g/mL	1.523	1.741	1.858
Vol% Settled Solids	%	46.7%	67.4%	86.0%
Density of Centrifuged Solids	g/mL	1.976	2.004	1.972
Vol% Centrifuged Solids	%	42.9%	65.5%	85.1%
Wt% Centrifuged Solids	%	55.7%	75.7%	90.4%
Supernatant Density	g/mL	1.179	1.218	1.188
Density of Settled Solids	g/mL	1.91	1.98	1.96
Wt% Settled Supernatant	%	44.3%	24.3%	9.6%
Wt% dissolved solids in supernatant	%	18.9%	24.1%	27.0%
Wt% total solids in Centrifuged Sludge	%	77.8%	75.3%	74.1%
Wt% Total Solids	%	51.8%	62.9%	69.6%
Wt% UDS	%	40.4%	51.1%	58.3%
Wt% UDS in Settled Sludge	%	68.8%	66.0%	63.9%
Wt% UDS in Centrifuged Sludge	%	72.5%	67.4%	64.4%
Average Particle Density	g/mL	2.67	2.95	3.12
Settled solids Density	g/mL	1.92	1.99	1.97
Centrifuged Solids Density	g/mL	1.98	2.02	1.98
Wt% centrifuged solids	%	55.8%	75.8%	90.5%
Wt% settled solids	%	58.8%	77.5%	91.2%
Vol% UDS	%	23.0%	30.1%	34.7%
Vol% UDS in settled solids	%	49.3%	44.4%	40.3%
Vol% UDS in centrifuged solids	%	53.7%	46.0%	40.8%

The settling behavior of the AZ-101 LAW melter feed can be characterized as “zone” or “hindered” settling. Depending on tank volume in the WTP, settling experiments indicate that a settled-solids layer with a high solids loading can form 24 hours after loss of agitation. This indicates that an operational constraint of several hours is required as the maximum time before evacuation from the unagitated tank to an agitated tank before slurry mobilization becomes extremely difficult.

After settling for 72 hours, the volume fraction of settled solids decreases as temperature increases. This behavior is most likely due to tighter particle packing as a result of particle dissolution at elevated temperatures. Because the settled-solids volume does not appear to significantly change before and after centrifugation, maximum packing appears to have been reached after settling for three days at 25°C. However, at 40°C, the maximum packing efficiency does not appear to be reached after three days of settling as the solids-layer volume appears to decrease approximately 10% after centrifugation at each sodium concentration.

Physical-properties testing reveals that, as expected, the quantity of total and undissolved solids (UDS) increases with sodium concentration. This is due to the increased quantity of GFC required for the melter-feed formulation at higher sodium concentrations. When the temperature is increased from 25°C to 40°C, the GFC or solids precipitated during the GFC addition appear to dissolve slightly. This is reflected by the increasing dissolved-solids content and decreasing undissolved-solids content as temperature increases at each sodium concentration.

At low sodium concentrations, AZ-101 LAW melter feed exhibits Newtonian rheological behavior. At 1.75 M Na at 40°C, the Newtonian viscosity at the low range was approximately 14 cP. At 2.75 M Na and 25°C, the Newtonian viscosity at the high range was approximately 80 cP. The high-concentration melter feed at 3.75 M Na appeared to behave as a power-law fluid. However, a good fit could be achieved with the Bingham model. At 25°C, the Bingham consistency was measured at 106 cP with a yield stress of 9 Pa. A fluid of this consistency is expected to be difficult to process in the WTP. However, when the temperature is increased to 40°C, the Bingham consistency drops to 58 cP, resulting in a fluid that is easier to process.

Glass-former chemicals were continuously mixed with an AZ-101 2.75 M Na pretreated waste sample. At intervals of 1 hour, 2 days, and 1 week, the rheology and pH of the sample were measured. Results from these tests are shown in Table S.5. The 2.75 M Na AZ-101 melter feed appears extremely thixotropic. The thixotropy is most likely due to precipitated solids that formed during the mixing/aging test process. These solids are suspected of being the cause of the high shear strengths observed in the baseline melter-feed rheology samples. During the mixing/aging test, the steady-state rheology of the fluid remained Newtonian with relatively low viscosities compared to the baseline measurements at the same sodium molarity.

Table S.5. Summary of 2.75 M Na AZ-101 LAW Melter-Feed Mixing/Aging Measurements

Description	Units	25°C	40°C
Viscosity (1-h mixing time)	cP	34.6	26.5
Viscosity (2-days mixing time)	cP	34.4	8.3
Viscosity (1-wk mixing time)	cP	19.6	45.1
pH (1-h mixing time at ambient)	--	7.6	NM
pH (1-day mixing time at ambient)	--	7.7	NM
pH (1-wk mixing time at ambient)	--	7.8	NM
NM—Not measured as part of scope.			

The particle-size distribution of a 1.75 M Na melter feed sample was measured. The particle-size distribution exhibits two major peaks, one in approximately the 0.5- to 1-μm range and the other in approximately the 10- to 30-μm range (see Figure S.1). Approximately 10 vol% of the particles are below 0.9 μm, 50 vol% (i.e., median value) below 13.3 μm, 90 vol% below 56.7 μm, and 95 vol% below 74 μm. With particle sizes below 100 μm, no significant process challenges with respect to particle settling are anticipated. The 50% sonication particle size result should be considered the primary particle size distribution because of the high repeatability of particle size results between subsamples. The samples were sonicated to break apart agglomerates of small particles and measure the primary particle size distribution of the suspension. The 50% value refers to the percentage of maximum sonication power applied to the samples.

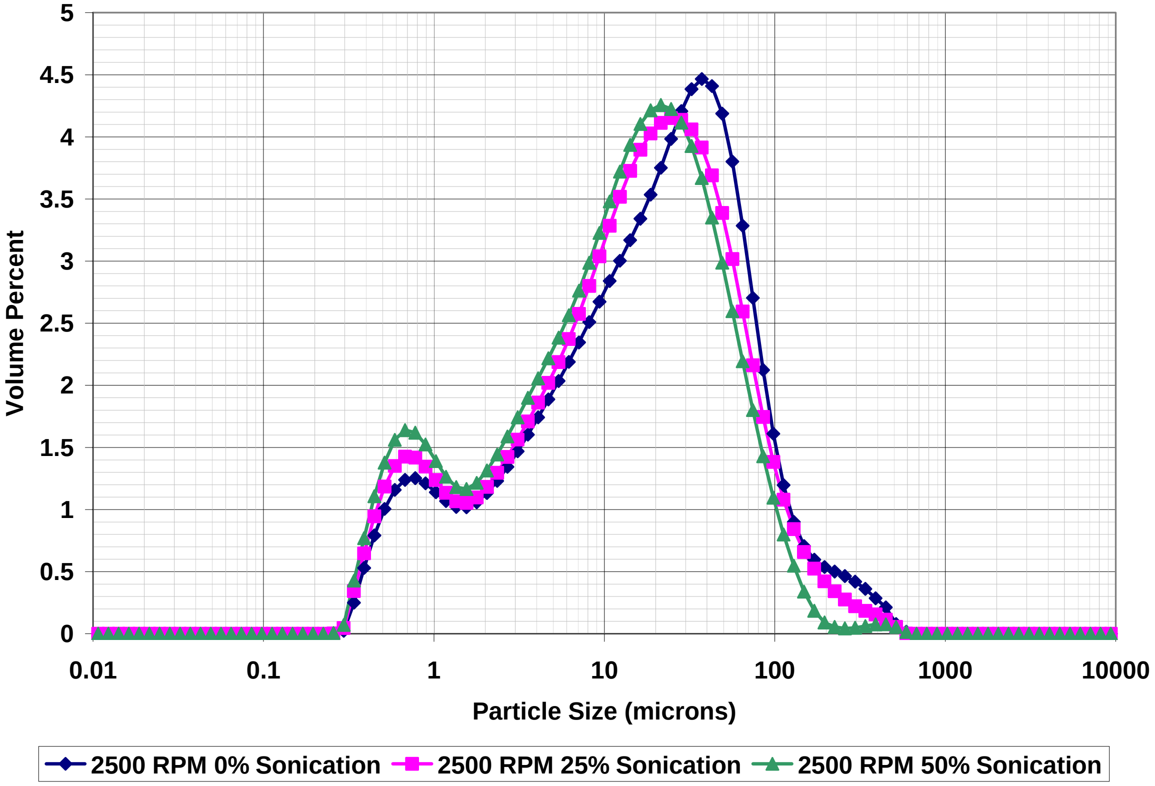

Figure S.1. Summary of AZ-101 1.75 M Na LAW Melter Feed and LAWB-83 Glass Former Mix Particle Size Distribution

Quality Requirements

PNWD implements the RPP-WTP quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Part 2.7. These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual*. The analytical requirements are implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

A matrix that cross-references the NQA-1 and 2a requirements with the PNWD's procedures for this work is given in Test Plan, TP-RPP-WTP-188 Rev 0, *AZ-101 (Envelope B)LAW Melter Feed Rheology Testing*. It includes justification for those requirements not implemented.

Experiments that are not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System" assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification, 24590-LAW-TSP-RT-02-009 Rev 0, BNI's QAPjP, PL-24590-QA00001, is not applicable since the work was not performed in support of environmental/regulatory testing, and the data will not be used as such.

PNWD addresses internal verification and validation activities by conducting an Independent Technical Review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

Issues

The results from this test raise the following issues in regard to processing these materials through the WTP:

- The 3.75 M Na melter feed suspensions at 40°C exhibited Newtonian behavior with viscosities that are within the current draft LAW melter feed bounding conditions of a Bingham plastic consistency index between 0.4 to 90 cP and a Bingham plastic yield index not to exceed 15 Pa[b]. This indicates that the material is relatively easy to transport. However, at 25°C, the 3.75 M Na melter-feed suspension possesses rheological properties that exceed the bounding window and could be difficult to transport.

- The AZ-101 LAW melter-feed shear-strength data indicate that difficulties could arise in operations that involve moving the material from a settled configuration. This is likely to happen during plant upset conditions. Examples of such operations include: 1) resuspending this material from a settled-solids configuration in a mixing vessel and 2) initiating pipeline flow with material that has settled in the pipe. Poloski et al. (2003) established a maximum bounding condition for shear strength at 625 Pa. When shear strength exceeds this value, process difficulties may be encountered. The timeframe by which transport difficulties may arise due to loss of process agitation has not been determined.
  - The settled-solids shear strength of the 1.75, 2.75, and 3.75 M Na melter-feed material is higher than expected. The measured shear strengths exceeded 18,600 Pa for the 1.75 M Na melter feed at 40°C and 11,600 Pa for the 2.75 and 3.75 M Na melter feed at 40°C.
  - This high shear strength could be the result of dropping the pH of the suspension with the addition of boric acid in the glass-former chemicals. A pH change from 13.5 to 7.5 is expected to precipitate aluminum hydroxide. Solids precipitation was observed in a decanted portion of melter-feed supernate. These precipitated solids may have bridged the particles of the settled insoluble glass-former chemicals, resulting in extremely high shear strengths. Such high shear strengths must be overcome by operational constraints in the WTP. If a tank with this melter feed loses agitation, the tank must be promptly evacuated to an agitated vessel. The chemical behavior underlying this phenomenon could be examined by solid-state NMR and other spectroscopic methods, leading to development of strategies to mitigate the formation of high shear strength settled solids.

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[b] Poloski A, H Smith, G Smith, and B Calloway. 2003. *Technical Basis for LAW Vitrification Stream Physical and Rheological Property Bounding Conditions.* WTP-RPT-098, Rev. A, Battelle—Pacific Northwest Division, Richland, WA.

Acronyms

BNI	Bechtel National Inc.
GFC	Glass-Former Chemicals
LAW	Low-Activity Waste
MFPV	Melter Feed Preparation Vessel
MFV	Melter Feed Vessel
N/A	Not Applicable
NIST	National Institute of Standards and Technology
PNWD	Battelle – Pacific Northwest Division
PSD	Particle-Size Distribution
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan
RPP	River Protection Project
R&T	Research and Technology
UDS	Undissolved Solids
VSL	Vitreous State Laboratory
WTP	Waste Treatment Plant
WTPSP	Waste Treatment Plant Support Project

Definitions

Apparent Viscosity – The measured shear stress divided by the measured shear rate.

Density – The mass per unit volume.

Interstitial Solution – The solution contained between the suspended solid particles of a sludge sample.

Newtonian Fluid – A fluid whose apparent viscosity is independent of shear rate.

Non-Newtonian Fluid – A fluid whose apparent viscosity varies with shear rate.

Rheogram/Flow Curve – A plot of shear stress versus shear rate.

Shear Strength – The minimum stress required to initiate fluid movement as determined by the vane method. This definition is different from "yield stress," which is defined below.

Sludge – Wet solids having little or no standing liquid (i.e., mud-like).

Slurry – A mixture of solids and solution.

Solution – A liquid phase possibly containing dissolved material.

Supernatant Liquid – A liquid phase overlying material deposited by settling, precipitation, or centrifugation.

Solids Settling Rate – The rate at which solids in a homogenized sample settle. This is typically the change in the settled-solids interface height as a function of time.

vol% Settled Solids – The percentage of the volume of the slurry sample that the settled solids occupy after settling for 72 hours under one gravity. These settled solids will contain interstitial solution.

vol% Centrifuged Solids – The volume of the solids layer that separates from the bulk slurry after 1 hour of centrifugation at 1000 gravities divided by the total sample volume on a percentage basis. These centrifuged solids will contain interstitial solution.

wt% Total Oxides – The percentage of the mass of the bulk sample that remains after converting all non-volatile elements to oxides. Some volatile elements such as cesium might be lost in this process.

wt% Dissolved Solids – The mass of dissolved species in the supernatant liquid divided by the total mass of the supernatant liquid on a percentage basis. This definition is the same as "wt% Dissolved Solids" from Table 4-2 (a) from the Research and Technology (R&T) plan, document number 24590-WTP-PL-RT-01-002, latest revision, for waste sample slurries. This is also the same as "wt% Oven Dried Solids" from Table 4-2 (b) from the R&T plan, document number

24590-WTP-PL-RT-01-002, latest revision, for the liquid-fraction analysis. This is also the same as the "wt% Soluble Solids" from Table 4-2 (c) from the R&T plan, document number 24590-WTP-PL-RT-01-002, latest revision, for the HLW solids analyses.

wt% Total Dried Solids – The percentage of the mass of the sample that remains after removing volatiles including free water by drying at 105 ± 5°C for 24 hours. This definition is the same as "wt% Total Dried Solids" from Table 4-2 (a) from the R&T plan, document number 24590-WTP-PL-RT-01-002, latest revision, for waste sample slurries.

wt% Undissolved Solids – A calculated value reflecting to the mass (on a percent basis) of solids remaining if all the supernatant liquid and interstitial solution could be removed from the bulk slurry.

Yield Stress – The minimum stress required to initiate fluid movement as determined by a flow curve using a rheological model. This definition is different from "shear strength," which is defined above. (Note: this is the same value as "Yield Strength" as delineated in Table 4.2a of the WTP R&T Plan, document number 24590-WTP-PL-RT-01-002, latest revision.)

Contents

Figures

Tables

1.0 Introduction

The objectives of this work were to obtain accurate measurement of solids concentration, densities, and rheological properties (in accordance with test plan TP-RPP-WTP-188 Rev 0) on actual AZ-101 pretreated low-activity waste (LAW Envelope B) samples and corresponding melter-feed samples. The physical and rheological properties of these process streams are important considerations in selecting flowsheet and processing equipment such as mixers, pumps, piping, and tanks. Measurements on actual waste are also required to verify and validate results obtained with simulants.

Actual samples from Tank AZ-101 were used in this testing. Multiple AZ-101 slurry samples were received from Hanford's 222-S laboratory. These slurry samples were composited and characterized by Urie et al. (2002). Next, the solids from the initial slurry were removed through a cross-flow filtration operation as described by Geeting et al. (2002). The low solids permeate from this operation was processed through cesium and technetium ion exchange columns. The cesium ion exchange work is described by Fiskum et al. (2003). The technetium ion exchange work is to be described in a future report by Burgeson et al.[a]

The resulting effluent stream from these ion exchange processes is similar to the cesium ion exchange effluent that will be processed in the plant and is termed "pretreated" AZ-101 LAW and is the focus of this document. The composition of the pretreated AZ-101 LAW after cesium ion exchange can be found in Table 3.5 of Fiskum (2003). The subsequent technetium removal process resulted in dilution of the sample from 4.87 M with respect to Na to 4.3 M Na. It is anticipated other minor compositional changes may have also occurred during the technetium ion exchange, but these should not have had a significant impact on the major components. A detailed compositional analysis of the effluent from the technetium ion exchange is anticipated in the future report by Burgeson et al.[a]

The pretreated AZ-101 LAW was received at a concentration of 4.3 M Na. The AZ-101 pretreated LAW was adjusted to various Na concentrations for physical and rheological property measurements. The purpose of adjusting the sodium concentration was to bound the physical and rheological property measurements about a Waste Treatment Plant (WTP) operating point of 2.75 M Na (Diener, 2003). The sodium concentrations tested include 1.75 M, 2.75 M, and 3.75 M Na AZ-101 pretreated LAW.

The physical and rheological properties were measured in accordance with the WTP project approved guidelines developed by Smith and Prindiville (2002). Rheological testing was conducted at 25°C and 40°C. Settling and physical-properties testing was conducted at ambient (nominally 23°C to 25°C) and 40°C. For this work, ambient is reported as 25°C.

Project-approved glass-former chemicals (Hansen and Schumacher 2003) were added to the 1.75 M, 2.75 M, and 3.75 M Na samples to produce a LAW "melter feed" stream. The detailed chemical

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[a] Burgeson IE, DL Blanchard Jr, and JR Deschane. *Small Column Testing of SuperLig® 639 for Removal of ^{99}Tc from Hanford Tank Waste Envelope A (241-AZ-101).* WTP-RPT-058, Rev A, Battelle—Pacific Northwest Division, Richland, Washington.

composition of the melter feed is to be included in a future report by Smith et al[b]. Physical and rheological properties of these melter-feed samples were measured. Mixing and aging studies were also conducted on the 2.75 M Na melter-feed sample. This testing entailed placing a 2.75 M Na pretreated LAW sample in a mixing vessel at a power-to-volume ratio consistent with that expected in the WTP. Glass formers were added, and the mixing continued for 1 week. During this week, rheograms were obtained after 1 hour, 1 day, and 1 week.

This report describes the experimental approach and results of the testing. Specifications for this work were provided in Test Specification Number 24590-LAW-TSP-RT-02-009. This report also provides the means of communicating results of testing conducted under test plan (TP-RPP-WTP-188).

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[b] H. D. Smith, R. J. Bates, P. R. Bredt, L. R. Greenwood, M. J. Schweiger, M. W. Urie, J. D. Vienna, D. R. Weier. Vitrification and Initial Product Testing of AP101 Pretreated LAW Envelope A Glass. WTP-RPT-092, Rev A, Battelle—Pacific Northwest Division, Richland, Washington.

2.0 Sample-Preparation Details

This section details preparation of the actual AZ-101 samples used for testing. Section 2.1 describes sodium concentration adjustment steps used to achieve the target Na concentrations. Section 2.2 describes the addition of Glass-Former Chemicals (GFC) to the pretreated feed to form the melter feed. Unless otherwise stated, all temperatures in this work are reported to ±2°C.

2.1 Pretreated Feed

The pretreated waste sample was received at a Na concentration of 4.3 M. The 4.3 M Na sample was diluted by adding deionized water to target Na concentrations of 1.75, 2.75, and 3.75 M. No precipitation was observed due to pH changes during the dilution. These samples are shown in Figure 2.1. Throughout this document, samples labeled with an "A" denote a concentration of 1.75 M Na, "B" denote a concentration of 2.75 M Na, and "C" denote a concentration of 3.75 M Na.


1.75 M Na AZ-101 Pretreated LAW | 2.75 M Na AZ-101 Pretreated LAW | 3.75 M Na AZ-101 Pretreated LAW

Figure 2.1. Photograph of 1.75, 2.75, and 3.75 M Na AZ-101 Pretreated Wastes

2.2 Melter Feed

After physical and rheological characterization of the pretreated feed, GFC were added to the 1.75, 2.75, and 3.75 M Na pretreated LAW samples. The purpose of these samples is physical and rheological characterization of the AZ-101 Envelope B LAW melter feed. A second 2.75 M Na sample was prepared as a melter feed for a mixing/aging study that is discussed in Section 4.4. Glass-former quantities were based on the formulation provided by the Vitreous State Laboratory (VSL) (LAWB-83). The VSL formulation was based on a 2.75 M Na feed on a mass per liter basis. The quantities of glass formers were first adjusted on a per liter basis to the target Na concentrations (1.75 and 3.75 M Na). The masses to be added to the 1.75 M Na samples were calculated using an adjustment factor of 0.636 (1.75 M Na/2.75M Na). The adjustment factor for the 3.75 M Na sample was 1.36 (3.75 M Na/2.75 M Na). These adjusted masses on a liter basis were then multiplied by the volume of sample to calculate how much glass formers to add to each sample. Table 2.1 lists the quantity and type of glass formers added to each of the two AZ-101 pretreated feed samples.

Before adding GFC, the individual dry-glass-former constituents were weighed into a vessel and mixed together at the formulation ratio (see Table 2.2) until homogeneous. The appropriate mass to add to each of the samples was then weighed into a separate container. The glass-former mixtures were then slowly added to the samples while the samples were stirred using a mechanical agitator. Following the glass-former addition, the samples were stirred for an additional hour. The initial agitator rotational rate was specified in Test Plan TP-RPP-WTP-188 Rev 0 by a relationship (see Equation 2.1) designed to keep the level of power input to the mixture per unit volume constant between WTP mixer designs and the lab-scale mixer. If the calculated rotational rate resulted in poor mixing or a large vortex, the agitator rate was further adjusted to achieve good mixing.

$$N^3 = \left(1.96 \times 10^9 \text{ rpm}^3 \cdot \text{cm}^2\right) \cdot \frac{V}{D_i^5} \tag{2.1}$$

where N is the impeller speed (rpm), V is the sample volume (mL), and D_i is the impeller diameter (cm).

For the physical and rheological characterization samples, a 1.5-in.-diameter magnetic stir bar in a 6.9-cm (2.7-in.) diameter glass jar was used for mixing (see Figure 2.2). The magnetic stir bar was maintained at approximately 350 rpm in accordance with Equation 2.1. The quantity of GFC added to the 3.75 M Na pretreated LAW sample was large enough to inhibit effective mixing with the magnetic stir bar. For this sample, good mixing was achieved by replacing the magnetic stirrer with an overhead stirrer with a 6.4-cm (2.5-in.) impeller rotating at approximately 180 rpm. For the mixing/aging sample, an enclosed spherical flask was used to minimize evaporation over the week of mixing (see Figure 2.3). The spherical flask had a diameter of 3.4 in (8.6 cm). To achieve good mixing, a 2.5-cm (1.0-in.) impeller was used, rotating at approximately 800 rpm. Mixing details are summarized in Table 2.3.

After stirring for 1 hour, samples were removed for physical and rheological testing. Mixing continued for a full week with the mixing/aging sample. Samples were drawn and rheologically characterized after 1 hour, 1 day, and 1 week of mixing. Physical properties and rheology results are described in Sections 3 and 4, respectively.

Table 2.1. GFC Formulation (LAWB-83) for AZ-101 Envelope B

Additive	Comment	2.75 M Na VSL Glass Formulation (LAWB-83) g GFC/L Pretreated LAW
Kyanite (Al_2SiO_5)	Raw Kyanite, 325 Mesh	156.19
Orthoboric Acid (H_3BO_3)	Technical Grade Granular	282.85
Wollanstonite ($CaSiO_3$)	Powder untreated, NYAD 325 Mesh	236.47
Hemetite—Red Iron Oxide (Fe_2O_3)	Red Iron III Oxide, 325 Mesh Prince Mgt.	75.90
Lithium Carbonate (Li_2CO_3)	Chemetall Foote Co. Tech. Grade	170.61
Olivine (Mg_2SiO_4 with some Fe_2SiO_4)	325 Mesh (#180)	95.58
Ground Silica Sand (SiO_2)	Sil-co-Sil 75, 200 Mesh	517.69
Rutile (TiO_2)	Premium Grade, Airfloated	23.62
Zincite—Zinc Oxide (ZnO)	KADOX-920	76.96
Zircon Sand ($ZrSiO_4$)	Flour 325 Mesh	75.90
Sugar	Reagent Grade Granular	29.61
Total	n/a	1741.38

Table 2.2. Quantity of GFC Formulation (LAWB-83) Added to AZ-101 Envelope B Pretreated LAW Samples

Pretreated Feed Sodium Concentration (M)	Description	Initial Volume of Sample	Target Mass of GFC Added	Actual Mass of GFC Added	Percent Deviation
1.75	Physical and Rheological Characterization	183.3	203.1	209.3	3.1
2.75	Physical and Rheological Characterization	184.3	320.9	321.0	0.031
3.75	Physical and Rheological Characterization	184.4	437.8	437.8	0
2.75	Mixing/Aging	75.0	130.7	130.7	0

Table 2.3. Guideline Reporting Format Mixing Details

Melter Feed ID: LAWB-83	
Processing Scale (lab/bench, pilot, or full): lab	
Activity/Property	**Data or Explanation**
Order of Chemical Additions	Dry glass formers combined then added to waste in mixing vessel
Mixing Time	1 h
Impeller Speed	1.75 M Na aliquot: ~350 rpm 2.75 M Na aliquot: ~350 rpm 3.75 M Na aliquot: ~180 rpm 2.75 M Na mixing/aging aliquot: ~800 rpm
Impeller Diameter	1.75 M Na aliquot: 3.8 cm (1.5 in.) 2.75 M Na aliquot: 3.8 cm (1.5 in.) 3.75 M Na aliquot: 6.4 cm (2.5 in.) 2.75 M Na mixing/aging aliquot: ~6.4 cm (~2.5 in.)
Tank Diameter	1.75 M Na aliquot: ~6.9 cm (~2.7 in.) cylindrical 2.75 M Na aliquot: ~6.9 cm (~2.7 in.) cylindrical 3.75 M Na aliquot: ~6.9 cm (~2.7 in.) cylindrical 2.75 M Na mixing/aging aliquot: ~8.6 cm (~3.4 in.) spherical
Number of Baffles	0
Size of Baffles	NA
Depth of Impeller	1.75 M Na aliquot: bottom of vessel using magnetic stirrer 2.75 M Na aliquot: bottom of vessel using magnetic stirrer 3.75 M Na aliquot: sample midpoint using overhead stirrer 2.75 M Na mixing/aging aliquot: sample midpoint using overhead stirrer

a) 1.75 M Na AZ-101 Envelope B pretreated LAW with corresponding quantity of GFC Formulation (LAWB-83)

b) 2.75 M Na AZ-101 Envelope B pretreated LAW with corresponding quantity of GFC Formulation (LAWB-83)

Figure 2.2. Photographs of the CFC (LAWB-83) and AZ-101 Envelope B Pretreated LAW Physical and Rheological Characterization Samples Before Mixing

c) 3.75 M Na AZ-101 Envelope B pretreated LAW with corresponding quantity of GFC Formulation (LAWB-83)

Figure 2.2 (Contd)

a) GFC (LAWB-83) and 2.75 M Na AZ-101 Envelope B pretreated LAW mixing/aging sample before mixing

Figure 2.3. Photographs of 2.75 M Na AZ-101 Envelope B Mixing/Aging Sample

b) 2.75 M Na AZ-101 Envelope B melter feed mixing/aging sample during mixing

Figure 2.3 (Contd)

3.0 Physical-Properties Testing

Samples of the AZ-101 pretreated feed and melter feed described in Section 2 were characterized for selected physical properties according to the methodology defined in Section 4 of 24590-WTP-GPG-RTD-001, *Guidelines for Performing Chemical, Physical, and Rheological Properties* M*easurements*. Section 3.1 of this report provides the general protocol, nomenclature, equations, and definitions from the guidelines document. The following physical properties were all measured at 25°C with selected properties measured at 40°C as noted and required by the Test Plan (TP-RPP-WTP-188 Rev 0):

- Density of the bulk slurries, settled solids, centrifuged solids, and centrifuged supernatant.
- The weight percent (wt%) and volume percent (vol%) settled solids, wt% and vol% centrifuged solids, wt% total solids, wt% total dried solids, and wt% undissolved solids (UDS).

Under the guideline methodology, settled solids are defined as the solids layer that separates from the bulk slurry after 3 days of gravity settling. Centrifuged solids are defined as the solids layer that separates from the bulk slurry after 1 hour of centrifugation at 1000 gravities. Weight percent oven-dried solids is defined as the percent of solids remaining after oven drying the centrifuged solids fraction at 105ºC. Weight percent total dried solids is defined as the percent of solids remaining after drying the bulk sample (solid and liquid fractions) at 105ºC.

3.1 Methodology for Measuring Physical Properties

For this testing, a known mass of each slurry was placed in triplicate in volume graduated centrifuge cones. The total mass (M_B) and volume (V_B) of the bulk slurry were recorded, and the density of the bulk slurry calculated ($\rho_B=M_B/V_B$). These results can be biased low due to entrained gas as well as an inability to clearly measure the total sample volume due to material smeared on the sides of the centrifuge tubes. Therefore, the bulk slurry densities were recalculated later in the work using volumes recorded following centrifugation. The samples were then allowed to settle for 3 days. Following settling, the volume of the settled solids (V_{SS}) and volume of the bulk sample (V_B) were recorded. The vol% settled solids was then calculated ($P_{VSS} = V_{SS}/V_B \times 100\%$).

The settled slurries were then centrifuged at approximately 1,000 times the force of gravity for 1 hour. Note that for the 40ºC set of measurements, the aliquots were removed from a temperature-controlled oven at 40ºC prior to the centrifugation process, which occurred at ambient temperature (~23°C). After centrifugation, the aliquots were returned to the oven where the 40ºC testing temperature was restored. All of the centrifuged supernatant was then transferred to a graduated cylinder, its mass (M_{CL}) and volume (V_{CL}) were recorded, and the density was calculated ($\rho_{CL}=M_{CL}/V_{CL}$). The mass (M_{CS}) and volume (V_{CS}) of the centrifuged solids were also recorded. In addition, the vol% centrifuged solids ($P_{VCS} = V_{CS}/V_B \times 100\%$) was calculated.

In many cases, centrifugation can result in the release of gas in the form of bubbles or foams. Therefore, comparison of the bulk-density measurements before and after centrifugation is very important in understanding the rheology of some samples. In addition, it is possible that not all of the gas is released from the slurry by centrifugation, so the density results following centrifugation may be biased low.

The centrifuged solids and supernatant aliquots were dried separately at 105°C for 24 hours. The mass of the dried centrifuged supernatant (M_{DCL}) and the mass of the dried centrifuged solids (M_{DCS}) were then measured. Assuming that all mass lost during the drying process is water and not another volatile component, the wt% total dried solids in the bulk slurry was calculated ($P_{MTS} = \{[(M_{DCL} \times M_S)/(M_{VL} \times M_B)]+[M_{DCS}/M_B]\} \times 100\ \%$), where M_{VL} is the mass of centrifuged liquid before drying. Waters of hydration or volatile organics can lead to low bias in M_{DCS}/M_{CS}. The wt% oven-dried solids was calculated from $P_{ODS} = M_{DCS} / M_{CS} \times 100\%$.

A calculation was then performed to determine the wt% solids in the samples, excluding all interstitial liquid. This is referred to as P_{MUDS}. The following equation was used:

$$P_{MUDS} = \left(1 - \frac{1 - \dfrac{M_{DCS}}{M_{CS}}}{1 - \dfrac{M_{DCL}}{M_{VL}}} \right) \times \frac{M_{CS}}{M_B} \times 100\ \% \tag{3.1}$$

This calculation assumes that: 1) the supernatant and the interstitial liquid had the same composition, and 2) all mass loss during the drying of the centrifuged solids was water loss from interstitial liquid.

The mass percent of UDS (P_{MUSS}) in the settled solids layer can be calculated from Equation 3.2.

$$P_{MUSS} = \frac{(P_{MUDS}/100) \cdot M_B}{M_B - (V_B - V_{SS})\rho_{CL}} \times 100\ \% \tag{3.2}$$

The mass percent of UDS (P_{MUCS}) in the centrifuged solids layer can be calculated from Equation 3.3.

$$P_{MUCS} = \frac{(P_{MUDS}/100) \cdot M_B}{M_B - (V_B - V_{CS})\rho_{CL}} \times 100\ \% \tag{3.3}$$

The average particle density (ρ_p) of the UDS can be calculated from Equation 3.4.

$$\rho_p = \frac{(P_{MUDS}/100)}{\dfrac{1}{\rho_B} - \dfrac{1-(P_{MUDS}/100)}{\rho_{CL}}} \tag{3.4}$$

The density of the settled solids (ρ_{SS}) can be calculated from Equation 3.5.

$$\rho_{SS} = \frac{1}{\frac{(P_{MUSS}/100)}{\rho_p} + \frac{1-(P_{MUSS}/100)}{\rho_{CL}}} \tag{3.5}$$

The density of the centrifuged solids (ρ_{CS}) can be calculated from Equation 3.6.

$$\rho_{CS} = \frac{1}{\frac{(P_{MUCS}/100)}{\rho_p} + \frac{1-(P_{MUCS}/100)}{\rho_{CL}}} \tag{3.6}$$

The mass percent of settled solids (P_{MSS}) in the sample can be calculated from Equation 3.7.

$$P_{MSS} = \frac{\rho_{SS} \cdot V_{SS}}{M_B} \times 100\ \% \tag{3.7}$$

The mass percent of centrifuged solids (P_{MCS}) in the sample can be calculated from Equation 3.8.

$$P_{MCS} = \frac{\rho_{CS} \cdot V_{CS}}{M_B} \times 100\ \% \tag{3.8}$$

The vol% of UDS (P_{VUDS}) in the sample can be calculated from Equation 3.8.

$$P_{VUDS} = \frac{(P_{MUDS}/100) \cdot \rho_B}{\rho_p} \times 100\ \% \tag{3.8}$$

The vol% of UDS (P_{VUSS}) in the settled solids can be calculated from Equation 3.9.

$$P_{VUSS} = \frac{(P_{MUSS}/100) \cdot \rho_{SS}}{\rho_p} \times 100\ \% \tag{3.9}$$

The vol% of UDS (P_{VUCS}) in the centrifuged solids can be calculated from Equation 3.10.

$$P_{VUCS} = \frac{(P_{MUCS}/100) \cdot \rho_{CS}}{\rho_p} \times 100\ \% \tag{3.10}$$

3.2 Analysis of Physical-Properties Uncertainty

Assuming instrument errors of ±0.002 g for mass measurments and ±0.05 mL for volume measurements, the error propagation assoicated with each of the above equations is reported using a Taylor series expansion approximation.(e) When performing the physical-properties procedure, three aliquots are taken from the initial bulk sample. The average value from the three subsamples and resulting error propagation value neglects subsampling and procedural errors. The standard deviation from these three measurments is calculated to provide an indication of the overall error assoicated with these measurments. A large standard deviation relative to the error propogation value and the reported result indicates that errors other than instrument errors (e.g., subsampling and procedural errors) were significant during phyical-properties measurement. A large error-propogation value relative to the reported result indicates that the sample matrix was not suitable for accurate measurments using the physcial properties measurment procedure. When the error propogation value and standard deviation are both small relative to the reported result, high confidence in the reported value is recognized.

3.3 Physical Properties of AZ-101 Envelope B Pretreated LAW

Physical-properties results of the LAW pretreated wastes at each sodium concentration can be found in Table 3.1. Physical properties were measured at both ambient (25°C) and 40°C. Because the LAW pretreated feed did not contain any significant quantity of UDS, many of the slurry-based physical-property measurements were not applicable to this sample. Consequentially, only the supernatant density and dissolved-solids content were measured. As expected, the density of the supernatant decreases with decreasing sodium concentration and temperature, and the dissolved-solids content increases with increasing sodium concentration. Depending on sodium concentration and temperature, the density of the supernatant ranged from 1.086 g/mL to 1.203 g/mL. The dissolved-solids content was measured at 12.1, 17.9, and 23.1 wt% for the 1.75, 2.75, and 3.75 M Na samples, respectively.

(e) Details on this approximation can be found at: http://physics.nist.gov/cuu/Uncertainty/index.html.

Table 3.1. Physical Properties of 1.75, 2.75, and 3.75 M Na AZ-101 Envelope B Pretreated Waste at 25°C and 40°C

Physical Property[a]	Units	1.75 M Na 25°C ± error (SD) 40°C ± error (SD)	2.75 M Na 25°C ± error (SD) 40°C ± error (SD)	3.75 M Na 25°C ± error (SD) 40°C ± error (SD)
Bulk Density	g/mL	1.095 ± 0.009 (0.003) 1.086 ± 0.009 (0.002)	1.150 ± 0.010 (0.004) 1.137 ± 0.010 (0.004)	1.203 ± 0.010 (0.001) 1.187 ± 0.010 (0.001)
Vol% Settled Solids	%	a	a	a
Density of Centrifuged Solids	g/mL	a	a	a
Vol% Centrifuged Solids	%	a	a	a
Wt% Centrifuged Solids	%	a	a	a
Supernatant Density	g/mL	1.095 ± 0.009 (0.003) 1.086 ± 0.009 (0.002)	1.150 ± 0.010 (0.004) 1.137 ± 0.010 (0.004)	1.203 ± 0.010 (0.001) 1.187 ± 0.010 (0.001)
Density of Settled Solids	g/mL	a	a	a
Wt% Settled Supernatant	%	a	a	a
Wt% dissolved solids in supernatant	%	12.1% ± 0.0% (0.1%) 12.1% ± 0.0% (0.1%)	17.9% ± 0.0% (0.2%) 17.9% ± 0.0% (0.2%)	23.1% ± 0.0% (0.6%) 23.1% ± 0.0% (0.6%)
Wt% total solids in Centrifuged Sludge	%	a	a	a
Wt% Total Solids	%	12.1% ± 0.1% (0.1%) 12.1% ± 0.1% (0.1%)	17.9% ± 0.1% (0.2%) 17.9% ± 0.1% (0.2%)	23.1% ± 0.1% (0.6%) 23.1% ± 0.1% (0.6%)
Wt% UDS	%	a	a	a
Wt % UDS in Settled Sludge	%	a	a	a
Wt% UDS in Centrifuged Sludge	%	a	a	a
Average Particle Density	g/mL	a	a	a
Settled solids Density	g/mL	a	a	a
Centrifuged Solids Density	g/mL	a	a	a
Wt% centrifuged solids	%	a	a	a
Wt% settled solids	%	a	a	a
Vol% UDS	%	a	a	a
Vol% UDS in settled solids	%	a	a	a
Vol% UDS in centrifuged solids	%	a	a	a

a—too little solids to quantify.

3.4 Physical Properties of AZ-101 Envelope B Melter Feed

Physical properties results of the LAW melter feed at each sodium concentration (see Figure 3.1) can be found in Table 3.2. Physical properties measurements were performed at both ambient (25°C) and 40°C. As expected, the quantity of total and UDS increases with sodium concentration due to the increased quantity of GFC required for the melter feed formulation at higher sodium concentrations. When the temperature is increased from 25°C to 40°C, the insoluble GFC appear to dissolve slightly. This is reflected by the increasing dissolved solids content and decreasing UDS content as temperature increases at each sodium concentration.

The volume fraction of settled solids decreases as temperature increases, most likely due to tighter particle packing as a result of particle dissolution at elevated temperatures. Because the settled-solids volume does not appear to significantly change before and after centrifugation, maximum packing appears to have been reached after settling for 3 days at 25°C. However, at 40°C, the maximum packing efficiency does not appear to be reached after 3 days of settling as the solids-layer volume appears to decrease approximately 10% after centrifugation at each sodium concentration.

Due to the relatively small quantity of supernatant present in the 3.75 M Na sample at 25°C, several of the physical-properties measurements, including average particle density, wt% centrifuged solids , wt% settled solids, vol% UDS, vol% UDS in settled solids, and vol% UDS in centrifuged solids possessed relatively large error values. With an increase in temperature to 40°C, the quantity of supernatant increased, thus lowering the measurement error.

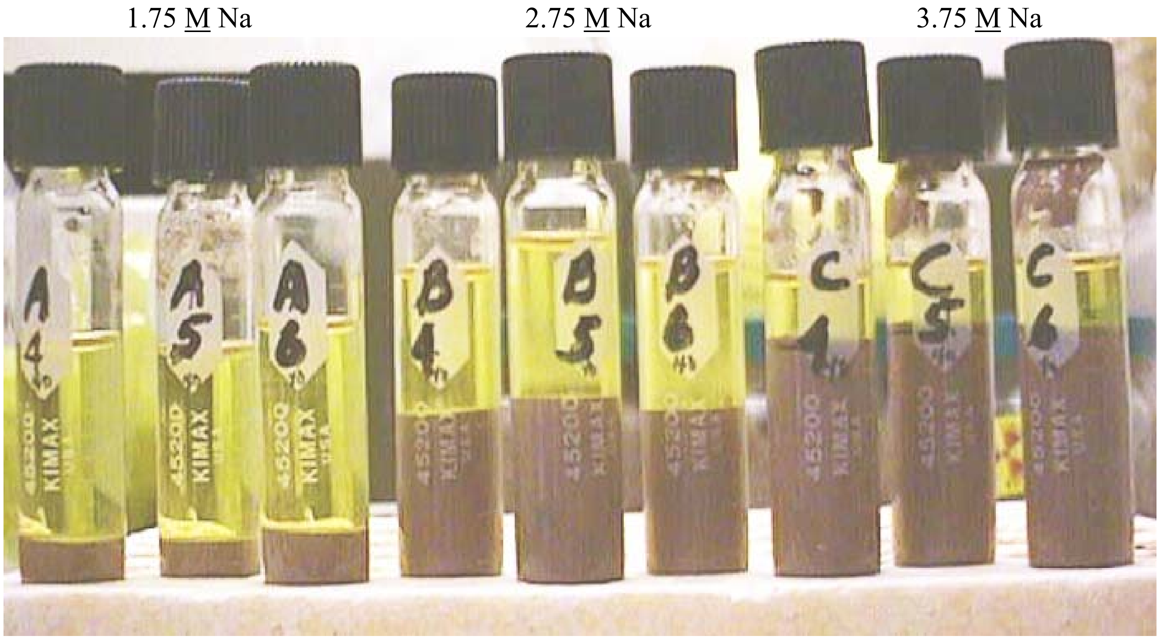


Figure 3.1. Photograph of AZ-101 Envelope B Melter Feed Physical-Property Samples

Table 3.2. Physical Properties of 1.75, 2.75, and 3.75 M Na AZ-101 Envelope B Melter Feed at 25°C and 40°C

Physical Property	Units	1.75 M Na	2.75 M Na	3.75 M Na
		25°C ± error (SD) 40°C ± error (SD)	25°C ± error (SD) 40°C ± error (SD)	25°C ± error (SD) 40°C ± error (SD)
Bulk Density	g/mL	1.534 ± 0.016 (0.001) 1.523 ± 0.017 (0.008)	1.736 ± 0.017 (0.006) 1.741 ± 0.016 (0.008)	1.890 ± 0.018 (0.014) 1.858 ± 0.018 (0.008)
Vol% Settled Solids	%	50.2% ± 1.2% (0.9%) 46.7% ± 1.2% (1.2%)	73.8% ± 1.2% (0.9%) 67.4% ± 1.1% (0.5%)	93.0% ± 1.3% (0.8%) 86.0% ± 1.3% (0.3%)
Density of Centrifuged Solids	g/mL	1.934 ± 0.041 (0.023) 1.976 ± 0.051 (0.030)	1.939 ± 0.026 (0.006) 2.004 ± 0.028 (0.033)	1.953 ± 0.020 (0.016) 1.972 ± 0.022 (0.013)
Vol% Centrifuged Solids	%	50.2% ± 1.2% (0.9%) 42.9% ± 1.2% (0.7%)	73.7% ± 1.2% (0.5%) 65.5% ± 1.1% (2.0%)	93.2% ± 1.3% (0.5%) 85.1% ± 1.3% (0.8%)
Wt% Centrifuged Solids	%	63.4% ± 0.0% (0.5%) 55.7% ± 0.0% (0.3%)	82.4% ± 0.0% (0.4%) 75.7% ± 0.0% (1.2%)	96.5% ± 0.0% (0.2%) 90.4% ± 0.0% (0.6%)
Supernatant Density	g/mL	1.151 ± 0.025 (0.007) 1.179 ± 0.023 (0.005)	1.171 ± 0.044 (0.011) 1.218 ± 0.033 (0.011)	1.092 ± 0.176 (0.018) 1.188 ± 0.076 (0.013)
Density of Settled Solids	g/mL	1.91 ± 0.04 (0.02) 1.91 ± 0.04 (0.02)	1.93 ± 0.02 (0.00) 1.98 ± 0.03 (0.01)	1.94 ± 0.02 (0.02) 1.96 ± 0.02 (0.01)
Wt% Settled Supernatant	%	36.6% ± 0.0% (0.6%) 44.3% ± 0.0% (0.3%)	17.6% ± 0.0% (0.4%) 24.3% ± 0.0% (1.2%)	3.5% ± 0.0% (0.2%) 9.6% ± 0.0% (0.6%)
Wt% dissolved solids in supernatant	%	16.0% ± 0.1% (0.0%) 18.9% ± 0.1% (0.1%)	18.8% ± 0.2% (0.2%) 24.1% ± 0.1% (0.1%)	20.5% ± 0.8% (0.6%) 27.0% ± 0.3% (0.4%)
Wt% total solids in Centrifuged Sludge	%	71.8% ± 0.1% (0.3%) 77.8% ± 0.1% (0.4%)	72.0% ± 0.0% (0.3%) 75.3% ± 0.0% (0.3%)	70.9% ± 0.0% (0.5%) 74.1% ± 0.0% (0.3%)
Wt% Total Solids	%	51.4% ± 0.0% (0.2%) 51.8% ± 0.1% (0.2%)	62.7% ± 0.0% (0.1%) 62.9% ± 0.0% (0.4%)	69.1% ± 0.0% (0.4%) 69.6% ± 0.0% (0.0%)
Wt% UDS	%	42.1% ± 0.0% (0.1%) 40.4% ± 0.0% (0.2%)	54.0% ± 0.1% (0.1%) 51.1% ± 0.0% (0.4%)	61.1% ± 0.3% (0.6%) 58.3% ± 0.1% (0.3%)
Wt% UDS in Settled Sludge	%	67.2% ± 1.5% (0.4%) 68.8% ± 1.7% (0.8%)	65.4% ± 0.9% (0.6%) 66.0% ± 0.9% (0.5%)	63.6% ± 0.8% (0.8%) 63.9% ± 0.7% (0.4%)
Wt% UDS in Centrifuged Sludge	%	67.2% ± 1.5% (0.4%) 72.5% ± 1.9% (0.5%)	65.6% ± 0.9% (0.3%) 67.4% ± 1.0% (0.5%)	63.6% ± 0.8% (0.8%) 64.4% ± 0.8% (0.3%)
Average Particle Density	g/mL	2.84 ± 0.25 (0.06) 2.67 ± 0.22 (0.07)	2.95 ± 0.26 (0.08) 2.95 ± 0.21 (0.07)	3.54 ± 1.17 (0.17) 3.12 ± 0.39 (0.02)

Table 3.2 (Contd)

Physical Property	**Units**	**1.75 M Na** **25°C ± error (SD)** **40°C ± error (SD)**	**2.75 M Na** **25°C ± error (SD)** **40°C ± error (SD)**	**3.75 M Na** **25°C ± error (SD)** **40°C ± error (SD)**
Settled solids Density	g/mL	1.92 ± 0.08 (0.02) 1.92 ± 0.08 (0.02)	1.93 ± 0.08 (0.00) 1.99 ± 0.07 (0.01)	1.95 ± 0.30 (0.02) 1.97 ± 0.12 (0.01)
Centrifuged Solids Density	g/mL	1.92 ± 0.08 (0.02) 1.98 ± 0.09 (0.03)	1.94 ± 0.08 (0.01) 2.02 ± 0.07 (0.02)	1.95 ± 0.30 (0.02) 1.98 ± 0.13 (0.01)
Wt% centrifuged solids	%	62.7% ± 3.0% (0.6%) 55.8% ± 3.0% (0.3%)	82.3% ± 3.8% (0.5%) 75.8% ± 3.0% (1.3%)	96.1% ± 15.1% (0.2%) 90.5% ± 5.9% (0.6%)
Wt% settled solids	%	62.7% ± 3.0% (0.6%) 58.8% ± 2.9% (0.9%)	82.5% ± 3.8% (0.9%) 77.5% ± 2.9% (0.3%)	96.1% ± 15.1% (0.2%) 91.2% ± 5.9% (0.4%)
Vol% UDS	%	22.8% ± 2.0% (0.5%) 23.0% ± 1.9% (0.6%)	31.8% ± 2.8% (0.8%) 30.1% ± 2.1% (1.0%)	32.7% ± 10.8% (1.4%) 34.7% ± 4.3% (0.3%)
Vol% UDS in settled solids	%	45.4% ± 4.5% (0.5%) 49.3% ± 4.7% (1.1%)	42.9% ± 4.2% (1.6%) 44.4% ± 3.5% (1.4%)	35.1% ± 12.9% (1.6%) 40.3% ± 5.6% (0.5%)
Vol% UDS in centrifuged solids	%	45.4% ± 4.5% (0.5%) 53.7% ± 5.2% (0.8%)	43.1% ± 4.2% (1.2%) 46.0% ± 3.7% (0.4%)	35.1% ± 12.9% (1.6%) 40.8% ± 5.7% (0.6%)

3.4.1 pH Measurements

The pH of the AZ-101 pretreated LAW and melter feeds was measured with a pH probe. The pH for the pretreated LAW was measured at 13.2, 13.4, and 13.6 for three Na concentrations, 1.75, 2.75, and 3.75 M, respectively (see Table 3.3). Since the GFC (see Table 2.1) contain significant amounts of acidic species, such as boric acid, the pH of the resulting melter feed interstitial liquid dropped significantly. The results of the pH measurement for the melter-feed material were 7.9, 7.5, and 7.1 for three Na concentrations of 1.75, 2.75, and 3.75 M, respectively. With this large drop in pH, solids precipitation is possible for amphoteric species such as aluminum hydroxide.

Table 3.3. pH of the AZ-101 Envelope B Pretreated LAW and Melter Feed

[Na], M	Pretreated LAW pH (at ambient)	Melter Feed pH (at ambient)
1.75	13.2	7.9
2.75	13.4	7.5
3.75	13.6	7.1

3.4.2 Settling Behavior

The settling behavior of the AZ-101 Envelope B melter feeds was investigated by agitating three ~10 mL samples of 1.75, 2.75, and 3.75 M Na melter feed in centrifuge cones. The samples were left undisturbed and allowed to settle. The solid/liquid interface volume was measured at various time intervals as specified by Smith and Prindiville (2002). The settling testing was performed at two temperatures, 25°C and 40°C.

The melter feeds were observed to settle in the "zone" or "hindered" settling regime. This regime occurs due to the particles interacting and settling as a mass. This behavior is characterized by the settled-solids layer height decreasing from the fully suspended volume to a final settled-solids volume. Hindered settling can often be modeled through Equation 3.11 (Renko 1998).

$$z = Az_0 + Bz_0 e^{-\frac{C}{z_0}t} \tag{3.11}$$

where z is the interface height at time, t, z_0 is the initial interface height, and A,B, and C are fitting parameters.

The derivative of this function with respect to time produces an equation for interfacial velocity as a function of time (see Equation 3.13). The maximum settling velocity occurs immediately after agitation stops and is described by Equation 3.14. Note that the maximum velocity is not a function of initial sample height.

$$v = \frac{dz}{dt} \tag{3.12}$$

$$v = -BCe^{-\frac{C}{z_0}t} \tag{3.13}$$

$$v_{\max} = -BC \tag{3.14}$$

Using this model, the maximum interface velocity for the AZ-101 melter feeds was calculated at each temperature. The resulting values are presented in Table 3.4. Brooks et al. (1997) recommend that settling data be nondimensionalized through the use of Equations 3.15 to 3.17. Nondimensionalizing provides a common basis for comparing settling data from different containers and geometries. The initial height for each of the settling experiments is provided in Table 3.5.

Table 3.4. Maximum Interface Settling Velocity of AZ-101 Envelope B Melter Feed

[Na], <u>M</u>	$\lvert V_{max}\rvert$ at 25ºC ± σ (cm/h)	$\lvert V_{max}\rvert$ at 40ºC ± σ (cm/h)
1.75	6.8 ± 0.3	12.0 ± 2.0
2.75	2.1 ± 0.3	3.2 ± 0.3
3.75	0.43 ± 0.08	0.77 ± 0.01

$$z^* = \frac{z}{z_0} \tag{3.15}$$

$$t^* = \frac{t \cdot v_{\max}}{z_0} \tag{3.16}$$

$$v^* = \frac{v}{v_{\max}} \tag{3.17}$$

Table 3.5. Initial Interface Height for AZ-101 Envelope B Melter Feeds

[Na], <u>M</u>	z_0 at 25ºC ± σ (cm)	z_0 at 40ºC ± σ (cm)
1.75	11.4 ± 0.1	10.9 ± 0.3
2.75	12.3 ± 0.4	12.9 ± 0.3
3.75	12.5 ± 0.2	12.5 ± 0.2

Using these dimensionless variables, the settling Equation 3.11 can be rewritten as Equation 3.18. The equation describing the interface velocity can be rewritten in dimensionless form as shown by Equation 3.19.

$$z^* = A^* + B^* e^{-C^* t^*} \tag{3.18}$$

where z^* is the dimensionless interface height at dimensionless time, t^*, and A^*,B^*, and C^* are fitting parameters.

$$v^* = e^{-C^* t^*} \tag{3.19}$$

where v^* is the dimensionless interface velocity at dimensionless time, t^*.

Using these dimensionless equations, the settling data were fit to Equations 3.18 and 3.19. The resulting model parameters are shown in Table 3.6. Good agreement between the data and Equation 3.18 were observed at each melter-feed concentration and temperature as the square of the correlation coefficient did not fall below 0.97.

Table 3.6. Settling-Velocity Model Fit Parameters for AZ-101 Envelope B Melter Feeds

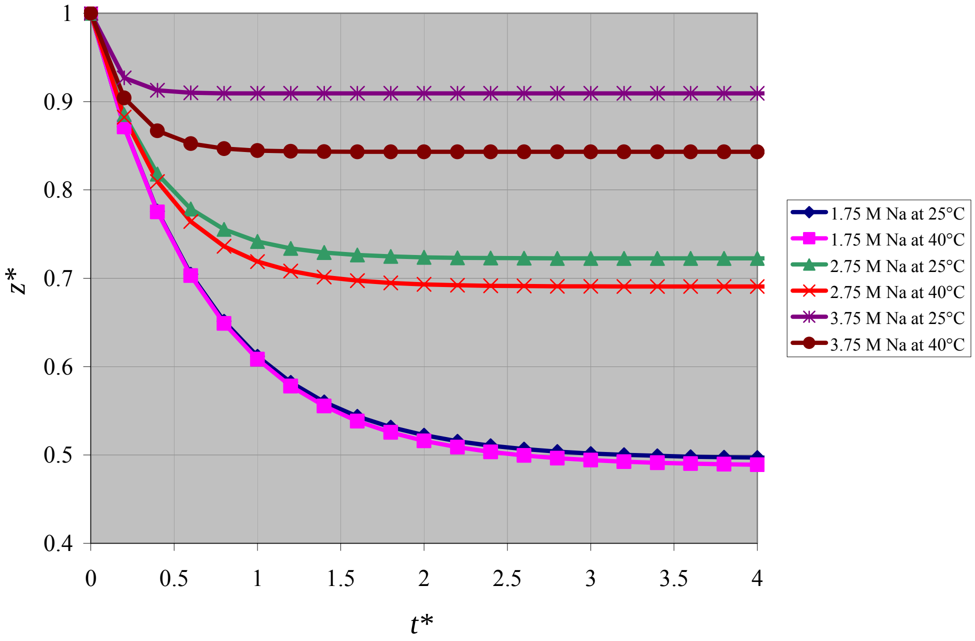
[Na], M	Temp (°C)	A^*	B^*	C^*	R^2
1.75	25	0.50	0.50	1.5	0.99
1.75	40	0.49	0.51	1.4	0.97
2.75	25	0.72	0.28	2.7	0.99
2.75	40	0.69	0.31	2.4	0.98
3.75	25	0.91	0.09	8.2	0.99
3.75	40	0.84	0.16	4.7	0.99

The model-fit data are presented graphically in Figure 3.2. As expected, the 1.75 M Na melter feed settled the fastest, followed by the 2.75 and 3.75 M Na samples, respectively. The 1.75 M Na sample settled at approximately the same dimensionless rate at both 25ºC and 40ºC. However, the maximum velocity of the 1.75 M Na sample at 40ºC was approximately double the 25ºC value. When converting to dimensional time, the 1.75 M Na melter feed at 40ºC will settle significantly faster than the 25ºC melter feed. At both 25ºC and 40ºC, the 1.75 M Na melter-feed solids layer settles to approximately 50% of the total sample volume.

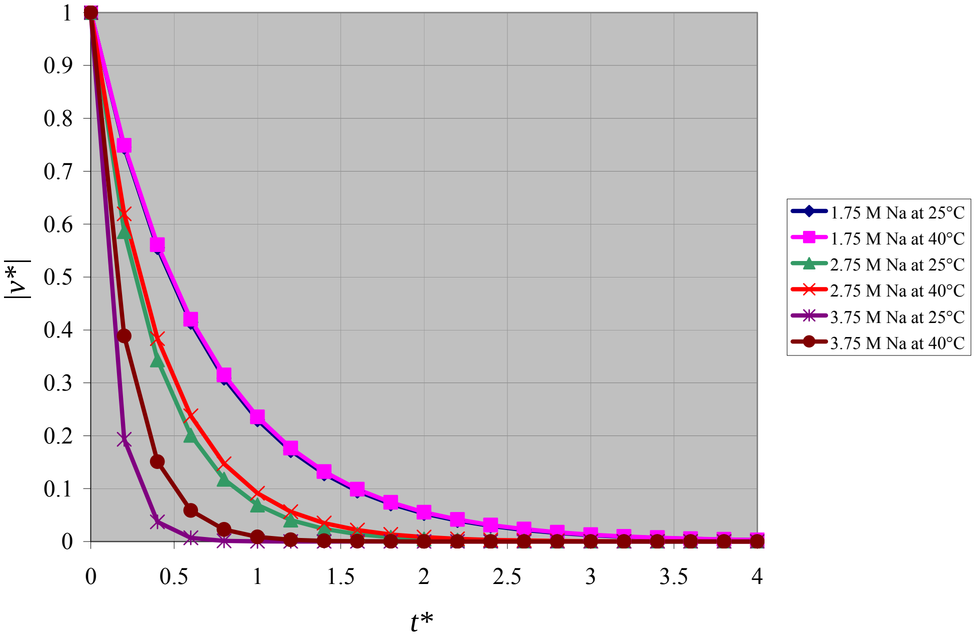
The 2.75 M Na melter feed at 40ºC settled at a faster dimensionless rate than the 25ºC melter feed. In addition, the maximum velocity of the 2.75 M Na sample at 40ºC was approximately 50% larger than the 25ºC value. When converting to dimensional time, the 2.75 M Na melter feed at 40ºC will settle significantly faster than the 25ºC melter feed. At 25ºC and 40ºC, the 1.75 M Na melter-feed solids layer settles to approximately 72% and 69% of the total sample volume, respectively.

The 3.75 M Na melter feed at 40ºC settled at a faster dimensionless rate than the 25ºC melter feed. In addition, the maximum velocity of the 3.75 M Na sample at 40ºC was approximately 80% larger than the 25ºC value. When converting to dimensional time, the 3.75 M Na melter feed at 40ºC settles significantly faster than the 25ºC melter feed. At 25ºC and 40ºC, the 1.75 M Na melter feed solids layer settles to approximately 91% and 84% of the total sample volume, respectively.

To illustrate the utility of dimensional analysis for settling measurements, Equation 3.18 and the parameters shown in Table 3.6 were used to predict the solid/liquid interface height as a function of initial sample height. The results from these prediction calculations are shown in Figure 3.3. The exponential term shown in Equation 3.13 indicates that the solid/liquid interface velocity depends on the initial sample height. As the initial sample height, z_0, increases, the exponent in Equation 3.13 becomes smaller, predicting smaller settling velocities and a longer amount of time required to settle to a particular volume-fraction settled solids. When the initial sample height is consistent with the WTP Melter Feed Preparation Vessel (MFPV) and Melter Feed Vessel (MFV) operating range (approximately 1.5 to 4.5 m [5 to 15 ft]), settling is predicted to occur on the order of several days rather than several hours as measured in the small-scale centrifuge cone tests.

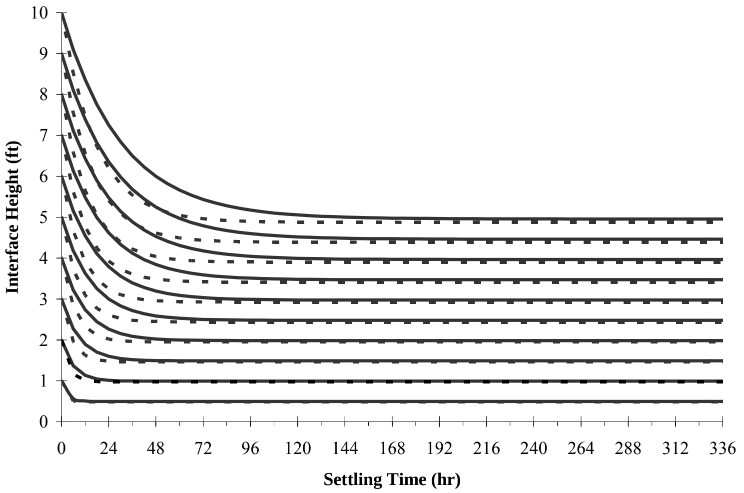


a) dimensionless solid/liquid interface height as a function of dimensionless time

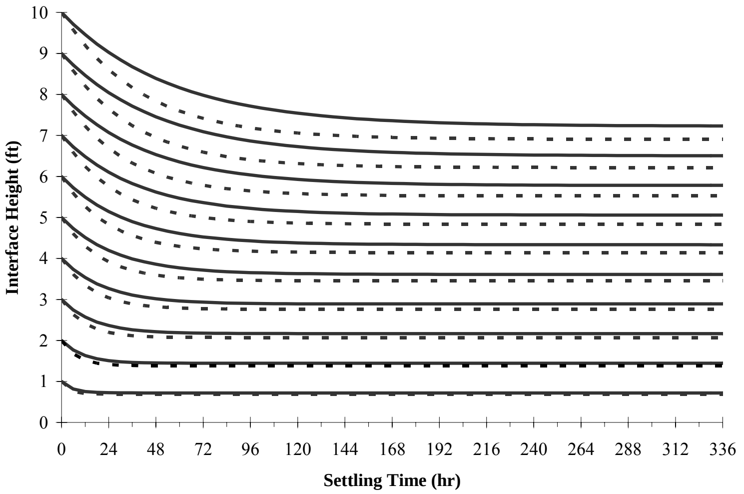


b) dimensionless solid/liquid interface velocity as a function of dimensionless time

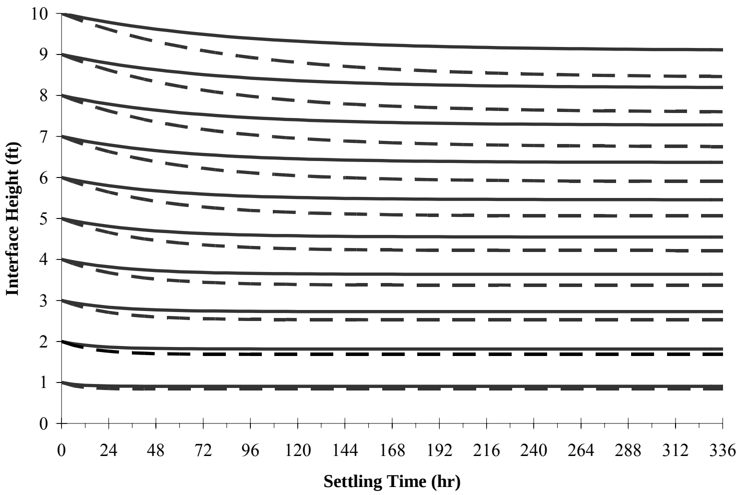
Figure 3.2. Sedimentation Curves for AZ-101 Envelope B Melter Feeds



a) 1.75 M AZ-101 Envelope B Melter Feed; solid line is at 25ºC; dashed line is at 40ºC; majority of settling occurs 3 to 6 days after loss of agitation



b) 2.75 M AZ-101 Envelope B Melter Feed; solid line is at 25ºC; dashed line is at 40ºC; majority of settling occurs 6 to 10 days after loss of agitation



c) 3.75 M AZ-101 Envelope B Melter Feed; solid line is at 25ºC; dashed line is at 40ºC; majority of settling occurs 10 days after loss of agitation

Figure 3.3. Predicted Sedimentation Curves for AZ-101 Envelope B Melter Feeds at Various Initial Mixing Heights

4.0 Rheology

Rheology is the study of the flow of matter. When a force (i.e., stress) is placed on an object, the object deforms or strains. Many relationships have been found relating stress to strain for various fluids. Flow behavior of a fluid can generally be explained by considering a fluid placed between two plates of thickness x (see Figure 4.1). The lower plate is held stationary while a force, F, is applied to the upper plate of area, A, that results in the plating moving at velocity, v. If the plate moves a length, ΔL , the strain, γ ,on the fluid can be defined by Equation 4.1.

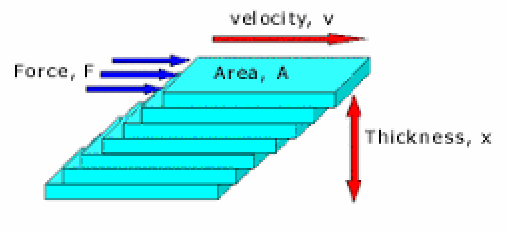


Figure 4.1. Diagram of Fluid Flow between Stationary and Moving Plates

$$\gamma = \frac{\Delta L}{\mathrm{x}} \tag{4.1}$$

The rate of change of strain (also called shear rate), $\dot{\gamma}$, can be defined by Equation 4.2. Since the shear rate is defined as the ratio of a velocity to a length, the units of the variable are the inverse of time, typically s^{-1}.

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{d}{dt}\left(\frac{\Delta L}{\mathrm{x}}\right) = \frac{\mathrm{v}}{\mathrm{x}} \tag{4.2}$$

Typical shear rates of food-processing applications can be seen in Table 4.1. Depending on the application, shear rates in the range of 10^{-6} to 10^{7} s^{-1} are possible. Human perception of a fluid is typically based on a shear rate of approximately 60 s^{-1}.

Table 4.1. Typical Shear Rates in Food-Processing Applications

Situation	Shear Rate Range (1/s)	Typical Applications
Sedimentation of Particles in a Suspending Liquid	$10^{-6} – 10^{-3}$	Medicines, paints, spices in salad dressing
Leveling due to surface tension	$10^{-2} – 10^{-1}$	Frosting, Paints, printing inks
Draining under gravity	$10^{-1} – 10^{1}$	Vats, small food containers
Extrusion	$10^{0} – 10^{3}$	Snack and pet foods, toothpaste, cereals, pasta, polymers
Calendering	$10^{1} – 10^{2}$	Dough sheeting
Pouring from a Bottle	$10^{1} – 10^{2}$	Foods, cosmetics, toiletries
Chewing and Swallowing	$10^{1} – 10^{2}$	Foods
Dip Coating	$10^{1} – 10^{2}$	Paints, confectionery
Mixing and Stirring	$10^{1} – 10^{3}$	Food processing
Pipe Flow	$10^{0} – 10^{3}$	Food processing, blood flow
Rubbing	$10^{2} – 10^{4}$	Topical application of creams and lotions
Brushing	$10^{3} – 10^{4}$	Brush painting, lipstick, nail polish
Spraying	$10^{3} – 10^{5}$	Spray drying, spray painting, fuel atomization
High speed coating	$10^{4} – 10^{6}$	Paper
Lubrication	$10^{3} – 10^{7}$	Bearings, gasoline engines

The shear stress applied to the fluid can be found by Equation 4.3. Since the shear stress is defined as the ratio of a force to an area, the units of the variable are pressures, typically expressed in Pa (N/m^2).

$$\tau = \frac{F}{A} \tag{4.3}$$

The apparent viscosity of the fluid is defined as the ratio of the shear stress to shear rate (see Equation 4.4). Since the viscosity is defined as the ratio of shear stress to shear rate, the units of the variable are Pa•s. Typically, viscosity is reported in units of centipoise (cP; where 1 cP = 1 mPa•s).

$$\eta(\dot{\gamma}) = \frac{\tau(\dot{\gamma})}{\dot{\gamma}} \tag{4.4}$$

For Newtonian fluids, the apparent viscosity is independent of shear rate (see Equation 4.5). Examples of the viscosity of common Newtonian materials can be seen in Table 4.2.

$$\tau = \eta\dot{\gamma} \tag{4.5}$$

where τ is the shear stress, η is the Newtonian viscosity, and $\dot{\gamma}$ is the shear rate.

Table 4.2. Viscosities of Several Common Newtonian Fluids

Material	Viscosity at 20°C (cP)
Acetone	0.32
Water	1.0
Ethanol	1.2
Mercury	1.6
Ethylene Glycol	20
Corn Oil	71
Glycerin	1,500

Fluids that do not behave as Newtonian fluids are referred to as non-Newtonian fluids. Rheograms or plots of shear stress versus shear rate are typically used to characterize non-Newtonian fluids. Examples of typical rheograms can be seen in Figure 4.2.

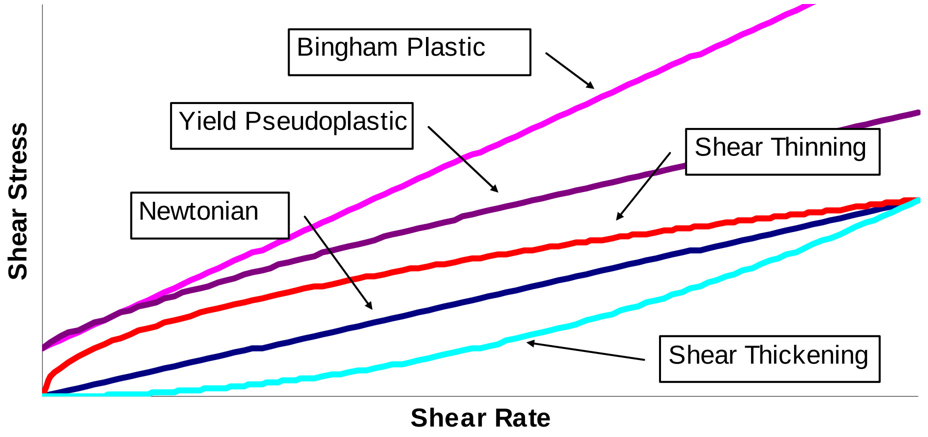


Figure 4.2. Rheograms of Various Fluid Types

Shear-thinning and shear-thickening fluids can be modeled by the Ostwald equation (see Equation 4.6). If n<1, then the material is referred to as pseudoplastic (shear thinning). If n>1, then that material is referred to as dilatant (shear thickening). These fluids exhibit decreasing or increasing apparent viscosities as shear rate increases, depending on whether the fluid is shear thinning or shear thickening, respectively. Since shear-thickening flow behavior is rare, shear-thickening behavior is often an indication of possible secondary flow patterns or other measurement errors.

$$\tau = m\dot{\gamma}^{n} \tag{4.6}$$

where *m* is the power law consistency coefficient, *n* is the power law exponent, and $\dot{\gamma}$ is the shear rate.

A rheogram for a Bingham plastic does not pass through the origin. When a rheogram possesses a non-zero y-intercept, the fluid is said to posses a yield stress. A yield stress is a shear-stress threshold that defines the boundary between solid-like behavior and fluid-like behavior. The fluid will not begin to flow until the yield stress threshold is exceeded. For Bingham plastic materials, once enough force has been applied to exceed the yield stress, the material approaches Newtonian behavior at high shear rates (see Equation 4.7).

$$\tau = \tau_O^B + \eta_P\dot{\gamma} \tag{4.7}$$

where τ_O^B is the Bingham yield stress, η_p is the plastic viscosity, and $\dot{\gamma}$ is the shear rate.

Fluids that exhibit a non-linear rheogram with a yield stress are typically modeled by the three-parameter Herschel-Bulkley equation (see Equation 4.8). Again, shear-thickening behavior is uncommon, and typically the Hershel-Bulkley power-law exponent is less than unity.

$$\tau = \tau_O^H + k\gamma^{b} \tag{4.8}$$

Where

τ_O^H = yield stress
k = Herschel-Bulkley consistency coefficient
b = Hershel-Bulkley power law exponent
γ = shear rate.

4.1 Equipment Details

Haake RS300 and M5 rheometers were used for the work described in this section. The RS300 and M5 systems have been configured with a temperature-controlled concentric cylinder rotational system. The sensor system consists of an inner cylinder that is placed inside an outer cylinder with a known annular gap distance. When the inner cylinder rotates, the resulting fluid resistance to the flow is measured electronically. When this signal is combined with the rotational rate, it can be mathematically transformed into shear-stress and shear-rate data. For the samples analyzed in this report, Haake Z41 (RS300 rheometer) and MVI (M5 rheometer) sensor systems were used.

The testing was conducted as follows. The samples were loaded into the sample container, and the shear rate was increased from 0 to 1000 s^{-1} in 5 minutes. The sample was held at a shear rate of 1000 s^{-1} for 1 minute. Lastly, the shear rate was decreased from 1000 to 0 s^{-1} in 5 minutes. The test was then immediately repeated with the same sample. If the subsequent data were in close agreement with the previous run, the testing for that sample was considered complete. If there was noticeable variation in the data, the sample was ramped through this cycle again until two consecutive similar data sets were obtained. The purpose of this repetition was to qualitatively determine if rheological changes occur while under the influence of shear. Shear history is often an important part of determining expected rheological behaviors. Once the previous sample was tested to the point of obtaining consistent data, it was removed, and a new sample was loaded for the next run.

The purpose of this set of testing parameters was to identify the rheological behavior and shear sensitivity of the materials. The first ramp cycle shows newly loaded or fresh sample behavior, including breakdown of sample structure through hysteresis, if present. Hysteresis is when the ramp-down curve is different from the ramp-up curve. An immediate repeat allows little or no time for the sample to recover. The complete cycle repeat with the used sample shows the effects of a shear history with a short time of recovery for the sample.

NIST-traceable Brookfield viscosity standard oils were used to verify the calibration of the rheometer systems. These data are shown in Table 4.3. A verified calibration check requires a deviation between measured and certified values less than 10% for viscosity standards above 10 cP and 15% for viscosity standards below 10 cP. The calibration check is valid for 30 days.

Table 4.3. Battelle—Pacific Northwest Division (PNWD) Rheometer Calibration Check Results

Rheometer System	Date	Certified Viscosity at 25°C	Measured Viscosity at 25°C	Percent Deviation
RS300	12/06/02	9.8	10.2	4.1%
RS300	1/29/03	98.0	98.7	0.7%
RS300	4/15/03	103.0	102.8	0.2%
M5	4/7/03	47.4	47.6	0.4%
M5	5/5/03	47.4	47.4	0.0%
M5	5/15/03	103.0	102.8	0.2%

4.2 Pretreated Waste

Rheograms from pretreated waste at various Na concentrations are shown in Figure 4.3 through Figure 4.8. Each figure provides a least-squares rheological model fit (see Section 4.0) for each increasing shear-rate rheogram. These wastes did not contain GFC. Results are summarized in Table 4.4. As expected, the viscosity of the waste increases with increasing Na concentration and decreasing temperature in a range of 1.1 to 2.4 cP. These wastes have the characteristics of low viscosity Newtonian fluids. Taylor Vortices developed at shear rates between 200 to 400 s^{-1}. This secondary flow pattern can be recognized by nonlinearity in the rheogram, resulting in an increase in slope, and leads to erroneous data at higher shear rates. Data above the shear rate causing Taylor Vortices have been discarded for the rheological model analysis.

Table 4.4. Rheological Model Fits for AZ-101 Pretreated LAW at Various Concentrations and Temperatures

Model/model Parameter	1.75 M Na at 25°C	1.75 M Na at 40°C	2.75 M Na at 25°C	2.75 M Na at 40°C	3.75 M Na at 25°C	3.75 M Na at 40°C
File Name	**120902_a**	**120902_e**	**121002_a**	**121002_e**	**121102_a**	**121102_e**
Newtonian:						
η – Newtonian viscosity (cP)	1.4	1.1	1.8	1.4	2.4	1.7
R^2 – correlation coefficient	0.9958	0.9914	0.9972	0.9948	0.9992	0.9984
Ostwald (or Power Law):						
m – the consistency coefficient ($mPa \cdot s^{-n}$)	n/a	n/a	n/a	n/a	n/a	n/a
n – the power law exponent	n/a	n/a	n/a	n/a	n/a	n/a
R^2 – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	n/a	n/a	n/a	n/a	n/a	n/a
η_p - the plastic viscosity (cP)	n/a	n/a	n/a	n/a	n/a	n/a
R^2 – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Herschel-Bulkley:						
τ_O^H - the yield stress (Pa)	n/a	n/a	n/a	n/a	n/a	n/a
k - the Herschel-Bulkley consistency coefficient ($mPa \cdot s^{-b}$)	n/a	n/a	n/a	n/a	n/a	n/a
b - the Hershel-Bulkely power law exponent	n/a	n/a	n/a	n/a	n/a	n/a
R^2 – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
n/a = not applicable						

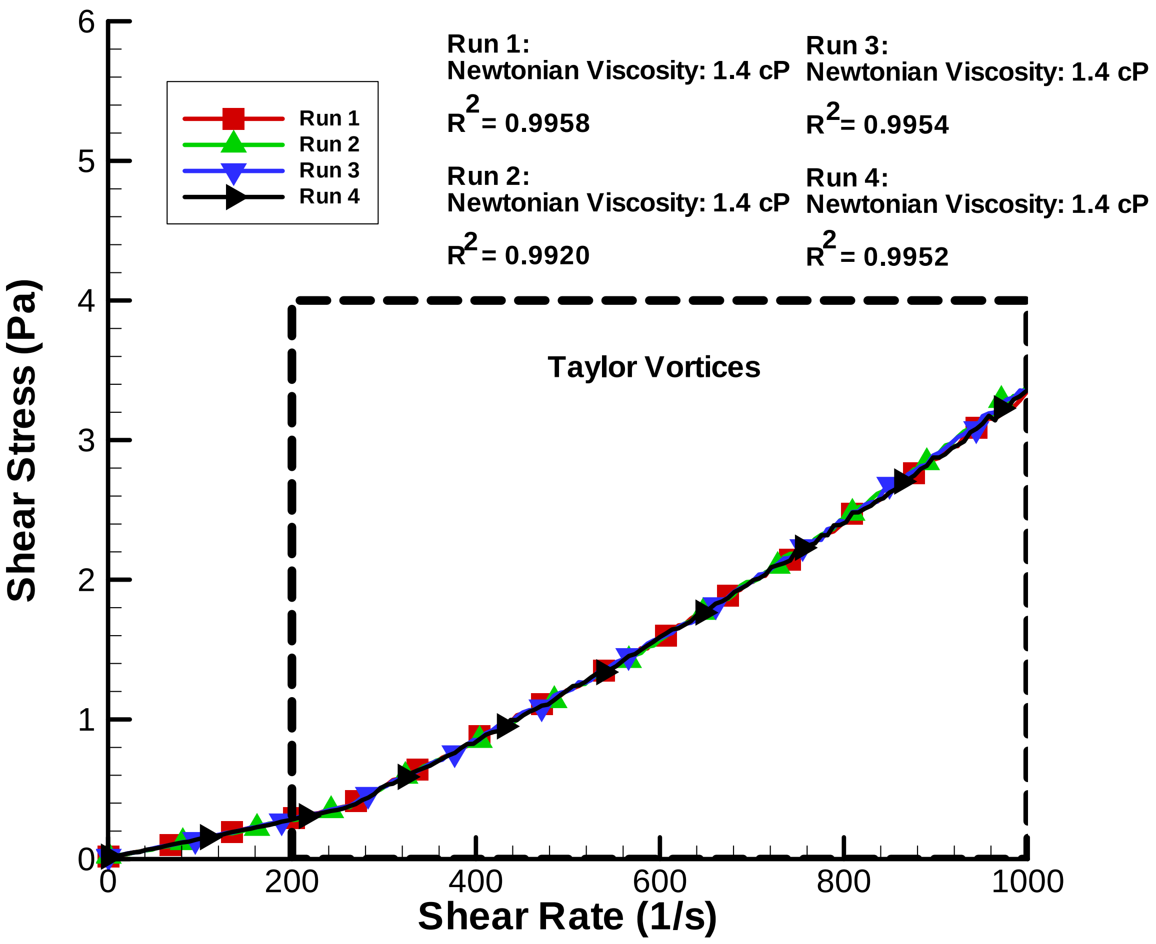


Figure 4.3. Flow Curve of 1.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 25°C

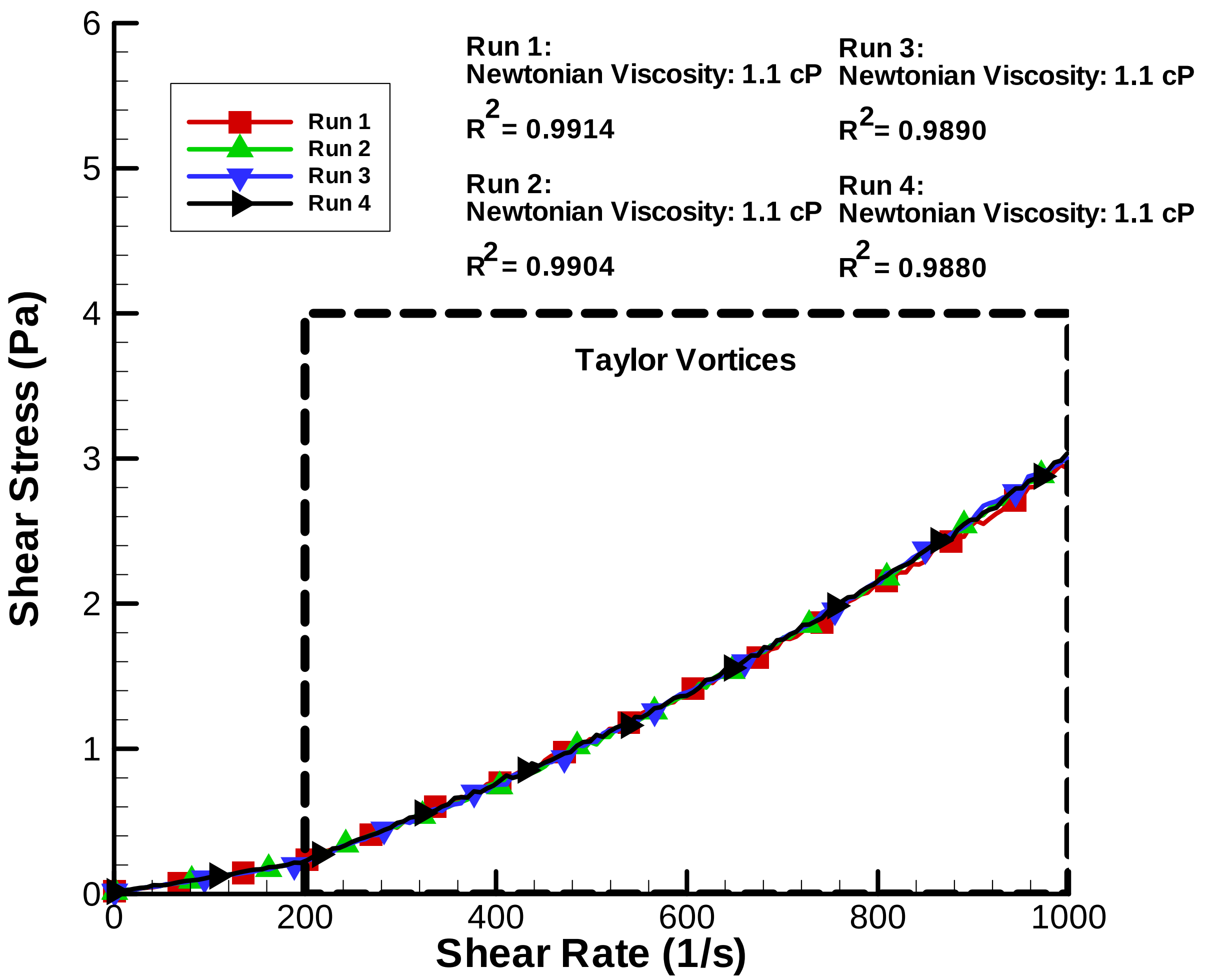


Figure 4.4. Flow Curve of 1.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 40°C

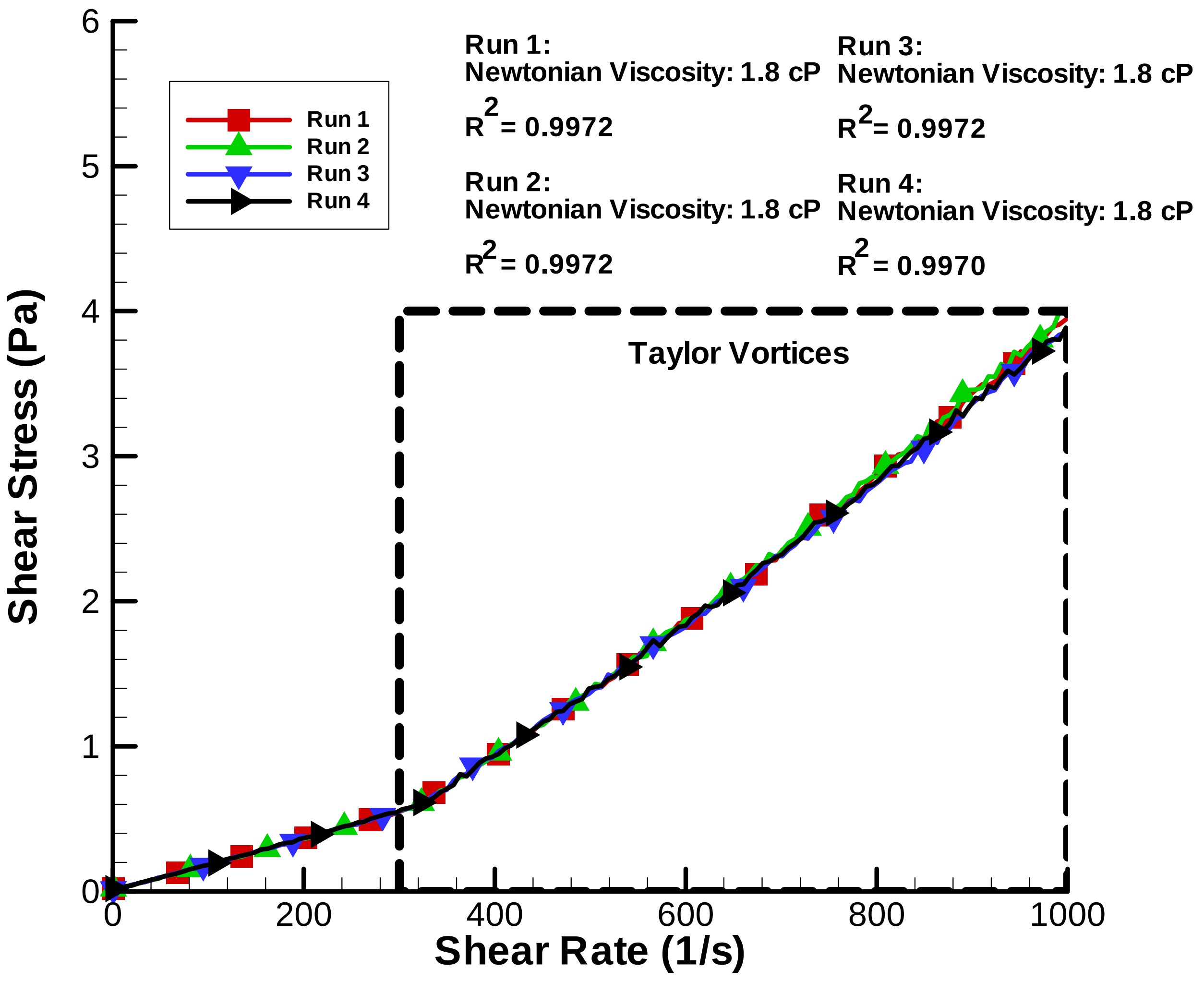


Figure 4.5. Flow Curve of 2.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 25°C

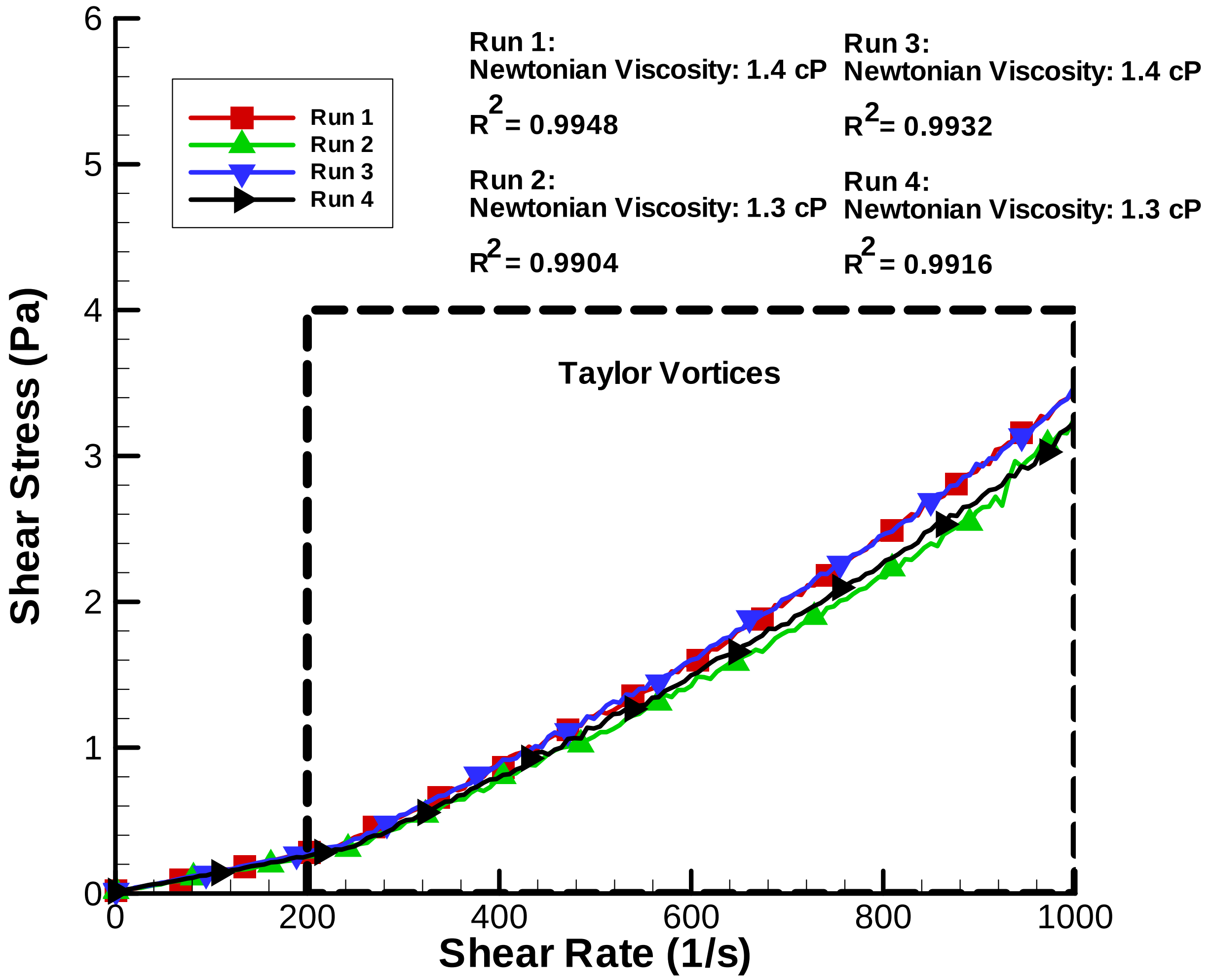


Figure 4.6. Flow Curve of 2.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 40°C

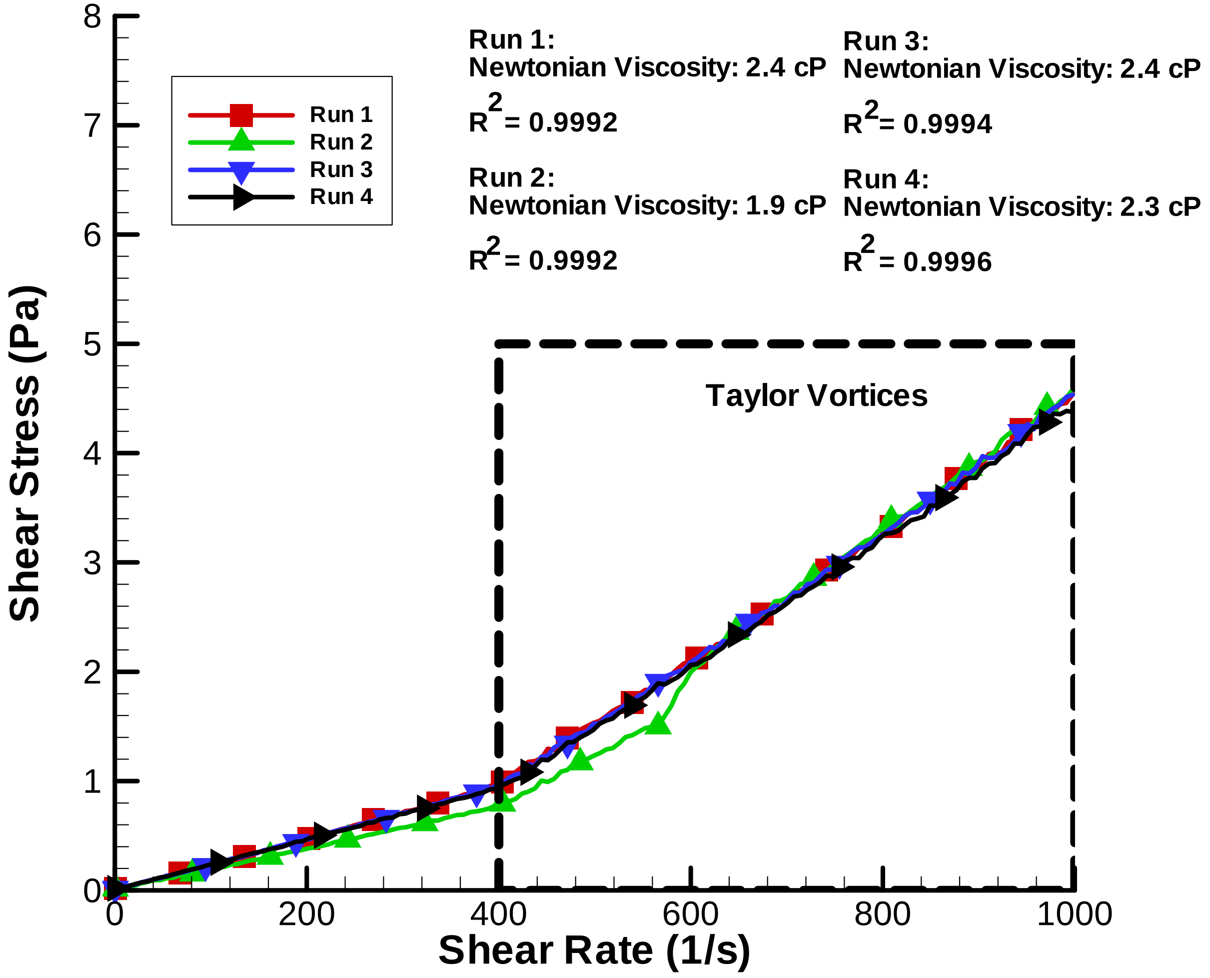


Figure 4.7. Flow Curve of 3.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 25°C

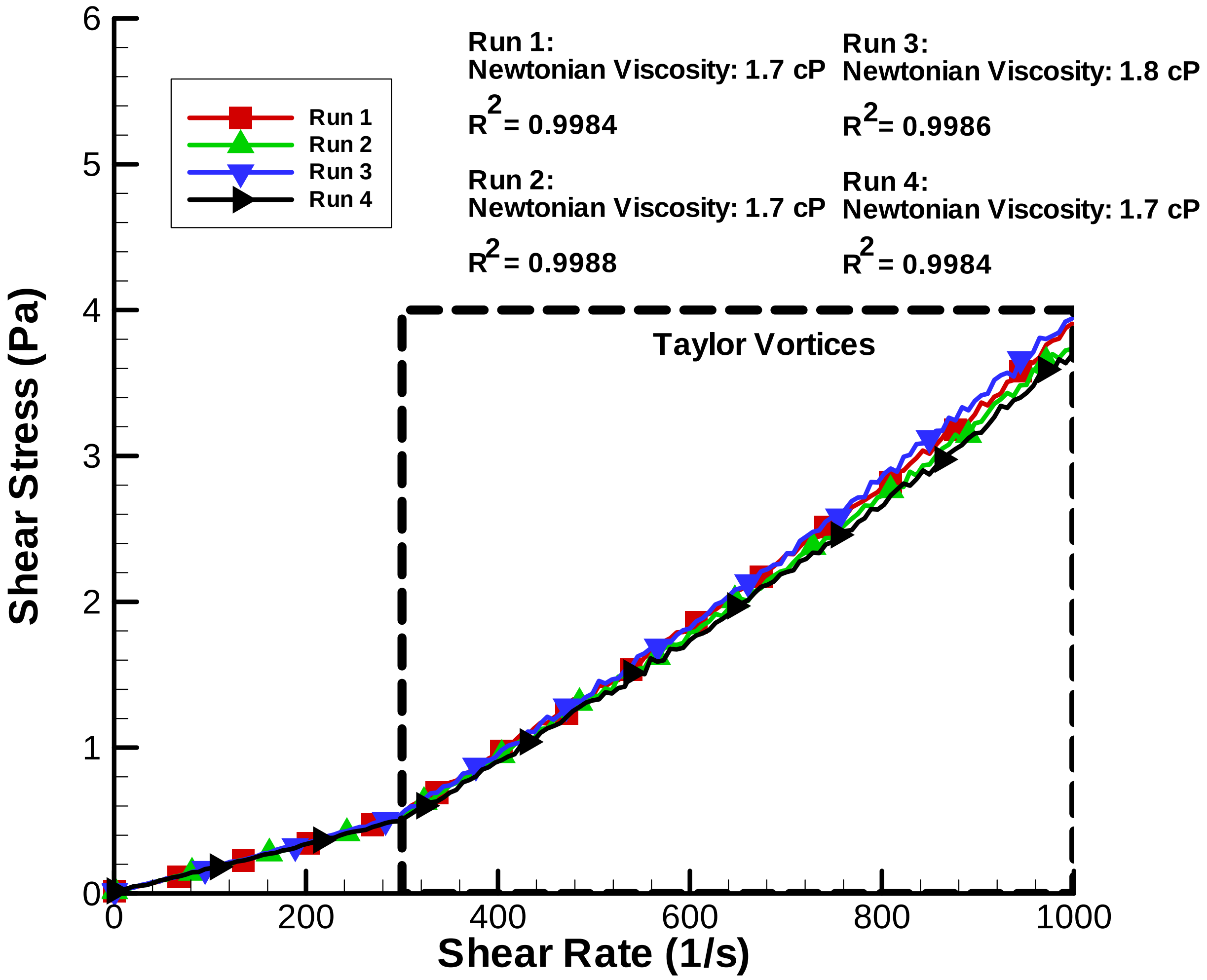


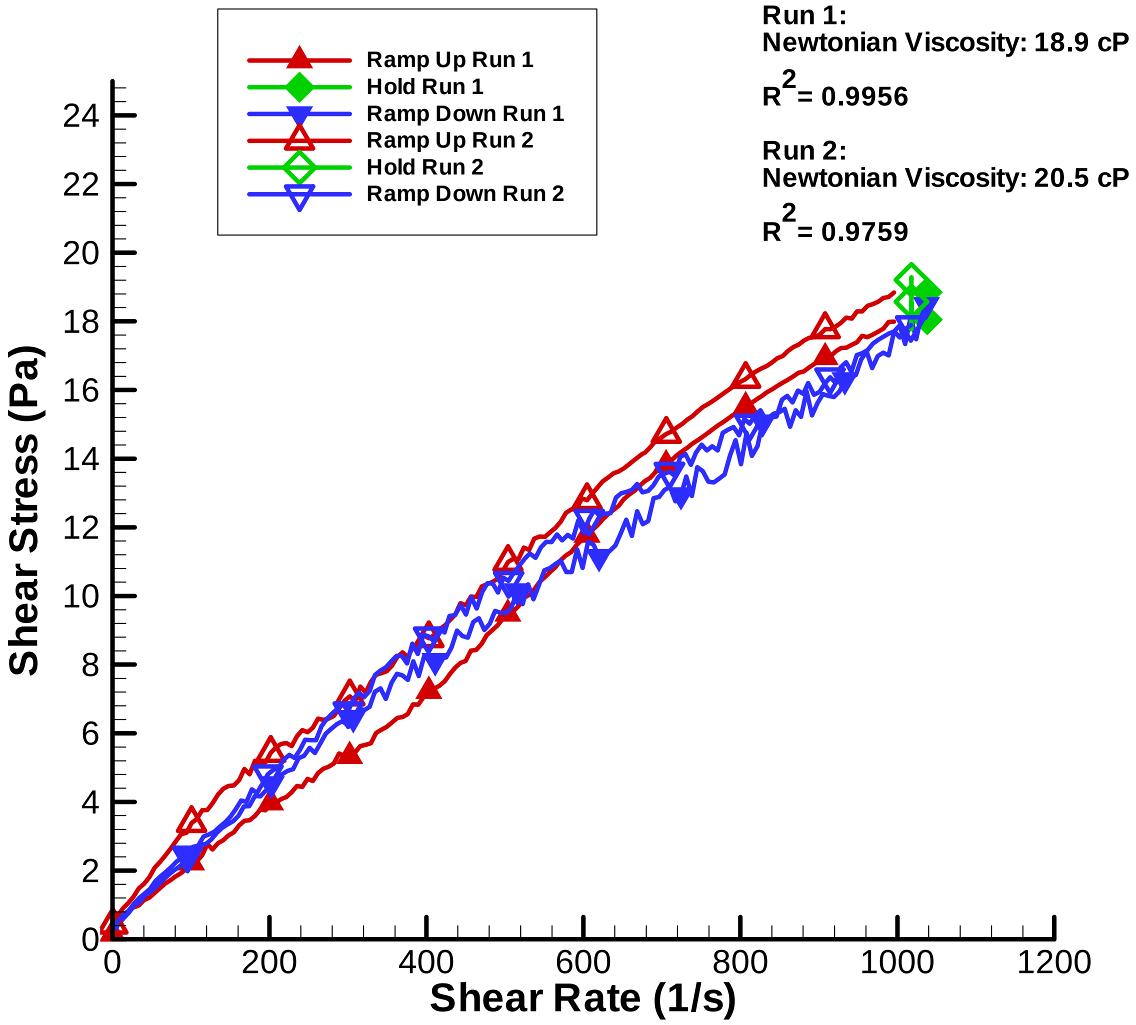
Figure 4.8. Flow Curve of 3.75 M Na AZ-101 Pretreated Waste (Without Glass Formers) at 40°C

4.3 Melter Feed

Rheograms for each of the AZ-101 melter-feed samples show strong Newtonian behavior at both temperatures and concentrations (see Figure 4.9 through Figure 4.14). Results are summarized in Table 4.5. As expected, the viscosity of the 1.75 M Na suspension is significantly less than the viscosity of the 3.75 M Na suspension. This is due to the higher concentration of GFC added to the 3.75 M Na sample and the higher viscosity of the 3.75 M Na pretreated waste. In addition, all suspensions showed strong temperature dependence. As seen in Figure 4.10, there is an increase in the sample viscosity during the ramp up and ramp down phases of the test. This apparent shear thickening is most likely due to a combination of evaporation of the interstitial fluid and settling of the solids particles during the run. Fortunately, the settling rate for the higher concentration suspensions was sufficiently slow during the remaining analyses, and these melter feeds can be adequately modeled as a Newtonian fluid. Newtonian model least-squares fits are presented in the rheograms. The first segment of each run (i.e., ramp-up) was used to determine flow characteristics.

Table 4.5. Rheological Model Fits for AZ-101 LAW Melter Feed at Various Concentrations and Temperatures

Model/model Parameter	**1.75 M Na at 25°C**	**1.75 M Na at 40°C**	**2.75 M Na at 25°C**	**2.75 M Na at 40°C**	**3.75 M Na at 25°C**	**3.75 M Na at 40°C**
File Name	**041603_d**	**041603_f**	**022503_a**	**022503_c**	**022603_d**	**022603_e**
Newtonian:						
η – Newtonian viscosity (cP)	18.9	13.5	80.0	32.6	118.7	72.2
R^2 – correlation coefficient	0.9956	0.9819	0.9807	0.8870	0.9750	0.9128
Ostwald (or Power Law):						
m – the consistency coefficient ($mPa\cdot s^{-n}$)	20.1	32.6	224.4	238.3	435.2	592.6
n – the power law exponent	0.99	0.87	0.84	0.70	0.80	0.68
R^2 – correlation coefficient	0.9958	0.9918	0.9950	0.9580	0.9998	0.9996
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	0.1	0.8	5.3	4.4	8.6	9.2
η_p - the plastic viscosity (cP)	18.7	12.3	72.1	26.1	105.9	58.4
R^2 – correlation coefficient	0.9958	0.9936	0.9966	0.9696	0.9946	0.9860
Herschel-Bulkley:						
τ_O^H - the yield stress (Pa)	0.3	2.1	3.9	4.0	0.1	0.7
k - the Herschel-Bulkely consistency coefficient ($mPa\cdot s^{-b}$)	15.8	13.1	104.6	34.2	432.2	526.6
b - the Hershel-Bulkely power law exponent	1.02	1.02	0.95	0.96	0.80	0.69
R^2 – correlation coefficient	0.9958	0.9892	0.9970	0.9698	0.9998	0.9996
n/a = not applicable						



Run 1:
Newtonian Viscosity: 18.9 cP

R^2 = 0.9956

Run 2:
Newtonian Viscosity: 20.5 cP

R^2 = 0.9759

Figure 4.9. Flow Curve of 1.75 M Na AZ-101 Melter Feed (With Glass Formers) at 25°C

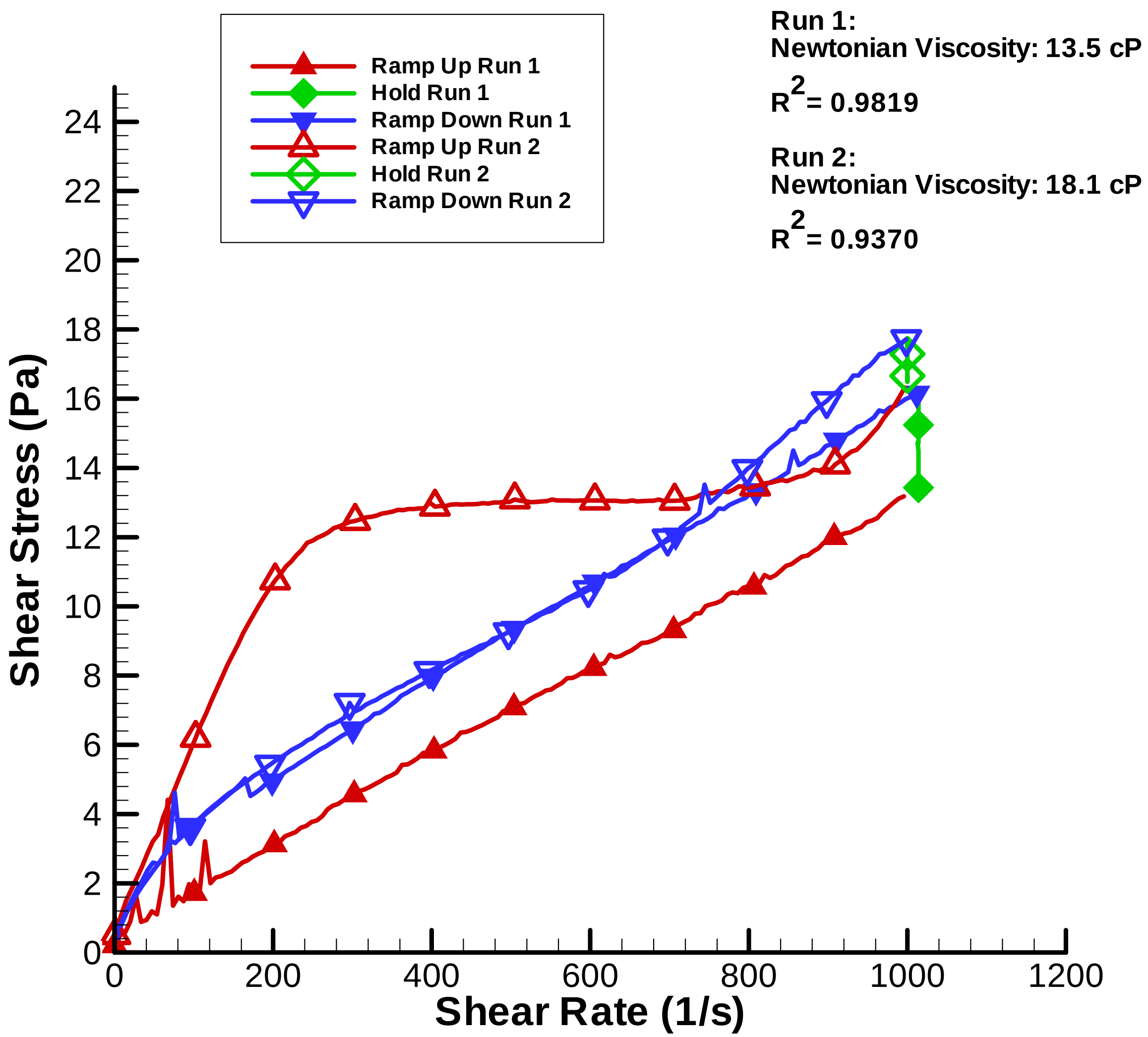


Figure 4.10. Flow Curve of 1.75 M Na AZ-101 Melter Feed (With Glass Formers) at 40°C

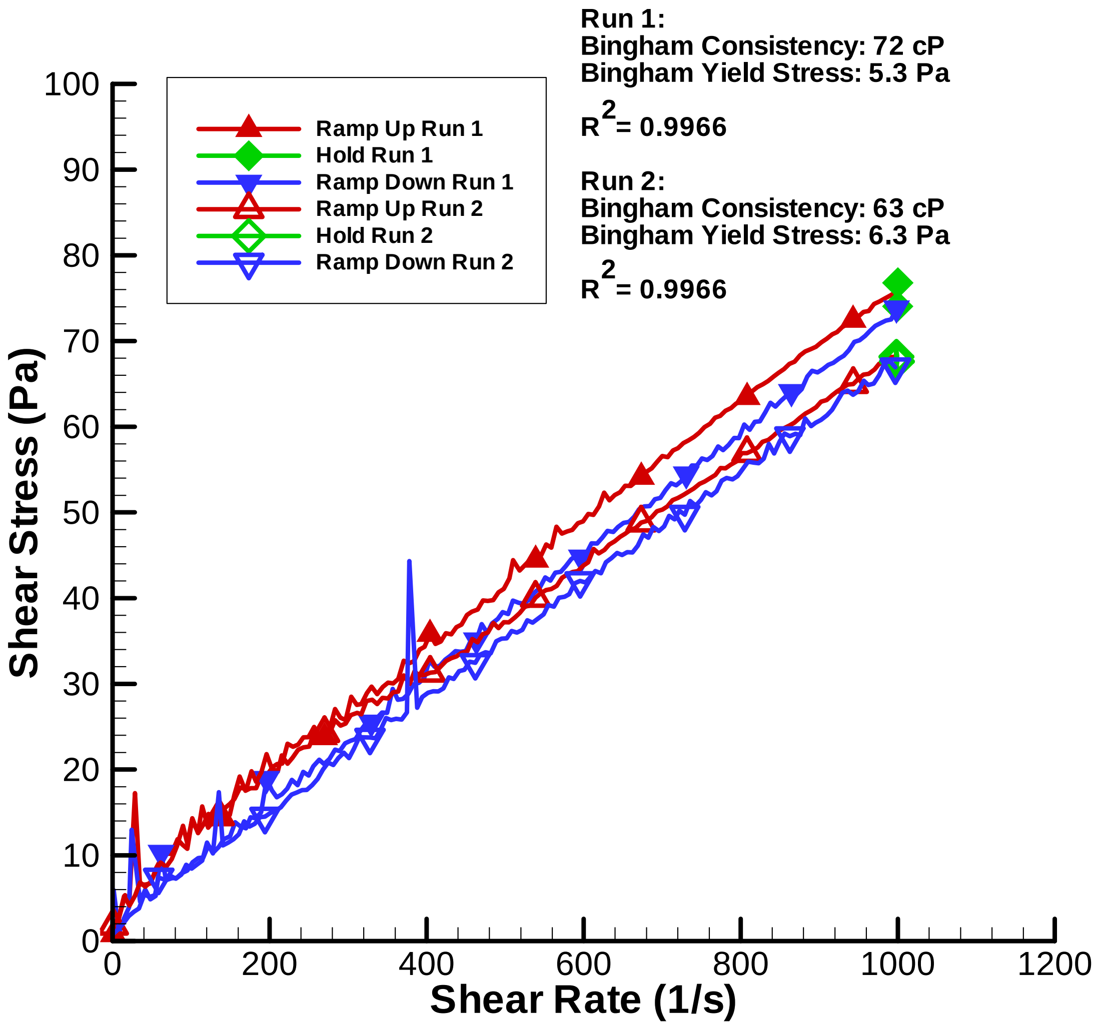


Figure 4.11. Flow Curve of 2.75 M Na AZ-101 Melter Feed (With Glass Formers) at 25°C

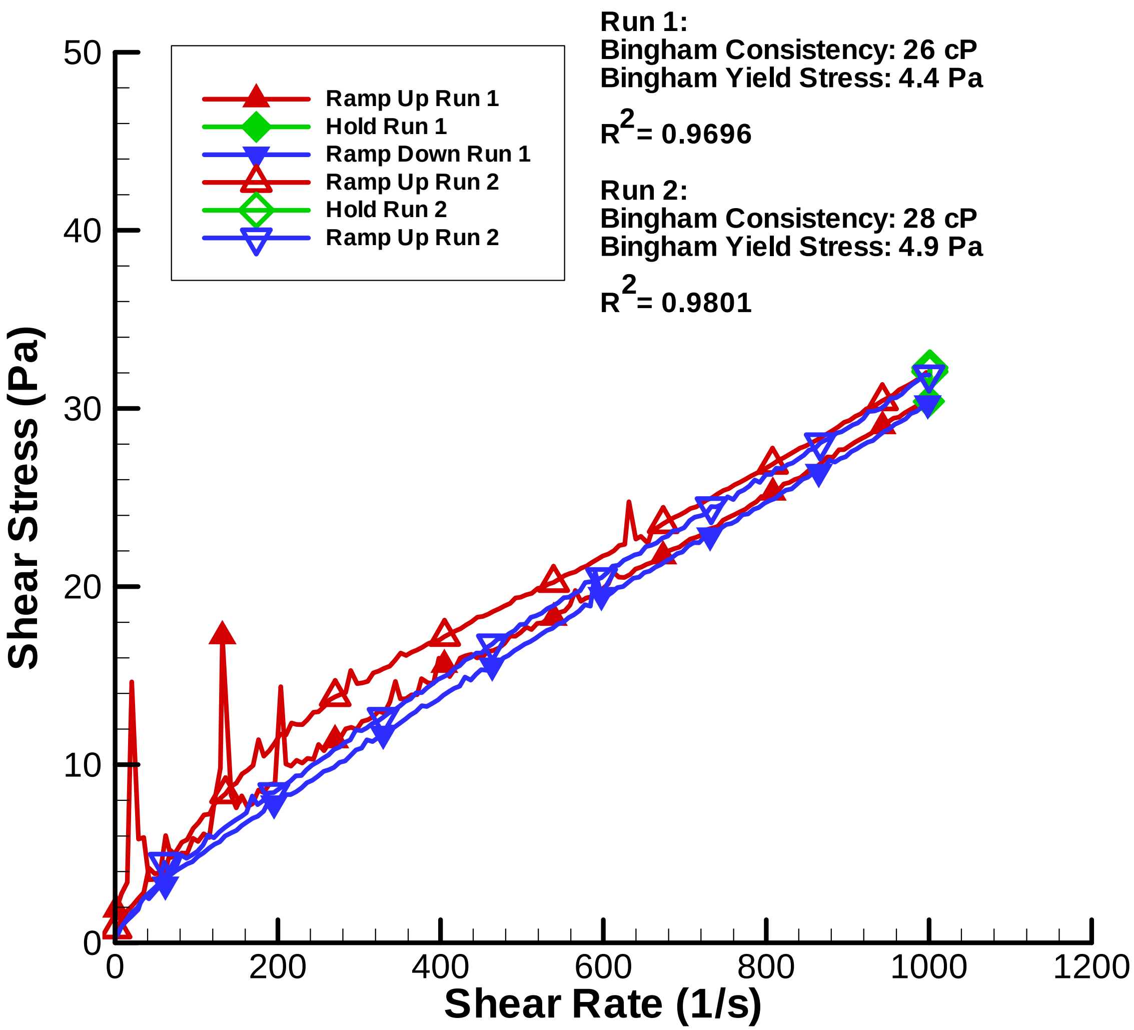


Figure 4.12. Flow Curve of 2.75 M Na AZ-101 Melter Feed (With Glass Formers) at 40°C

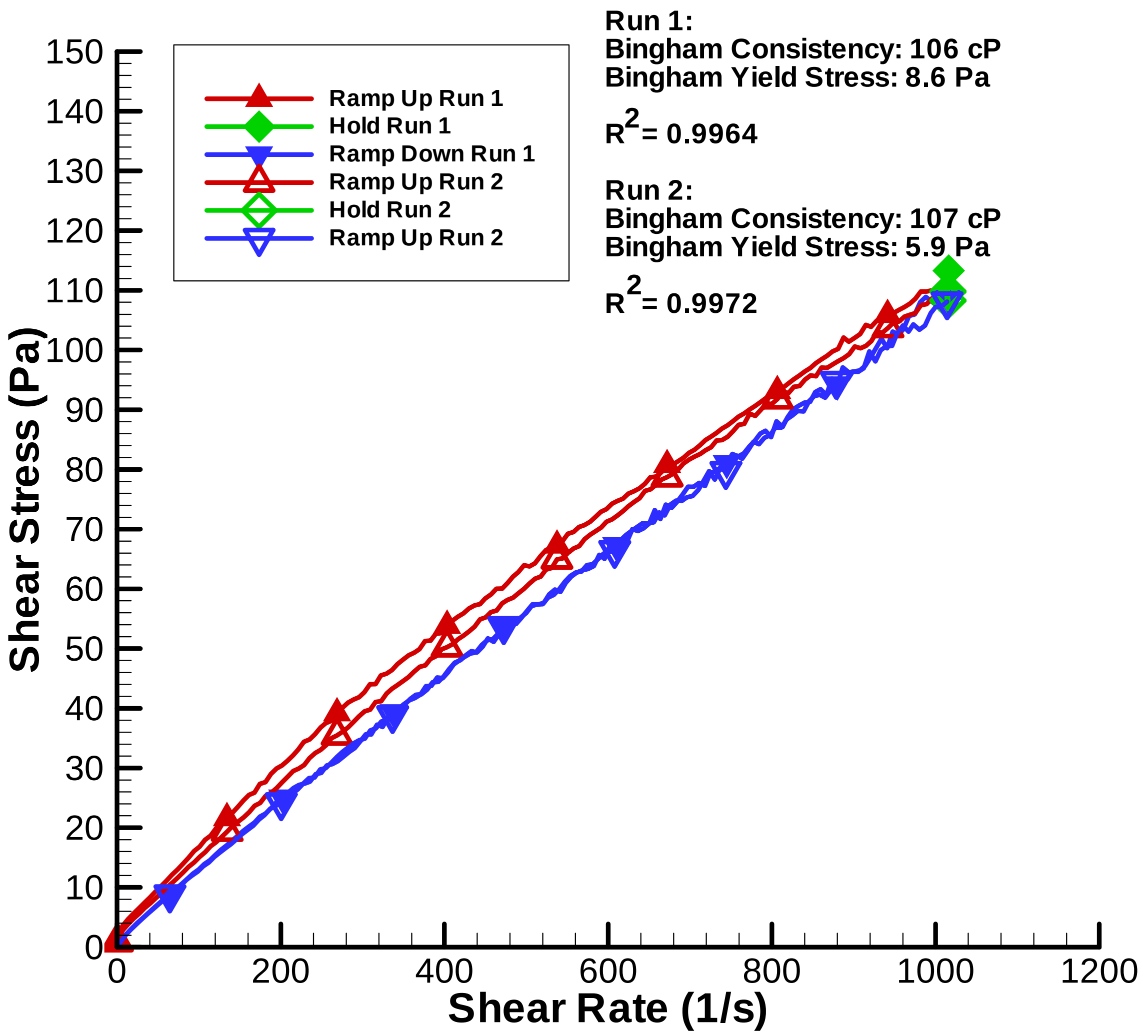


Figure 4.13. Flow Curve of 3.75 M Na AZ-101 Melter Feed (With Glass Formers) at 25°C

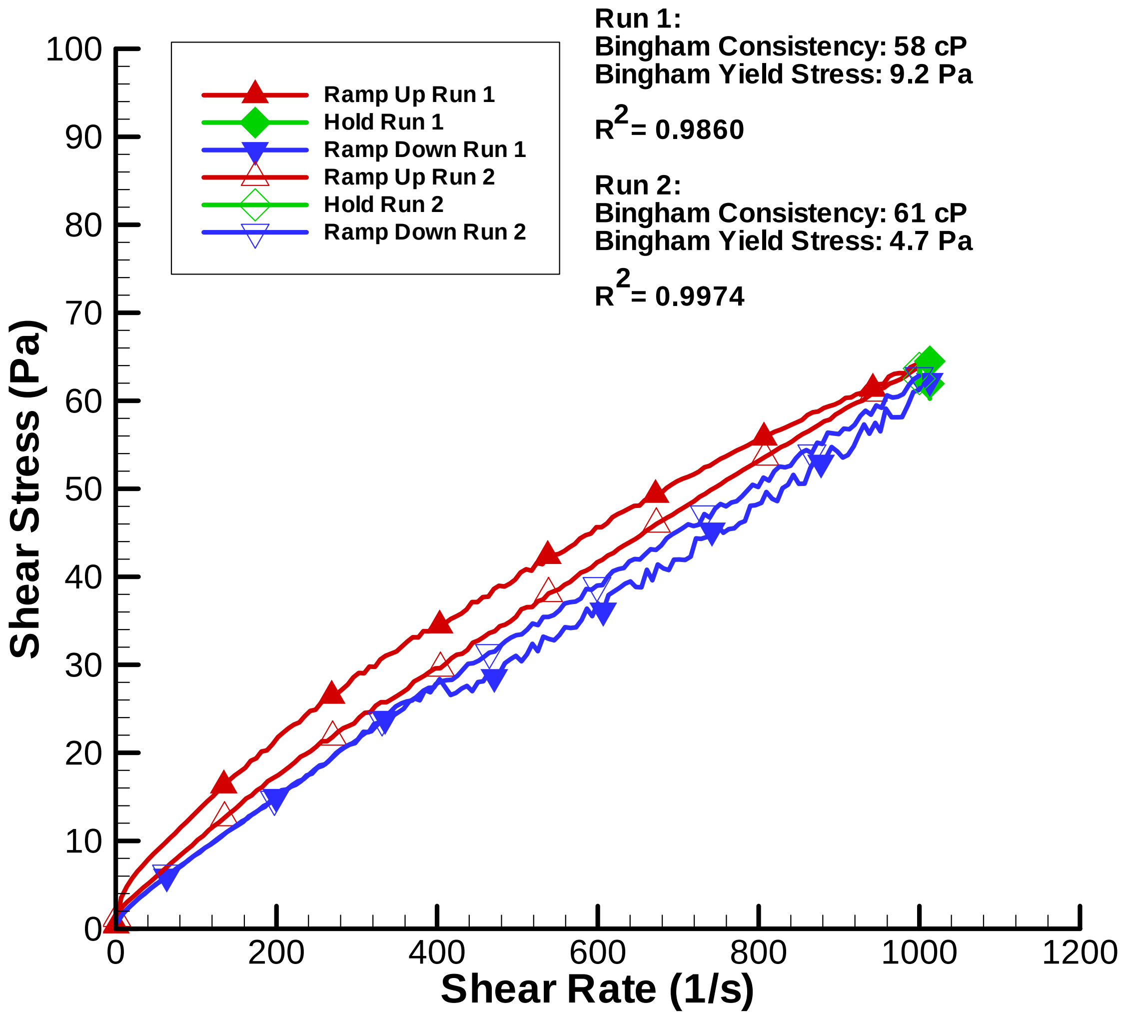


Figure 4.14. Flow Curve of 3.75 M Na AZ-101 Melter Feed (With Glass Formers) at 40°C

4.4 Mixing/Aging

This section describes rheological measurements performed on 2.75 M AZ-101 melter-feed material that was mixed for a week with selected measurements performed after 1 hour, 2 days, and 1 week of mixing. GFC, as formulation LAWB-83, were added to a 2.75 M Na AZ-101 pretreated LAW sample with target quantities consistent with Table 2.1. The sample was then mixed with the impeller system discussed in Section 2.2 for a period of 1 hour at ambient temperature (~23°C). The rheology of this sample was then measured at 25°C and 40°C. The remaining sample continued to mix for a period of 2 days. The rheology was again measured at 25°C and 40°C. Finally, the remaining sample continued to mix for a period of 5 additional days (total of 1 week). The rheology was then measured a third time. Figure 4.15 through Figure 4.20 present the mixing/aging rheograms at 25ºC and 40ºC over 1-hour, 2-days, and 1-week intervals. Deionized water was added to these samples to keep a constant volume while mixing, thus minimizing error due to evaporation.

As originally intended, rheological measurements were to be taken after 1 day of mixing. Due to instrument problems, the mixing duration was extended to 2 days. A Haake RS-300 system with a Z-41 sensor was used for the 1-hour measurements while a Haake M5 system with a MVI sensor was used for the remaining mixing/aging measurements. The Z-41 and MVI sensors possess comparable performance capabilities.

Several shear-rate ramps were performed on the sample material to assess the degree of thixotropy (or time-dependence) of the material. The 1-hour mixed sample shows little evidence of thixotropy as both runs nearly overlay each other at both temperatures of 25ºC and 40ºC. However, melter-feed measurements made after 2 days of mixing exhibit significant thixotropy at both 25ºC and 40ºC. This is seen by the fact that successive runs on the sample material result in significantly lower rheological parameters. Physically, this indicates that a weak structure may have formed in the sample while being mixed for 2 days. As the material is brought to a relatively high shear in the viscometer, the structure breaks down, lowering the initial measured rheological properties. This structure could be the result of a weak structure that formed from precipitated solids during the mixing period (Barnes 1997). As the material is sheared multiple times, the flow curves become repeatable, and a steady-state flow curve can be observed. The steady state rheological parameters from the mixing/aging phase of the AZ-101 melter feed characterization can be found in Table 4.7. Non-steady-state results are not reported as several factors including shear history, sample aging, etc. result in non-repeatable results.

When the thixotropic behavior of the mixing/aging sample is examined and compared to the baseline 2.75 M Na AZ-101 melter-feed results presented in Section 4.3, several interesting observations can be made:

- Firstly, the 1-hour mixed samples possessed lower rheological results from the results reported in Section 4.3. This is explained by the fact that rheological properties of the 1-hour mixed samples were immediately measured while the baseline samples reported in Section 4.3 aged for a period of time after mixing for 1 hour.

- Initially, the 2-day mixed sample at 25ºC has rheological properties that approach the results presented in Section 4.3. However, as the sample is sheared, the rheological properties drop to a value similar to the 1-day mixed values. At 40ºC, the rheological properties of the 2-day mixed sample begin less than the baseline values and the 1-hour mixed sample. As the sample is sheared, the rheological properties drop further. This can be explained by a temperature dependence of a material that is precipitating over time.

- The 1-week mixed sample at 25ºC has rheological properties that initially approach the baseline values reported in Section 4.3. After shearing, the rheological properties drop but remain increased over the 1-hour and 2-day mixed measurements.

- At 40ºC, the 1-week mixed sample has rheological properties that initially approach the baseline values reported in Section 4.3. After shearing, the rheological properties drop below the 1-hour mixed properties but are elevated compared to the 2-day mixed measurements.

These results indicate that shear history (i.e., mixing history), age, and temperature have significant effects on the rheological properties of the 2.75 M Na AZ-101 melter feed. This behavior can be explained by the formation of a slow-forming, temperature-sensitive, solid precipitate. This hypothesis is substantiated by evidence of solids precipitation in containers of decanted supernate. This precipitation was observed during the shear-strength testing on the AZ-101 melter feed and is explained more thoroughly in Section 4.5.

The pH of the melter feed was also measured during the mixing/aging portion of the study. Results of these measurements are shown in Table 4.6. The pH of the sample is slightly elevated when compared to the reported value of 7.5 (see Section 3.2.2) throughout the mixing/aging process. Therefore, the observed changes in the rheological behavior during the week mixing/aging period may be associated with slight changes in pH.

Table 4.6. pH of Mixed/Aged 2.75 M Na AZ-101 Melter Feed

pH at ambient		
1-hour after GFC addition	**1-day after GFC addition**	**1-week after GFC addition**
7.6	7.7	7.8

Table 4.7. Rheological Model Fits for AZ-101 LAW Melter Feed at Various Mixing Durations and Temperatures

Model/model Parameter	2.75 M Na at 25°C 1 Hour Mixing	2.75 M Na at 40°C 1 Hour Mixing	2.75 M Na at 25°C 2 Days Mixing	2.75 M Na at 40°C 2 Days Mixing	2.75 M Na at 25°C 1 Week Mixing	2.75 M Na at 40°C 1 Week Mixing
File Name	**043003_a**	**043003_b**	**050203_d**	**050203_f**	**050703_b**	**050703_d**
Newtonian:						
η – Newtonian viscosity (cP)	34.6	26.48	34.36	8.329	45.05	19.64
R^2 – correlation coefficient	0.9916	0.9841	0.9702	0.9647	0.9316	0.9374
Ostwald (or Power Law):						
m – the consistency coefficient (mPa·s^{-n})	71.21	26.48	112.9	32.53	301.2	147.7
n – the power law exponent	0.8901	1.0	0.8187	0.7922	0.71	0.6967
R^2 – correlation coefficient	0.9982	0.9841	0.9898	0.9920	0.9964	0.9932
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	1.233	1.557	2.834	0.7458	5.382	2.551
η_p - the plastic viscosity (cP)	32.76	24.33	30.09	7.205	36.93	16.2
R^2 – correlation coefficient	0.9958	0.9944	0.9972	0.9974	0.9960	0.9980
Herschel-Bulkley:						
τ_O^H - the yield stress (Pa)	0	1.557	3.269	0.6834	2.992	1.951
k - the Herschel-Bulkely consistency coefficient (mPa·s^{-b})	71.21	24.33	21.67	8.659	121.1	34.5
b - the Hershel-Bulkely power law exponent	0.8901	1.0	1.047	0.974	0.8332	0.8939
R^2 – correlation coefficient	0.9982	0.9944	0.9974	0.9974	0.9996	0.9990
n/a = not applicable						

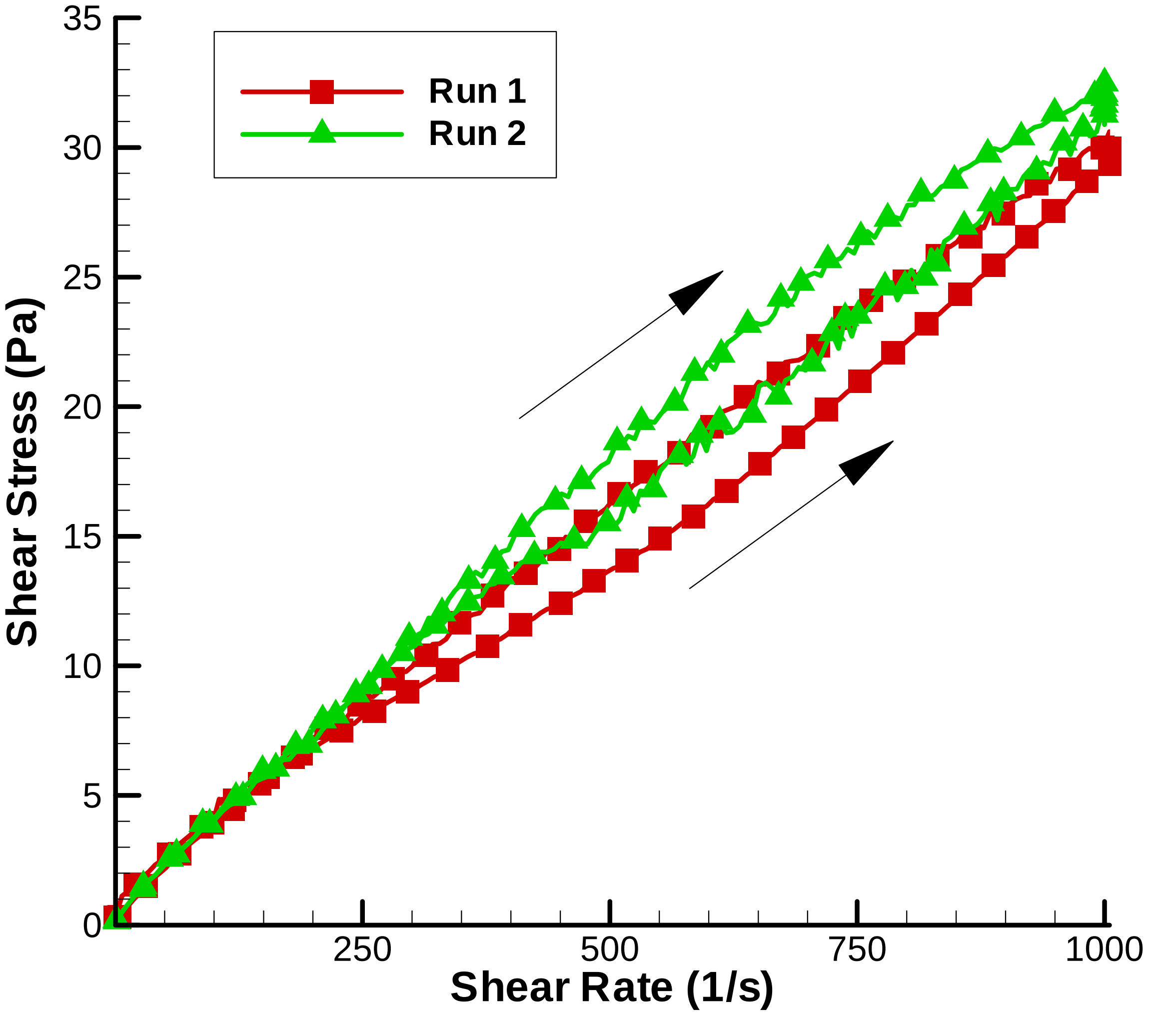


Figure 4.15. Flow Curve of 2.75 M Na AZ-101 Melter Feed (1 Hour Mixing with Glass-Former Chemicals) at 25°C

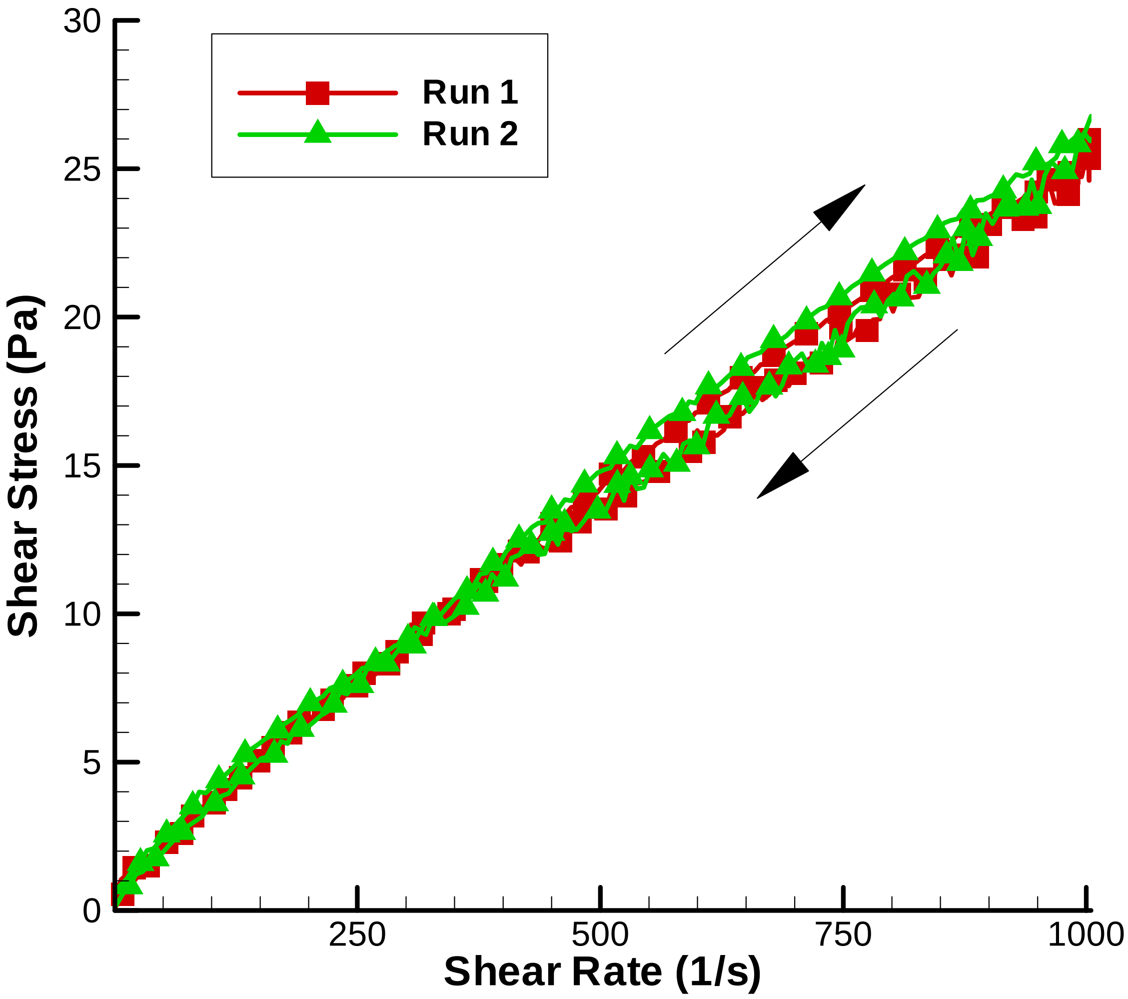


Figure 4.16. Flow Curve of 2.75 M Na AZ-101 Melter Feed (1 Hour Mixing with Glass-Former Chemicals) at 40°C

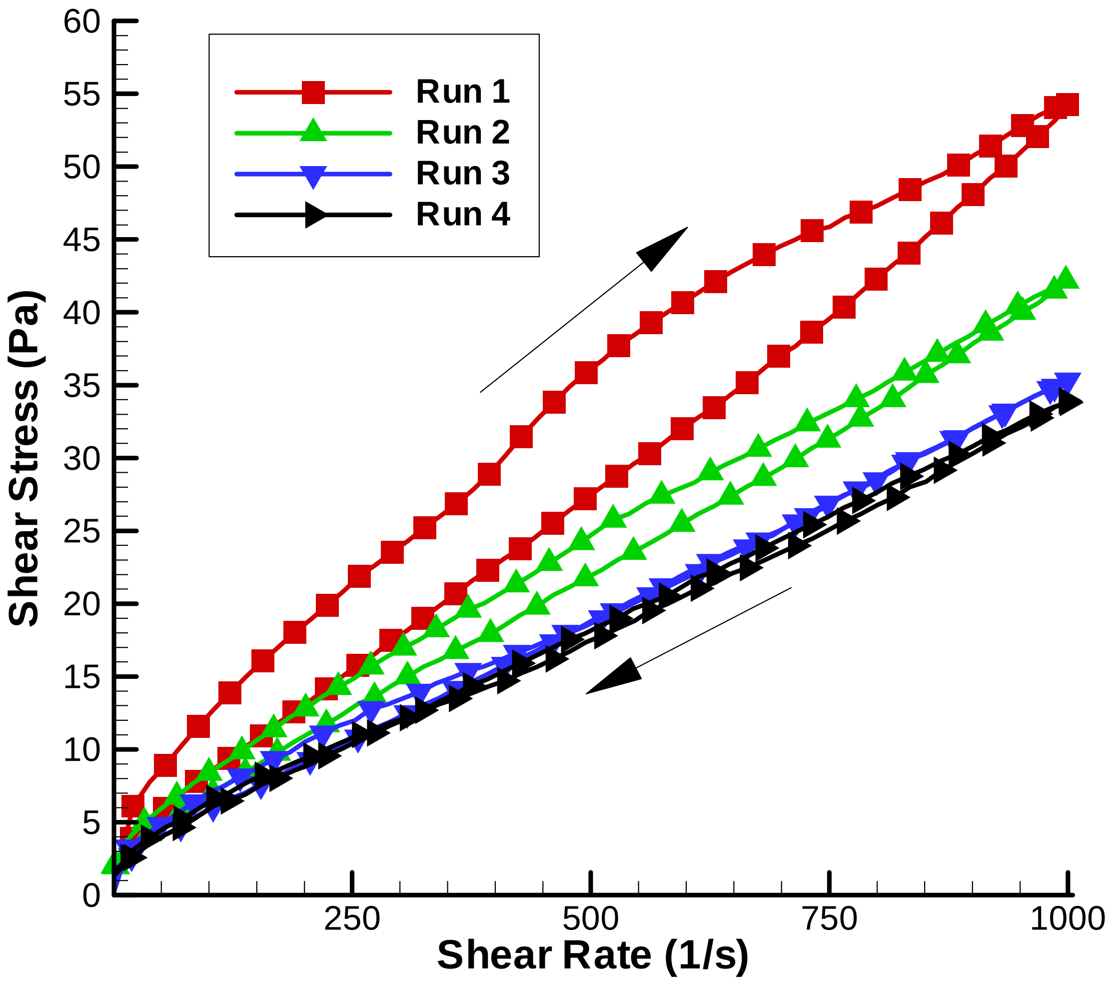


Figure 4.17. Flow Curve of 2.75 M Na AZ-101 Melter Feed (2 Days Mixing with Glass-Former Chemicals) at 25°C

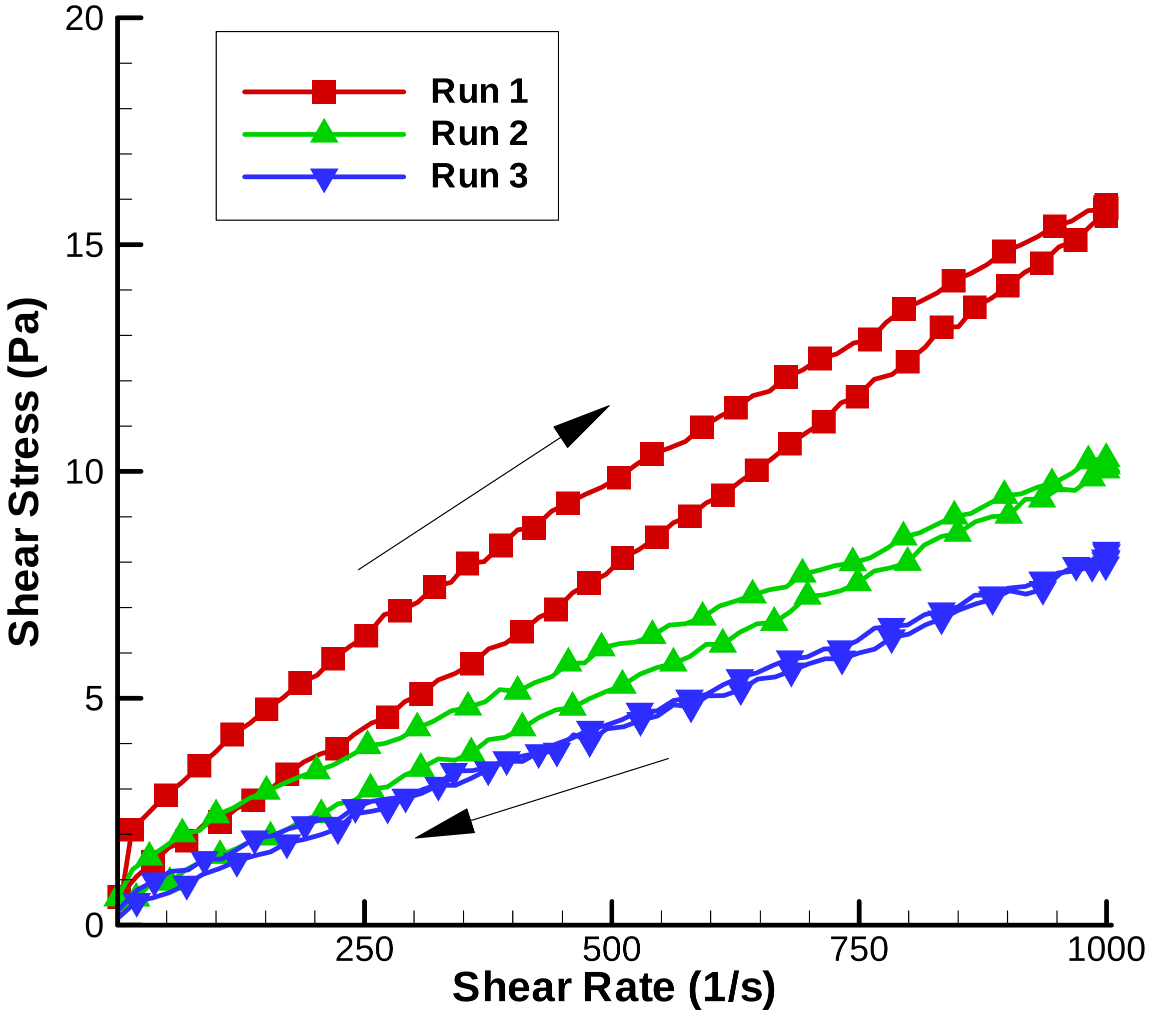


Figure 4.18. Flow Curve of 2.75 M Na AZ-101 Melter Feed (2 Days Mixing with Glass-Former Chemicals) at 40°C

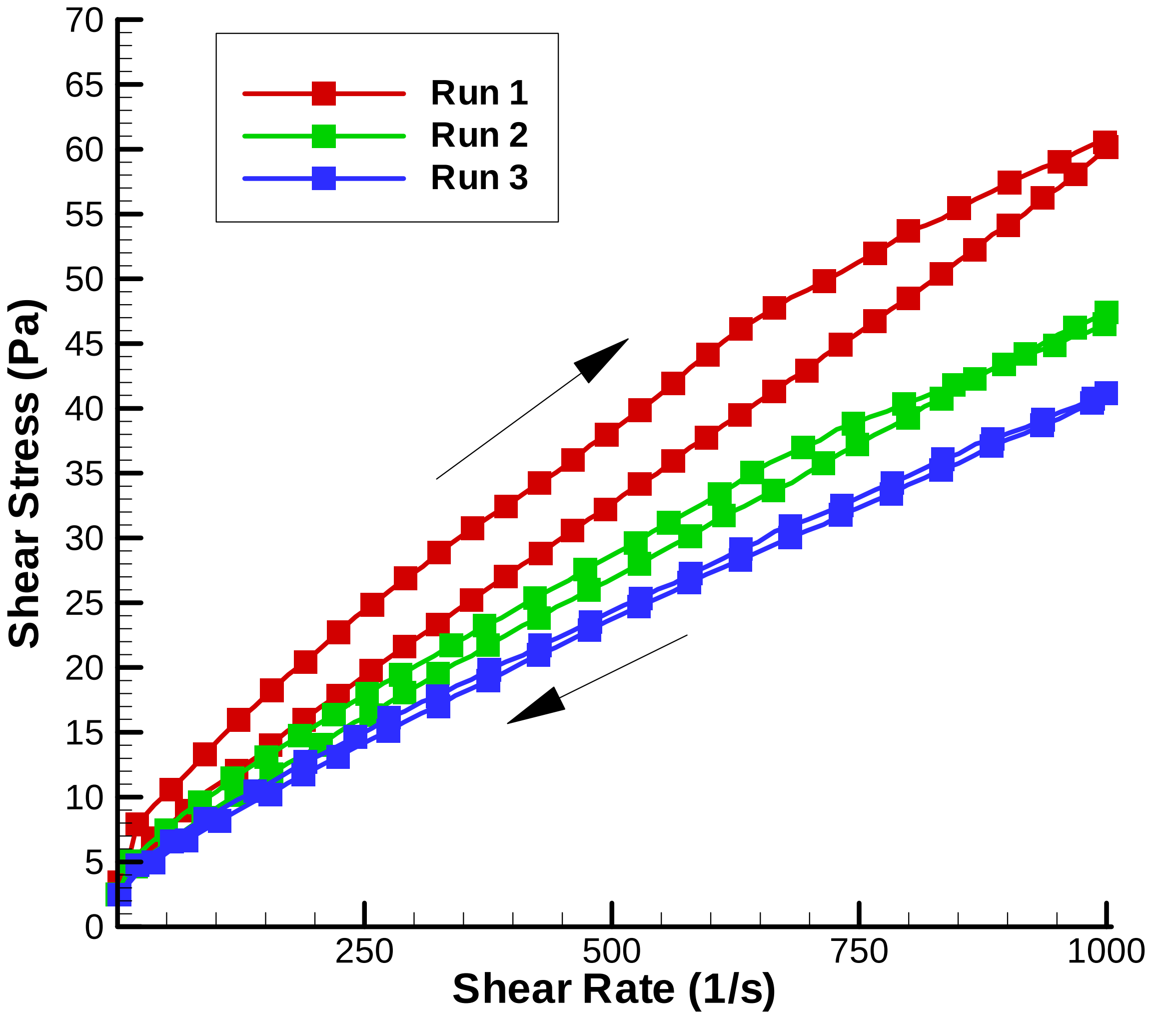


Figure 4.19. Flow Curve of 2.75 M Na AZ-101 Melter Feed (1 Week Mixing with Glass-Former Chemicals) at 25°C

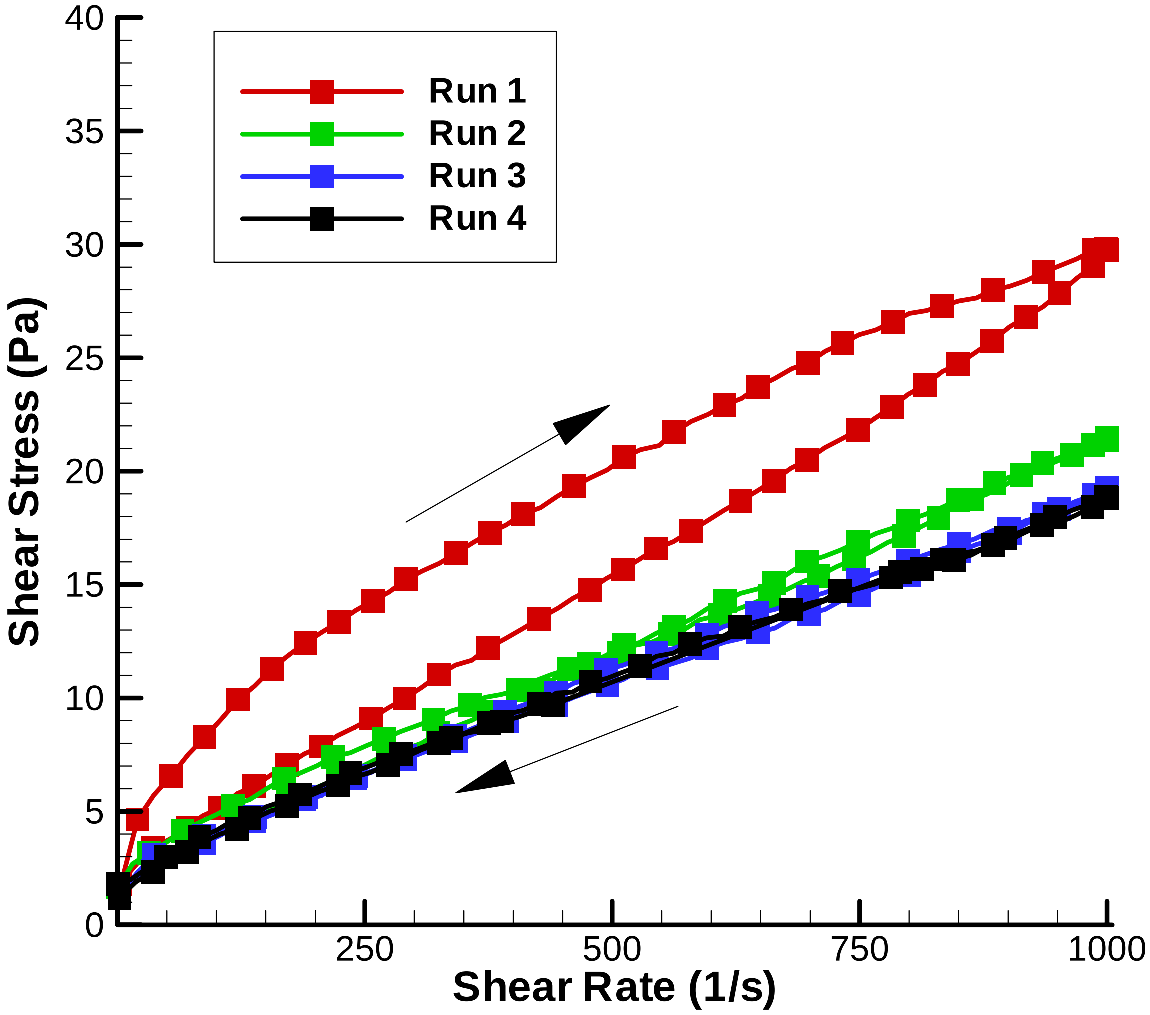


Figure 4.20. Flow Curve of 2.75 M Na AZ-101 Melter Feed (1 Week Mixing with Glass-Former Chemicals) at 40°C

5.0 Shear Strength

According to *Guidelines for Performing Chemical, Physical, and Rheological Properties* M*easurements* (24590-WTP-GPG-RTD-001 Rev 0), the shear strength is defined as the minimum stress required to initiate fluid movement as determined by the vane method. Materials that possess a shear strength exhibit solid-like behavior at low stresses and fluid-like behavior at high stresses. During the solid-like behavior, the material behaves elastically, where a material will strain to a point at a given stress. When the stress is removed in the elastic regime, the material will return to its initial state. The shear strength is regarded as the transition between the elastic behavior and viscous flow.

At sufficiently high solids concentrations, solid/liquid multiphase systems usually exhibit a shear strength. In these systems, the solid particles are usually attracted to each other through electrostatic forces. This creates a network of attracted particles (e.g., a flocculated structure) that can impede viscous flow at low stresses. Viscous flow is achieved when the applied stress is high enough to break apart the structure. Examples of materials that exhibit shear strength include cements, soils, paints, pastes, and various food products (Liddell and Boger 1996).

Many methods have been developed to evaluate yield stress. These methods produce varying results based on the rheological technique and assumptions used in the evaluation. To explain these variations, the concept of static and dynamic yield stress is introduced (Figure 5.1). Static and dynamic yield stresses can be explained by assuming that there are two structures present in yield stress exhibiting fluids. One structure is insensitive to shear rate and defines the dynamic yield stress associated with a flow curve. This dynamic yield stress is found by extrapolating data from a conventional rheogram (i.e., shear stress/shear rate) to zero shear rate. The extrapolation can be made through the use of rheological model equations.

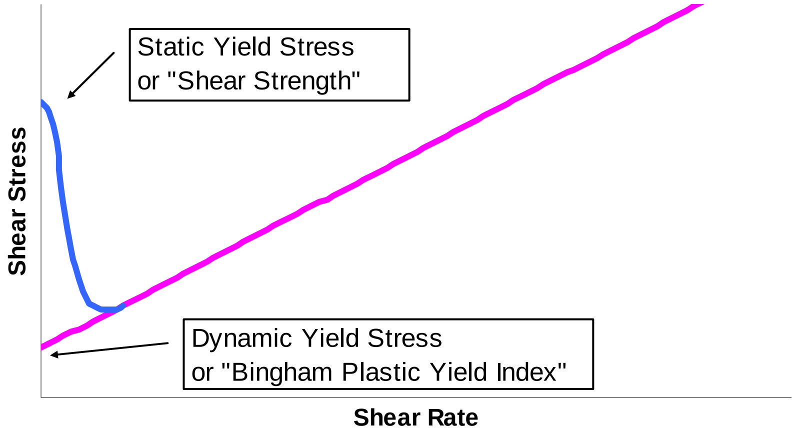


Figure 5.1. Rheogram Illustrating the Concept of Dynamic and Static Yield Stress

However, a secondary weak network structure is also present that forms while the fluid is at rest. The second structure is sensitive to shear rate and breaks down as the fluid is sheared. Combined, these two stresses define the static yield-stress value. The use of a rheogram to measure this secondary structure requires accurate experimental data at low shear rates. Due to slip flow, inertial effects, etc., this is often difficult with conventional viscometers. Consequently, direct measurement of static yield stress or shear strength using a shear vane has been developed. Measurements using this technique are discussed in detail in Section 5.

Use of the static and dynamic yield-stress values varies with application. For instance, the dynamic yield-stress value extrapolated from a rheogram should be used when performing pipeline head-loss calculations. The static yield stress should be used for process restart applications where the secondary structure could form while the fluid is a rest. Static yield stress or shear strength can be directly measured using a shear-vane technique. Since shear-strength values are discussed in this section, values of shear strength for common food items as measured by the vane method are given in Table 5.1. This table should provide a reference point for the magnitude of shear-strength values discussed in this section.

Table 5.1. Shear Strength of Various Common Materials

Material	Shear Strength (Pa)		
Baby food, peaches	22.9	±	3.4
Spaghetti sauce, Brand B	24.8	±	3.4
Spaghetti sauce, Brand A	26.3	±	4.5
Tomato puree, Brand B	30.0	±	4.2
Baby food, pears	31.8	±	5.0
Tomato puree, Brand A	34.4	±	3.7
Tomato ketchup, Brand B	43.2	±	3.4
Apple sauce, Brand B	48.2	±	4.7
Tomato ketchup, Brand A	51.3	±	5.0
Baby food, carrots	64.0	±	4.0
Apple sauce, Brand A	77.3	±	0.0
Mustard, Brand A	82.5	±	5.3
Mustard, Brand B	103.8	±	5.0
Mayonnaise, Brand B	163.8	±	4.2
Mayonnaise, Brand A	204.4	±	5.0

5.1 Measurement Equipment and Theory

Direct measurement of shear strength can be made by slowly rotating a vane immersed in the sample material and measuring the resulting torque as a function of time. The torque can be converted to a shear stress by making several assumptions (Liddell and Boger 1996). Firstly, the material is assumed to be sheared only along the cylinder defined by the dimensions of the vane. This assumption has been shown to be only a slight oversimplification. The actual diameter of the sheared surface may be up to 5% larger than the vane dimensions (Bowles 1977, p. 99; Keentok 1982; Keentok et al. 1985). Secondly, it is assumed that the stress is distributed uniformly over the cylindrical sheared surface. Although the stress actually peaks sharply at the vane tips (Barnes and Carnali 1990; Keentok et al. 1985), it has been shown that the error due to this assumption is minimal (Alderman et al. 1991; Avramidis and Turain 1991; James et al. 1987; Nguyen and Boger 1985a; Nguyen and Boger 1985b; Nguyen and Boger 1983). Therefore, a good approximation of the measured stress can be calculated from Equation 5.1 where K is the vane constant defined in Equation 5.2.

$$\tau = T / K \tag{5.1}$$

$$K = \frac{\pi D^3}{2}\left(\frac{H}{D} + \frac{1}{3}\right) \tag{5.2}$$

where

τ = calculated shear strength (Pa)
T = measured torque (Nm)
K = shear vane constant (m^3)
D = shear vane diameter (m)
H = shear vane height (m).

In addition, the shear vane must be immersed in the test material such that wall and end effects are negligible. Figure 5.2 shows an accepted material testing geometry to minimized wall and end effects (Dzuy and Boger 1985). These geometry requirements were confirmed before material testing.

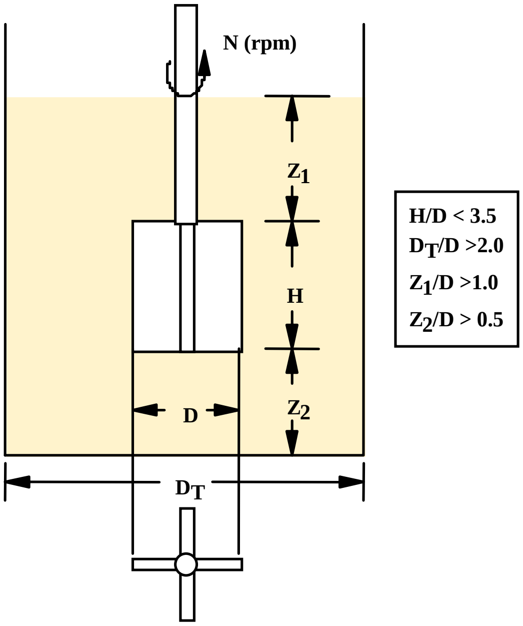


Figure 5.2. Geometrical Requirements of a Shear Vane

A typical stress-time profile is shown in Figure 5.3. The profile shows an initial linear region, followed by a non-linear region, a stress maximum, and a stress-decay region. The shape of the stress-time profile can be explained from a consideration of the network bonds within the material. The initial linear region represents the elastic deformation of the network bonds. The non-linear region represents visco-elastic flow (also called creep flow), where the network bonds are stretched beyond their elastic limit, and some of the bonds begin to break. The linear and non-linear regions are separated by point τ_y. At the maximum stress, τ_s, the majority of the bonds are broken, and the material begins to flow as a fully viscous fluid. The network typically collapses, and stress decay is observed.

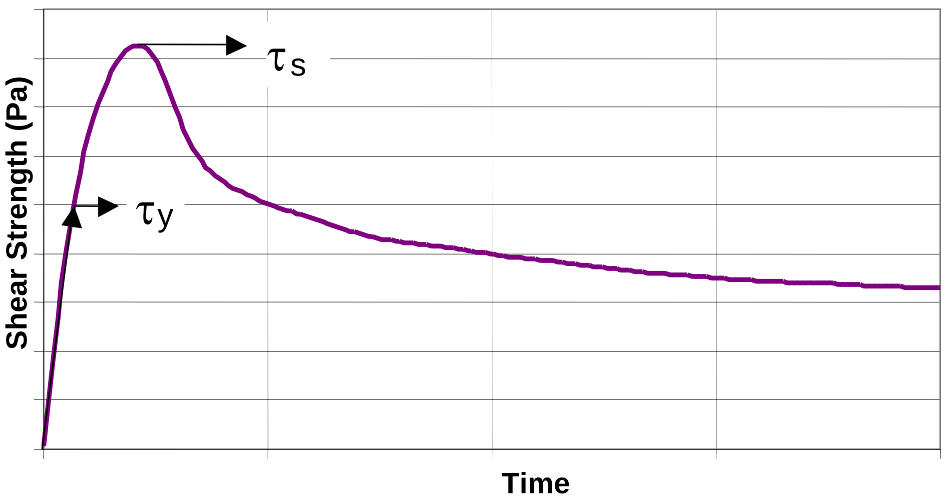


Figure 5.3. Typical Response of a Shear Vane

From this response, two shear strengths can be defined, one corresponding to the transition between elastic and visco-elastic flow, τ_y, and the other corresponding to the transition between visco-elastic and fully viscous flow, τ_s. Most researchers regard the transition between visco-elastic and fully viscous flow as the definitive shear strength of the material. In this report, shear strength will be defined by the transition between visco-elastic and fully viscous flow, τ_s.

5.2 System Validation and Calibration

Initially, a viscosity standard (Brookfield 98cP oil, lot# 010702) was measured with the cup/cylinder geometry on the Haake RS300 rheometer. While this does not implicitly test the vane geometry, it assures that the torque detection system used by the viscometer is functioning and calibrated properly. As expected, Newtonian behavior of the standard was observed with a measured viscosity of 98.7 cP at 25°C. This viscosity was measured over a shear-rate range of 0 s^{-1} to 1000 s^{-1}. This measured viscosity results in approximately 1% error from the documented viscosity of 98 cP at 25°C. This error is within the allowable 10% value specified in PNWD Test Instruction TI-RPP-WTP-207, "AZ-101 (Envelope B) Melter Feed and Rheology Testing" and is typical of this particular viscometer model.

5.3 Results from Shear-Strength Measurements

With the calibration of the Haake RS300 rheometer established, shear-strength measurements were taken on the settled solids from the 1.75, 2.75, and 3.75 M Na melter-feed samples. The shear vanes were immersed in the settled solids according to the geometrical requirements outlined in Figure 5.2. The shear used for this report were four bladed with dimensions of D=1.6 cm H=1.6 cm. The rotational speed of the viscometer was set at a constant 0.3 RPM (0.0314 rad/s). The resulting shear stress/time curves are shown in Figure 5.4.

These shear-strength results indicate that the settled solids can form a very cohesive layer that is difficult to shear. Initially, the 1.75 M Na sample produced a shear strength of 950 Pa while the 3.75 M Na sample had a shear strength of 2,430 Pa. Interestingly, the 2.75 M Na sample possessed a shear strength that exceeded the scale of the viscometer. The top scale of the viscometer with the 1.6 × 1.6 cm (0.63 × 0.63 in.) shear vane is approximately 11,600 Pa.

This apparent inconsistency in the trend of shear strength with Na concentration was probably the result of partial agitation of the samples prior to the analysis. The researcher performing this work noted that he had trouble getting the sample into the glovebox where the instrument was located. He knocked the sealed jars on their side in the process. Since the jars were sealed no material was lost. However, the settled solids had been disturbed so the analysis needed to be repeated.

The samples were mixed and allowed to settle for two additional days. A second shear-strength run was then performed. For this set of runs, all of the samples exceeded the top scale of the of the viscometer/shear vane system at 11,600 Pa. The 1.75 M Na sample was then run a third time with a smaller shear vane (D=1.6 cm H=0.8 cm) to extend the measurement scale of the technique. Again, this run exceeded the top scale of the of the viscometer/shear vane system at 18,600 Pa. These results are summarized in Table 5.2.

It should be noted that viscosity calibration standards were run before and after the shear-strength runs. The viscosity calibration checks were in tolerance, indicating that the instrument was functioning properly. In addition, the viscometer/shear vane system was run with an empty sample container, and a value of zero shear strength was measured. This indicates that the instrument was configured properly with the shear vane during the actual waste measurements.

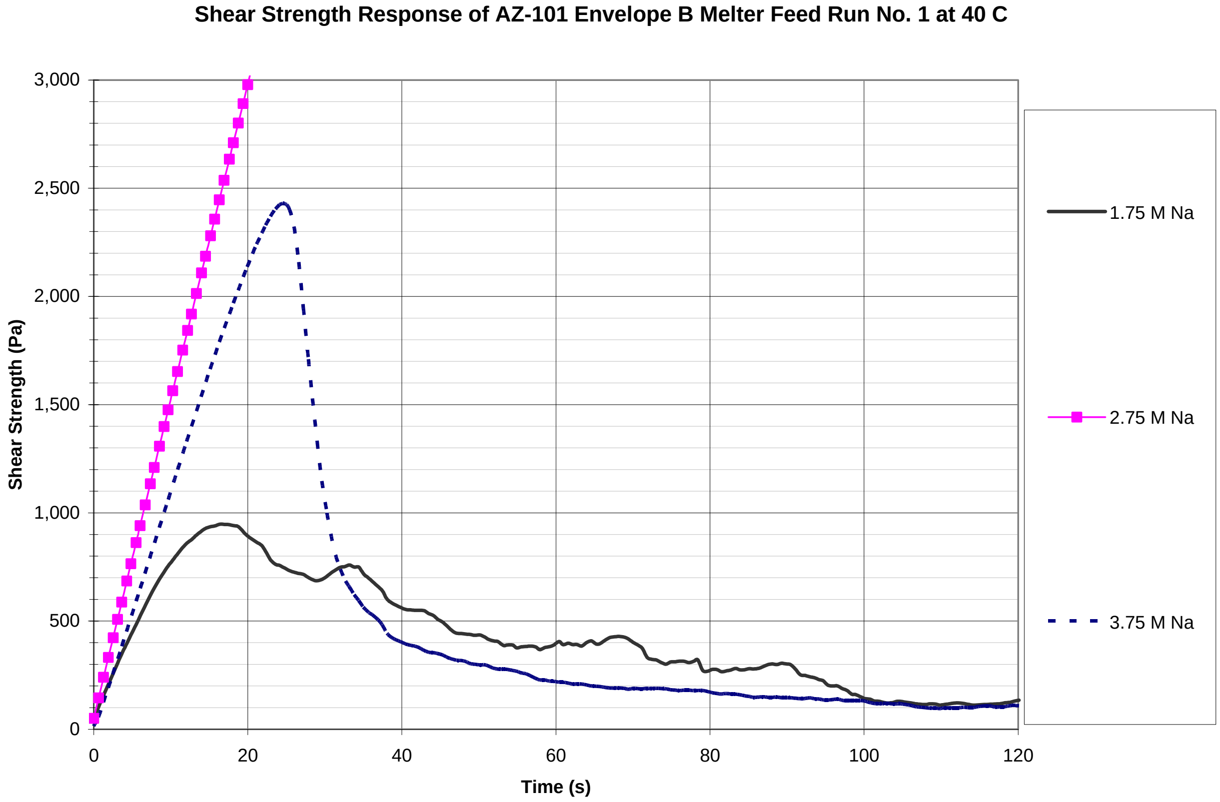
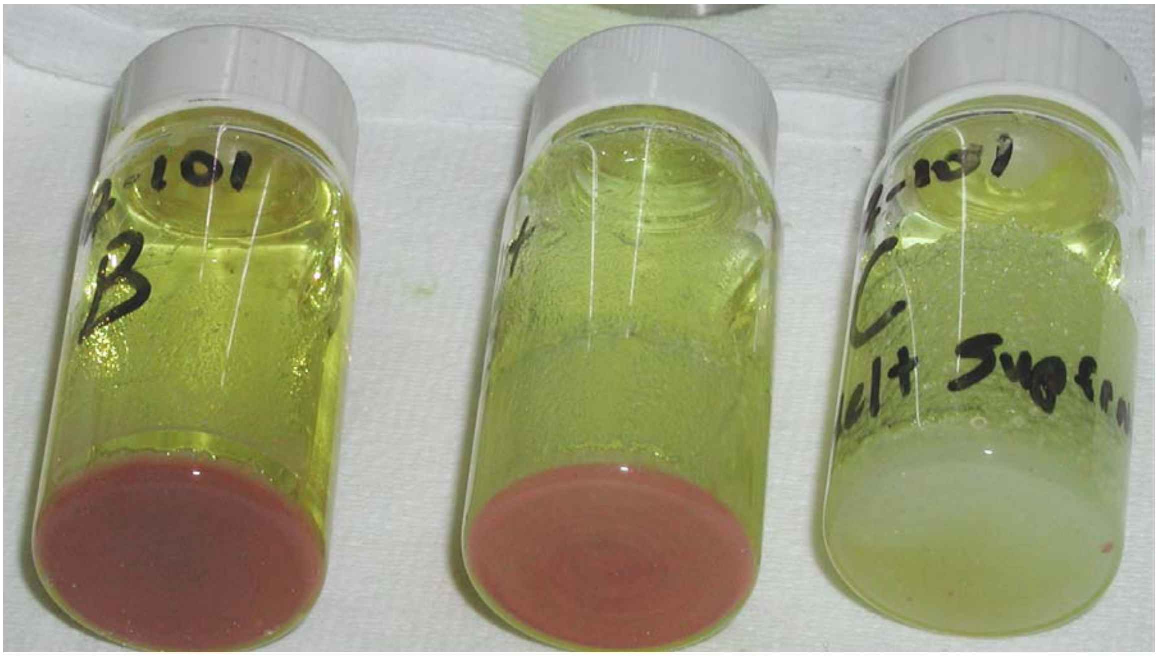


Figure 5.4. Shear Strength Response of 1.75, 2.75, and 3.75 M Na AZ-101 Melter Feed Settled Solids Run No. 1. Sample Were Partially Agitated Prior to Analysis.

Table 5.2. Summary of Shear Strength Data at 40°C

Sample	**Temp.**	**Shear Strength (Pa)**		
		Run 1[a]	**Run 2**	**Run 3**
1.75 M Na	40°C	2,430	>11,600	>18,600
2,75 M Na	40°C	>11,600	>11,600	n/a
3.75 M Na	40°C	950	>11,600	n/a
n/a – not applicable a, samples partially agitated				

The shear-strength results indicate that the AZ-101 melter feed is very time dependent with respect to shear strength. The shear strength can be measured at reasonable levels (i.e. ~900 Pa) and then reach exceedingly high levels (~>18,000 Pa) in a time span of 48 hours. This is most likely due to a solids-precipitation reaction that is bridging the melter-feed particles into a solid monolith over time. This solid precipitation was observed during shear-strength sample preparation when free-standing supernate was decanted from the settled-solids layer. The decanted supernate was placed in individual glass scintillation vials. A crystalline material was observed to be forming in the vials as shown in Figure 5.5. This precipitated material may be the source of the high shear-strength measurements.

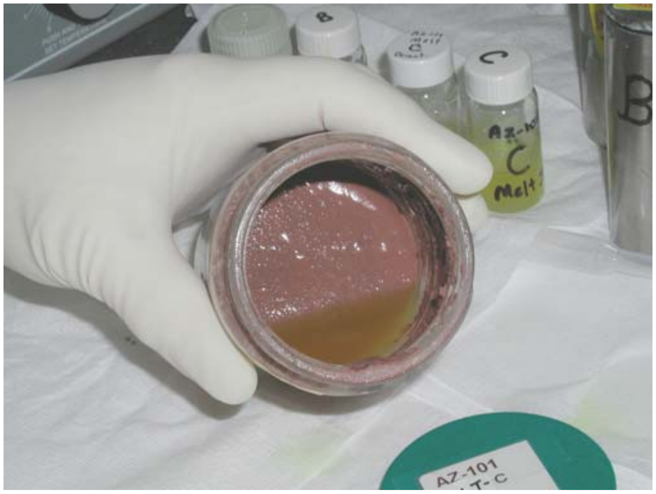


note: precipitates are white solids; red coloration is due to residual melter feed from decanting

Figure 5.5. Crystalline Precipitate Observed from Decanted AZ-101 Envelope B Melter Feed

The high shear strength of the settled solids was also observed visually throughout the AZ-101 Envelope B melter feed characterization. This can be seen from Figure 5.6. When the settled solids were tilted to the side, the settled-solids layer remained parallel to the bottom of the container, and no deformation due to gravity was observed. In addition, when the settled solids were mixed with a spatula, significant force needed to be applied to mobilize the slurry. When sheared with the spatula, the settled solids broke off in chucks leaving a large depression in the settled solids layer. This behavior is indicative of a material with a large shear stress and substantiates the measured results.

a) Settled solids layer when tilted to one side.



b) Settled solids layer before mixing.

c) Settled solids layer during mixing.

Figure 5.6. High Shear Strength of AZ-101 Envelope B Melter Feed During Mixing

6.0 Particle-Size Distribution

The particle-size distributions (PSDs) of the 1.75 M Na melter feed sample that was mixed for 1 hour after glass-former chemicals addition is described in this section. A Malvern MS-2000 particle-size analyzer was used to measure the PSD of this sample.

6.1 Instrument Description

The Malvern MS-2000 particle-size analyzer measures particle diameter by scattered light from a laser beam projected through a stream of the sample particles diluted in a suspending medium. The amount and direction of light scattered by the particles is measured by an optical detector array and then analyzed to determine the size distribution of the particles. This measurement is limited to particles with diameters between 0.02 and 2000 μm.

6.2 Calibration Checks

The performances of both instruments were checked against a National Institute of Standards and Technology (NIST)-traceable standard from Duke Scientific Corporation. This standard consists of polystyrene microspheres dispersed in deionized water. This standard was run as a calibration check before the sample was analyzed. Results from these standard tests are presented in Table 6.1. To check the functionality of the instrument, a close fit of the D_{50} value is typically required (approximately 10%). The D_{50} value represents the particle diameter where 50% of the particles are smaller than this value. The D_{10} and D_{90} values represent the particle diameter where 10% and 90% of the particles are smaller than these values, respectively, and are used to quantify the edges of the total distribution. The instrument calibration was verified when the measured D_{50} value was within ±0.3% of the NIST-certified value.

Table 6.1. Particle-Size Analyzer Calibration Data

49.8 ± 0.8 μm NIST Traceable Particle Size Standard		**Measured Diameter (μm)**	**Coefficient of Variation Between Five Runs**
Malvern MS-2000	D_{10}	46.506	0.24%
	D_{50}	49.952	0.21%
	D_{90}	56.598	0.56%

6.3 Operating Conditions

The PSD of the 1.75 M Na melter-feed sample was measured in the Malvern MS-2000 at a pump rotational rate of 2500 RPM. The pump rotational speed has an effect on the resulting particle size distribution by applying shearing forces to agglomerated particles. The shearing forces break apart agglomerates such that the primary particle size distribution can be measured. The higher the pump speed the more shearing forces are applied. Further deagglomeration can be achieved through sonication. The samples were then sonicated with two progressively increasing levels of ultrasonic waves (25% setting and 50% setting) while flowing at a pump rotational rate of 2500 RPM. The PSD during sonication was then measured at each of these sonication levels. The ultrasonic energy input is used to determine the shear sensitivity of the slurry to investigate whether flocculation/deagglomeration is occurring. Analyses were repeated on five separate samples under all flow/sonication conditions.

6.4 Suspending Medium

The suspending medium should be chosen such that the particle size distribution is not altered through particle dissolution. The suspending medium for the AZ-101 analyses was related to an AZ-101 simulant tank supernatant used for particle size analysis in WTP-RPT-048, Rev. 0 (Urie et al. 2002). However, the simulant recipe was altered to produce a 1.75 M Na solution. To mimic the composition of the melter feed supernate, boric acid, lithium carbonate, and sugar were added to the simulant in a quantity consistent with Table 2.1. These chemicals are expected to be soluble in the 1.75 M Na simulant. The filtered simulant was then used as a suspending medium in the particle-size instrument. This suspending medium should have similar ionic content to the actual 1.75 M Na AZ-101 Env B interstitial liquid and minimize the potential for dissolution of the solid particles.

6.5 Results

The PSD summary of the five samples in the flow cell circulating at a pump speed of 2500 RPM and sonication levels of 0%, 25%, and 50% are shown in Table 6.2. The D_{10}, D_{50}, and D_{90} values along with the associated coefficient of variation between these five subsamples is presented. A target value for the coefficient of variation of 15% for the D_{10} and D_{90} values and 10% for the D_{50} value should indicate little variation between subsamples. These target values were achieved with a pump setting of 2500 RPM and sonication level of 50%.

Table 6.2. Summary of Volume PSD Data

Pump speed / Sonication level	D_{10} (μm)	Coefficient of Variation	D_{50} (μm)	Coefficient of Variation	D_{90} (μm)	Coefficient of Variation
2500 RPM/0% sonication	1.3	24.4%	19.3	23.1%	79.5	14.0%
2500 RPM/ 25% sonication	1.1	22.0%	15.8	24.2%	69.8	15.4%
2500 RPM/ 50% sonication	0.9	10.1%	13.3	7.3%	56.7	10.2%

At a pump setting of 2500 RPM and 0% sonication, the coefficient of variation between the five subsamples is relatively large, indicating large differences between the measurements taken for each aliquot. These difference can either be due to varying degrees of flocculation or subsampling errors. Differences due to flocculation will be eliminated by increasing the sonication level for subsequent measurements. In addition, the measured particle sizes exceed 105 μm, which is the maximum size of the typical glass-forming chemicals used by the WTP. This can be seen in the measured PSD shown in Figure 6.1.

At a pump setting of 2500 RPM and 25% sonication, the coefficient of variation between the five subsamples remains relatively large, indicating large differences between the measurements taken for each aliquot. Again, these differences can either be due to varying degrees of flocculation or subsampling errors. In addition, the measured particle sizes often exceed 105 μm, which is unexpected based on the mesh size of typical glass-former chemicals. These PSD runs can be seen in Figure 6.2.

Lastly, at a pump setting of 2500 RPM and 50% sonication, the coefficient of variation between the five subsamples drops significantly into the target ranges discussed above. These results indicate little difference between the measurements of the five aliquots. Due to the increased level of sonication, the high coefficients of variation in the previous measurements can be attributed to flocculation rather than subsampling errors. In addition, the resulting PSD appears consistent with the mesh sizes of the glass-former chemicals used in the melter feed. These PSD runs can be seen in Figure 6.3.

Due to the repeatability between five subsamples, the 2500 RPM and 50% sonication measurements should be considered the fundamental PSD. The average PSD for each sonication level is shown in Figure 6.4. From this figure, one can see that as the level of sonication increases, the quantity of large particles decreases, and the quantity of small particles increases. Three modes can be seen in the fundamental PSD. One peak is seen at approximately 0.7 μm and another peak at approximately 20 μm. A small third peak is observed at approximately 400 μm; this mode is most likely a small amount of flocculated particles that are not completely deagglomerated at 50% sonication. The cumulative PSD is shown in Figure 6.5. This representation of the particle-size measurements indicates that the D_{95} value for the fundamental distribution is approximately 74 μm. The D_{95} value is commonly used as a conservative value of particle size for various engineering calculations.

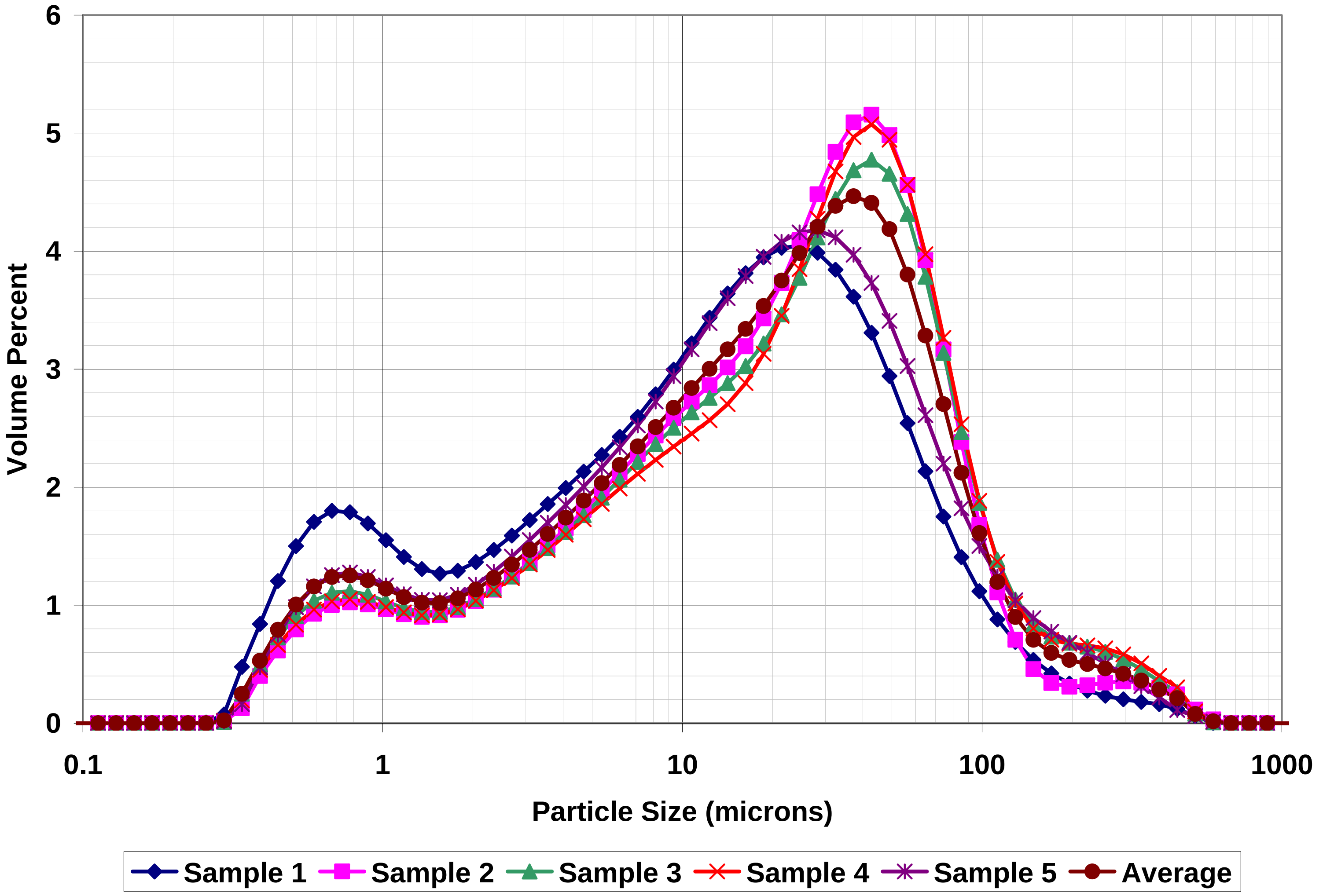


Figure 6.1. PSD of 1.75 M Na AZ-101 Envelope B Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 0%

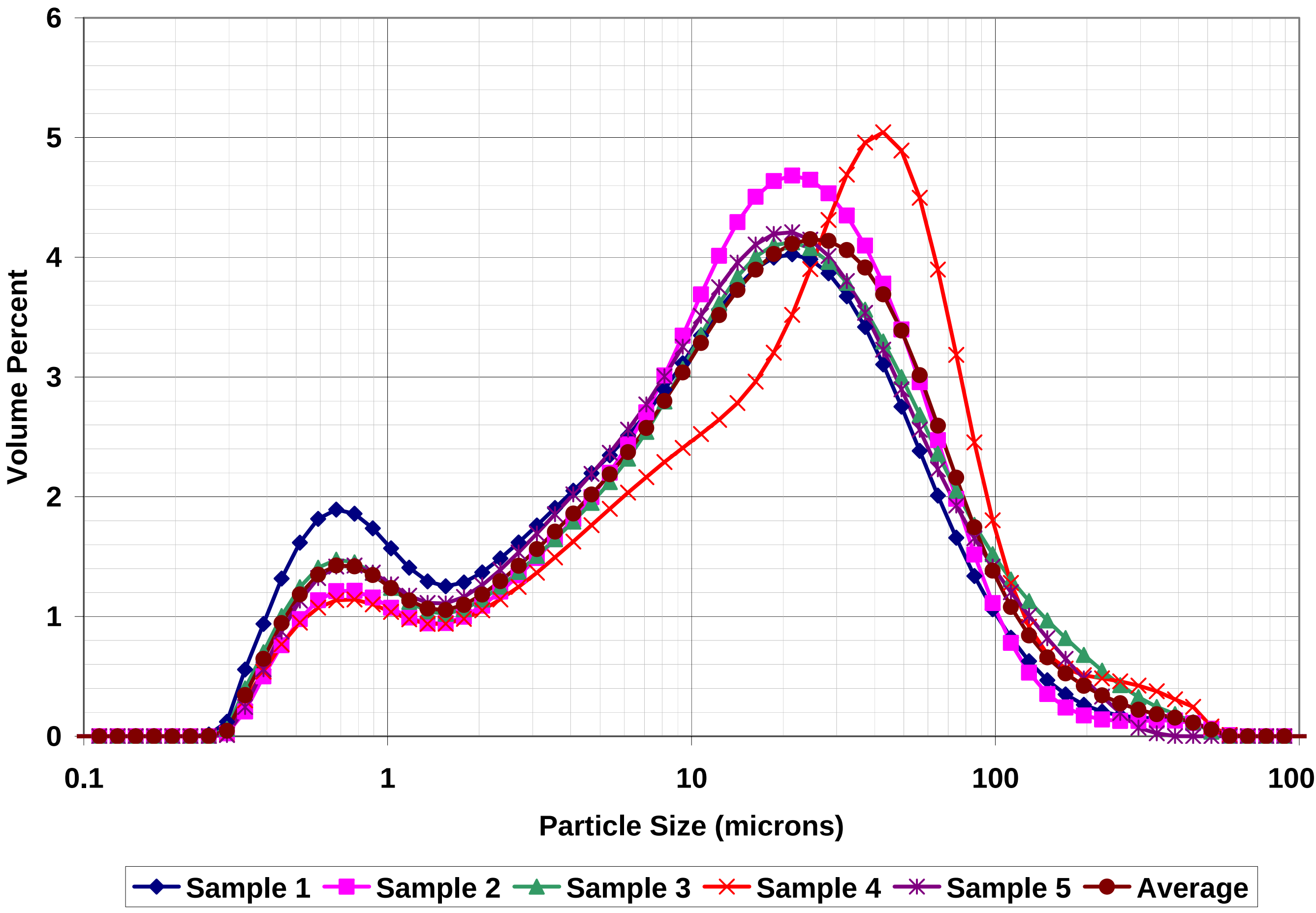


Figure 6.2. PSD of 1.75 M Na AZ-101 Envelope B Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 25%

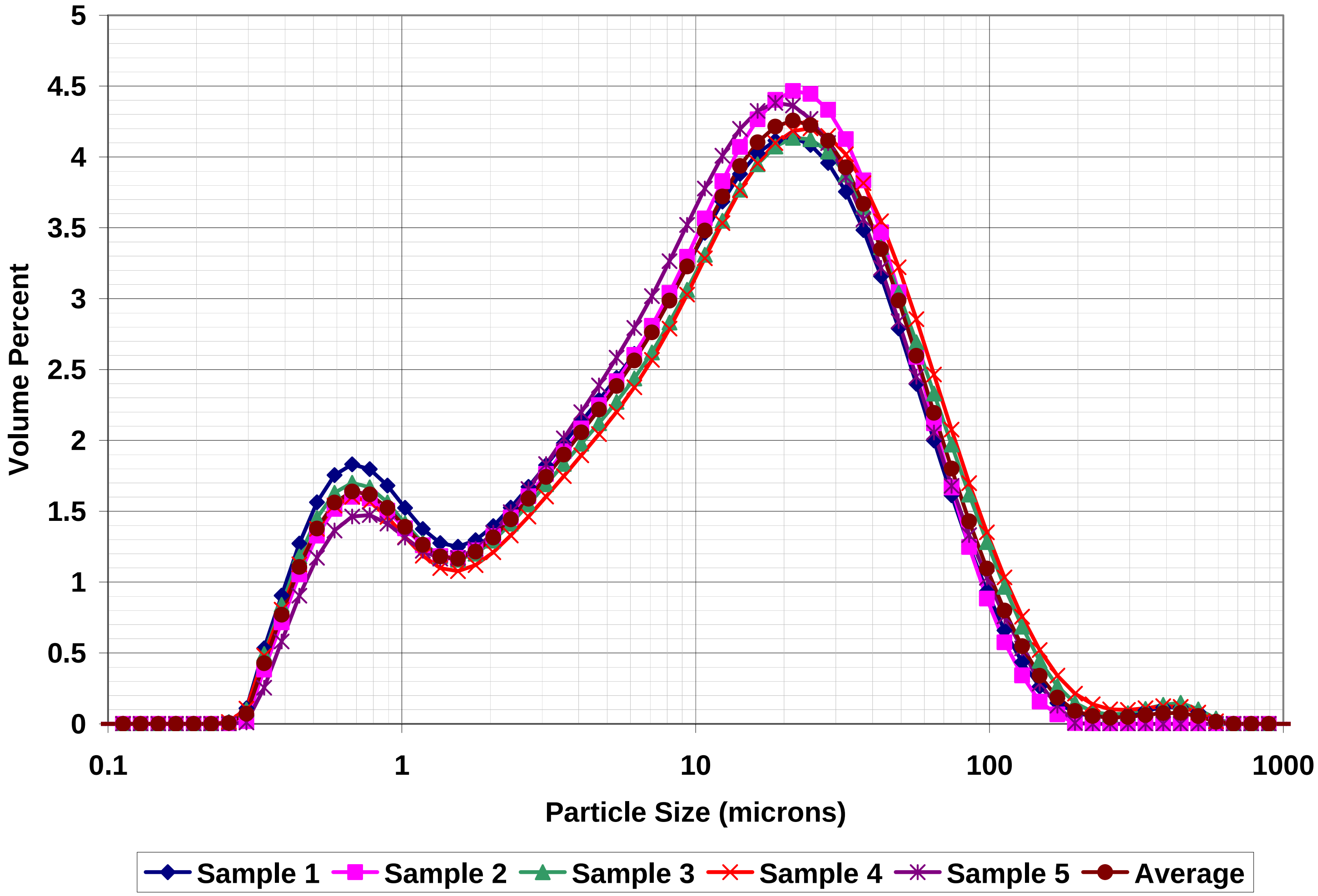


Figure 6.3. PSD of 1.75 M Na AZ-101 Envelope B Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 50%

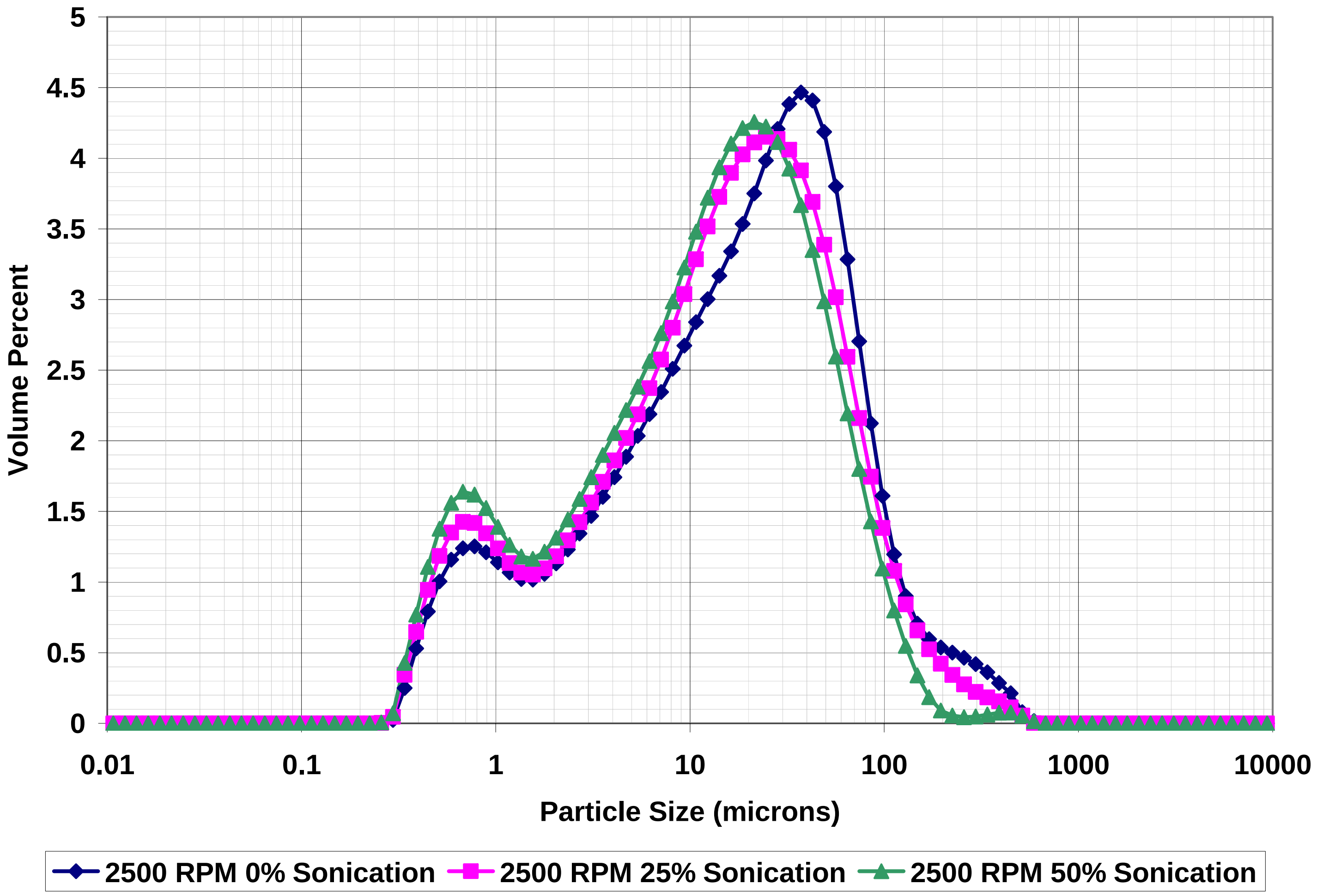


Figure 6.4. Average PSD of 1.75 M Na AZ-101 Envelope B Melter Feed at a Pump Setting of 2500 RPM and Varying Levels of Sonication

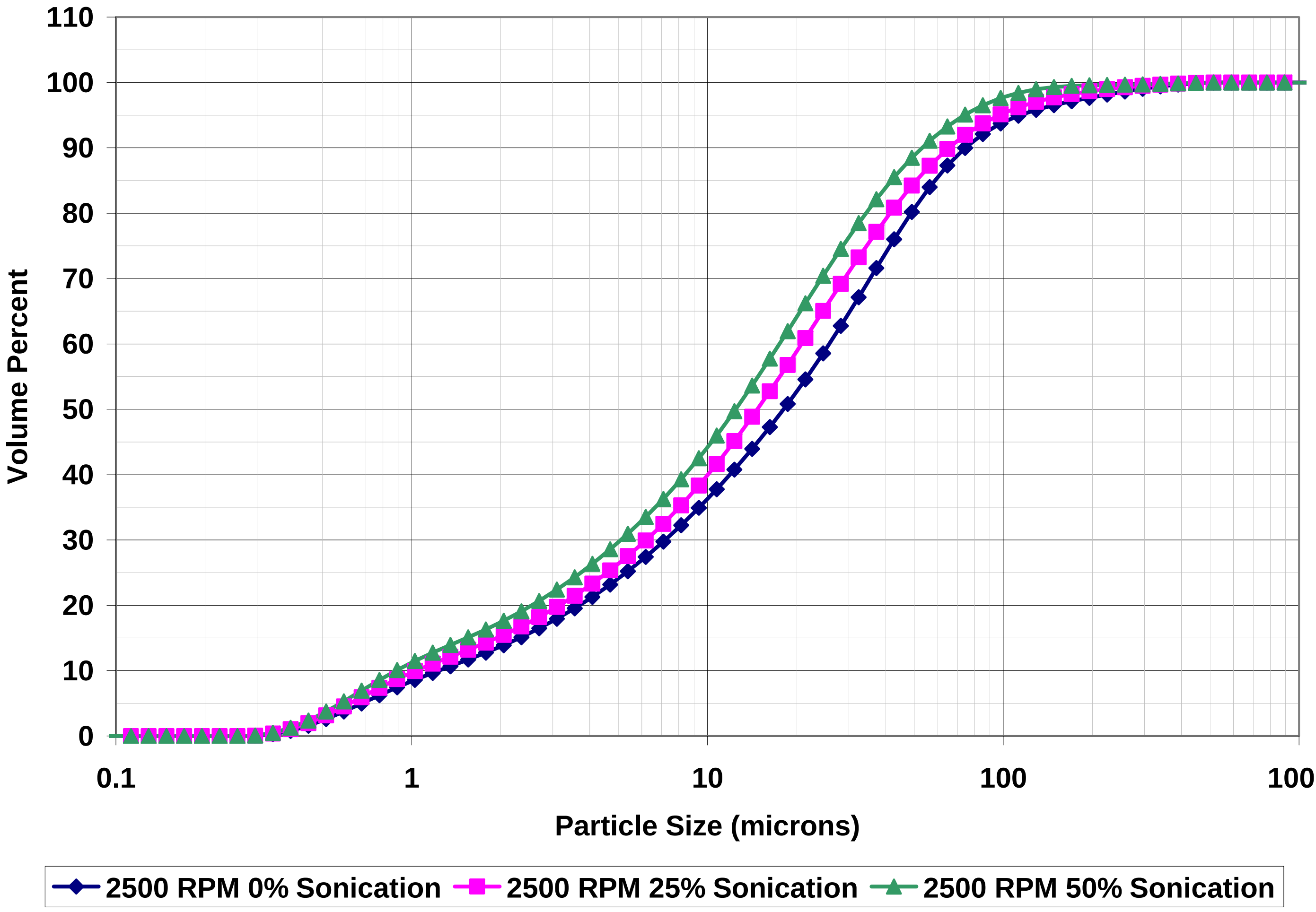


Figure 6.5. Average Cumulative PSD of 1.75 M Na AZ-101 Envelope B Melter Feed at a Pump Setting of 2500 RPM and Varying Levels of Sonication

7.0 Conclusions

A sample of AZ-101 pretreated LAW sample was received at an initial sodium concentration of 4.3 M. The sample was diluted to 1.75, 2.75, and 3.75 M Na concentrations. Physical-properties analyses on these samples indicate a density ranging from 1.10 to 1.20 g/mL with dissolved-solids contents ranging from 12% to 23% and pH ranging from 13.2 to 13.6 as concentration increases from 1.75 to 3.75 M Na. No precipitated solids were measured or observed in these samples. Flow curves from these samples indicate that the fluid should be characterized as a low viscosity Newtonian fluid with the maximum measured viscosity of 2.4 cP.

When glass-former chemicals were added to the AZ-101 pretreated LAW, the pH of the solution dropped from the 13.2 to 13.6 range to a 7.9 to 7.1 range as Na concentration increases from 1.75 to 3.75 M. This is most likely due to the relatively large quantity of boric acid in the LAWB-83 melter feed formulation. Such a large change in pH can result in significant solids precipitation. This solids precipitation was observed in decanted AZ-101 supernate that was separated from the settled solids layer for shear-strength analysis. It is hypothesized that these precipitated solids bridge the insoluble glass-former chemicals, resulting in extremely high measured shear strengths exceeding 18,000 Pa. Materials with shear strengths of this magnitude will be extremely difficult to mobilize in the WTP. To avoid this situation during WTP operation, the melter-feed solids must constantly be suspended and not allowed to settle. If loss of agitation occurs in the WTP, operational controls must be in place to transfer this material to an operational mixing tank before the solids can settle.

The settling behavior of the AZ-101 LAW melter feed can be characterized as "zone" or "hindered" settling. Depending on tank volume in the WTP, settling experiments indicate that a high-solids-loading settled-solids layer can form 24 hours after loss of agitation. This indicates that an operational constraint of several hours is required as the maximum time before evacuation from the unagitated tank to an agitated tank before slurry mobilization becomes extremely difficult.

After settling for 72 hours, the volume fraction of settled solids decreases as the temperature increases. This behavior is most likely due to tighter particle packing as a result of particle dissolution at elevated temperatures. Because the settled-solids volume does not appear to significantly change before and after centrifugation, maximum packing appears to have been reached after settling for 3 days at 25°C. However, at 40°C, the maximum packing efficiency does not appear to be reached after 3 days of settling as the solids-layer volume appears to decrease approximately 10% after centrifugation at each sodium concentration.

Physical-properties testing reveals that, as expected, the quantity of total and UDS increases with sodium concentration. This is due to the increased quantity of GFC required for the melter-feed formulation at higher sodium concentrations. When the temperature is increased from 25°C to 40°C, the insoluble GFC appear to dissolve slightly. This is reflected by the increasing dissolved-solids content and decreasing undissolved-solids content as the temperature increases at each sodium concentration.

At low sodium concentrations, AZ-101 LAW melter feed exhibits Newtonian rheological behavior. At 1.75 M Na at 40°C, the Newtonian viscosity at the low range was approximately 14 cP. At 2.75 M Na at 25°C, the Newtonian viscosity at the high range was approximately 80 cP. The high-concentration melter feed at 3.75 M Na appeared to behave as a power-law fluid. However, a good fit could be achieved with the Bingham model. At 25°C, the Bingham consistency was measured at 106 cP with a yield stress of 9 Pa. A fluid of this consistency is expected to be difficult to process in the WTP. However, when the temperature is increased to 40°C, the Bingham consistency drops to 58 cP, resulting in an easier-to-process fluid.

During the mixing/aging test with the 2.75 M Na AZ-101 melter feed, the fluid appears extremely thixotropic. This thixotropy is most likely due to precipitated solids that formed during the mixing/aging test process. These solids are suspected of being the cause of the high shear strengths observed in the baseline melter-feed rheology samples. During the mixing/aging test, the steady-state rheology of the fluid remained Newtonian with relatively low viscosities compared to the baseline measurements at the same sodium molarity.

The PSD of a 1.75 M Na melter feed sample was measured. The PSD exhibits two major peaks, one in approximately the 0.5- to 1-μm range and the other in approximately the 10- to 30-μm range. Approximately 10 vol% of the particles is below 0.9 μm, 50 vol% (i.e., median value) below 13.3 μm, 90 vol% below 56.7 μm, and 95 vol% below 74 μm. With particle sizes below 100 μm, no significant process challenges with respect to particle settling are anticipated.

8.0 References

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Appendix A

Table A.1 Contains compositional data for analytes listed in 24590-WTP-GPP-RTD-001, “Guidelines for Performing Chemical, Physical, and Rheological Properties Measurements”, Table 12, Sheet 1. With the exception of the 4.3 M Pretreated AZ-101 LAW, these compositions have been calculated based on dilutions levels and glass former chemical additions.

Table A.1. Composition of AZ-101 Pretreated LAW Waste and AZ-101 Melter Feed

Sample	4.3 M Pretreated AZ-101 LAW	1.75 M Pretreated AZ-101 LAW	2.75 M Pretreated AZ-101 LAW	3.75 M Pretreated AZ-101 LAW	1.75 M AZ-101 LAW Melter Feed	2.75 M AZ-101 LAW Melter Feed	3.75 M AZ-101 LAW Melter Feed
Bulk Density (g/ml)		1.095	1.150	1.203	1.534 g/ml[a]	1.736 g/ml[b]	1.890 g/ml[c]
Sodium Molarity of LAW Waste or Pretreated Waste:	4.3	1.75	2.75	3.75	1.75	2.75	3.75
Oxides Loading of Pretreated HLW Sludge or Melter Feed (g ox/L):					704.0	956.0	1148
pH	13.8[d]						

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[a] One liter of Melter Feed made from 1.75 molar sodium pretreated waste contains 0.702 liters of the pretreated waste. Density MF

[b] One liter of Melter Feed made from 2.75 molar sodium pretreated waste contains 0.606 liters of the pretreated waste. Density MF

[c] One liter of Melter Feed made from 3.75 molar sodium pretreated waste contains 0.5344 liters of the pretreated waste. Density MF

[d] calculated from [OH$^-$] = 0.63 M

Sample	**4.3 M Pretreated AZ-101 LAW**	**1.75 M Pretreated AZ-101 LAW**	**2.75 M Pretreated AZ-101 LAW**	**3.75 M Pretreated AZ-101 LAW**	**1.75 M AZ-101 LAW Melter Feed**	**2.75 M AZ-101 LAW Melter Feed**	**3.75 M AZ-101 LAW Melter Feed**
Analyte:	mg/L (LAW)	mg/L (LAW)	mg/L (LAW)	mg/L (LAW)	mg/L (LAW MF)	mg/L (LAW MF)	mg/L (LAW MF)
Cations							
Ag	<0.50						
Al	5,300	2,200	3,400	4,600	23,000	32,000	38,000
As	14	5.5	8.6	12	3.9	5.2	6.3
B	7.8	3.2	5.0	6.8	22,000	30,000	36,000
Ba	<0.20						
Be	<0.2						
Bi	<2						
Ca	<5.0				36,000	49,000	58,000
Cd	<0.3						
Ce	<4						
Co	<1						
Cr	570	230	360	500	29	40	48
Cs							
Cu	<0.5						
Dy	<1						
Eu	<2						
Fe	<0.50				26,000	35,000	42,000
Hg							
K	3,800	1,500	2,400	3,300	1,100	1,500	1,800
La	<1					1,100	
Li	<0.60				14,000	19,000	23,000
Mg	<2.0				12,000	17,000	20,000
Mn	<1				82	110	130
Mo	85	35	54	74	24	33	40
Na	99,000	40000	63,000	86,000	30,000	40,000	48,000
Nd	<2						
Ni	<0.6				130	180	220

Sample	**4.3 M Pretreated AZ-101 LAW**	**1.75 M Pretreated AZ-101 LAW**	**2.75 M Pretreated AZ-101 LAW**	**3.75 M Pretreated AZ-101 LAW**	**1.75 M AZ-101 LAW Melter Feed**	**2.75 M AZ-101 LAW Melter Feed**	**3.75 M AZ-101 LAW Melter Feed**
P	480	200	310	420	140	190	220
Pb	6.6	2.7	4.2	5.8	1.9	2.6	3.10
Pd	<15						
Pr							
Pt							
Rb							
Rh	<6						
Ru	<22						
S	5,500	2200	3500	4,800	1,600	2,100	2,600
Sb	<10						
Se	<5						
Si	52	21	33.58	46	160,000	220,000	260,000
Sn	44	18	28.14	38	12.6	17	21
Sr	<0.30						
Ta							
Te	<10						
Th	<5.4E-2						
Ti	2.6	1.0	1.63	2.2	6,200	8,500	10,000
Tl	<10						
U	<0.012				13.6	18	22
V	1.4	0.55	0.86	1.2	0.4	0.52	0.63
W	51	21	33	44	14.6	20	24
Y	<1						
Zn	1.6	0.67	1.1	1.4	28,000	37,000	45,000
Zr	1.9	0.79	1.2	1.7	17,000	23,000	27,000
Carbon Analyses							
TIC							
TOC	340	140	220	300	100	130	160
Anions							

Sample	**4.3 M Pretreated AZ-101 LAW**	**1.75 M Pretreated AZ-101 LAW**	**2.75 M Pretreated AZ-101 LAW**	**3.75 M Pretreated AZ-101 LAW**	**1.75 M AZ-101 LAW Melter Feed**	**2.75 M AZ-101 LAW Melter Feed**	**3.75 M AZ-101 LAW Melter Feed**
F	1,900	770	1,200	1,700	540	740	890
Cl	<130						
Br	680	280	440	600	200	270	320
NO2	62,000	25,000	40,000	54,000	18,000	24,000	29,000
NO3	53,000	22,000	34,000	46,000	15,000	21,000	25,000
PO4	1,600	650	1,000	1,400	460	620	750
SO4	16,000	6,700	11,000	14,000	4700	6,400	7,700
CN							
NH3	4.2	1.7	2.69	3.7	1.2	1.6	2.0
Free OH							
Total OH	1.1E+04	4,500	7,000	9,600	3100	4,300	5,100
Radioisotopes	mCi/L (LAW)	mCi/L (LAW)	mCi/L (LAW)	mCi/L (LAW)	mCi/L (LAW)	mCi/L (LAW)	mCi/L (LAW)
H-3	3.2E-02	1.3E-02	2.1E-02	2.8E-02	9.3E-03	1.3E-02	1.5E-02
C-14	1.9E-03	7.8E-04	1.2E-03	1.7E-03	5.5E-04	7.4E-04	9.0E-04
Cr-51	<0.0004						
Fe-59	<0.00002						
Ni-59							
Co-60	1.7E-05	6.8E-06	1.1E-05	1.47E-05	4.8E-06	6.5E-06	7.8E-06
Ni-63							
Se-79	1.4E-04	5.7E-05	9.0E-05	1.2E-04	4.0E-05	5.4E-05	6.5E-05
Y-88	<0.00001						
Sr-90	1.60E-01	6.5E-02	1.0E-01	1.4E-01	4.6E-02	6.2E-02	7.5E-02
Sr-90/Y-90							

Sample	4.3 M Pretreated AZ-101 LAW	1.75 M Pretreated AZ-101 LAW	2.75 M Pretreated AZ-101 LAW	3.75 M Pretreated AZ-101 LAW	1.75 M AZ-101 LAW Melter Feed	2.75 M AZ-101 LAW Melter Feed	3.75 M AZ-101 LAW Melter Feed
Nb-94/95							
Tc-99[e]							
Ru-103	<0.00005						
Ru-106							
Sn-113	<0.00007						
Sb-125	10.E-03	4.1E-03	6.4E-03	8.7E-03	2.8E-03	3.9E-03	4.7E-03
Sn-126							
Sb\Sn-126	2.2E-03	9.1E-04	1.4E-03	1.9E-03	6.4E-04	8.6E-04	1.0E-03
I-127							
I-129							
C-133	<0.25						
Cs-134	<0.00002						
Cs-135							
Cs-137	3.6E-02	1.4E-02	2.3E-02	3.1E-02	1.0E-02	1.4E-02	1.7E-02
Ce-144	<0.0003						
Sm-151	6.0E-05	2.5E-05	3.9E-05	5.3E-05	1.7E-05	2.3E-05	2.8E-05
Eu-152	<0.00002						
Eu-154	<0..00002						
Eu-155	<0.0002						
Pa-231							
U-233	<9.6E-6						
U-234	<2.1E-6						
U-235	<4.1E-9						
U-236	<1.6E-8						
U-238	<8.1E-9						
Np-237	1.1E-05	4.5E-06	7.0E-06	9.6E-06	3.1E-06	4.3E-06	5.1E-06

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[e] Data currently under review.

Sample	4.3 M Pretreated AZ-101 LAW	1.75 M Pretreated AZ-101 LAW	2.75 M Pretreated AZ-101 LAW	3.75 M Pretreated AZ-101 LAW	1.75 M AZ-101 LAW Melter Feed	2.75 M AZ-101 LAW Melter Feed	3.75 M AZ-101 LAW Melter Feed
Pu-236	<0.00000006						
Pu-238	1.1E-06	4.3E-07	6.8E-07	9.3E-07	3.0E-07	4.1E-07	5.0E-07
Pu-239	9.2E-06	3.8E-06	5.9E-06	8.1E-06	2.6E-06	3.6E-06	4.3E-06
Pu-240	<1.2E-3						
Pu-239/240							
Pu-241	5.2E-05	2.1E-05	3.4E-05	4.6E-05	1.5E-05	2.0E-05	2.4E-05
Pu-242	<0.0000002						
Pu-241/Am-241							
Am-241	6.8E-07	2.8E-07	4.3E-07	5.9E-07	1.9E-07	2.6E-07	3.2E-07
Am-241, Am-243							
Am-242							
Am-243	<0.0000002						
Cm-242	<0.00000005						
Cm-243							
Cm-244							
Cm-243/244	<0.0000001						
Sum of alpha (TRU) = S (Pu-238, Pu-239, Pu-240, Am-241)	1.1E-05	4.5E-06	7.0E-06	9.6E-06	3.1E-06	4.3E-06	5.1E-06
Total alpha							
Total beta	9.2E-01	3.7E-01	5.9E-01	8.0E-01	2.6E-01	3.6E-01	4.3E-01
Total gamma							

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