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Rheological and Physical Properties of AZ-101 HLW Pretreated Sludge and Melter Feed

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ACCEPTED FOR
WTP PROJECT USE

Battelle—Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by Test Specification 24590-HLW-TSP-RT-02-013 Rev. 0 and Test Plan TP-RPP-WTP-192 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

12-19-03
Date

Summary

Objectives

This document describes work performed under Battelle—Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-192 Rev 0 "AZ-101 (Envelope D) 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 physical and rheological properties of these process streams are important considerations in selecting flowsheet and processing equipment such as mixers, pumps, piping, and tanks. The first stream considered was the pretreated high-level waste (HLW) stream that consists of the AZ-101 slurry of washed and leached solids from the cross-flow ultrafiltration process. The second stream is the HLW melter-feed material. This material consists of the pretreated HLW 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) (Smith and Prindiville 2002). Pretreated AZ-101 material at an undissolved solids (UDS) concentration of 10.3-wt% was the source material for these measurements. The 10.3-wt% UDS sample was concentrated to 22-wt% UDS via decanting. This sample was tested for shear strength as a function of gel time using a Haake M5 rheometer fitted with a shear-vane impeller. The pretreated sludge was then subsampled and diluted with AZ-101 HLW pretreated supernate to two other UDS concentrations (10-wt% and 15-wt%). Settling behavior was determined for the 10- and 15-wt% UDS samples at ambient hot cell temperature (~36°C). The settling behavior of the 22-wt% UDS sample was not determined since this sample consists of settled solids after a sedimentation period of several days. Lastly, a Haake M5 rheometer with a temperature-controlled water bath was used to measure the rheological properties of the 10-, 15-, and 22-wt% UDS samples at 25°C and 40°C. Due to a low quantity of available sample material, these samples were recovered, returned to the initial source container, and decanted to 20-wt% UDS.

The 20-wt% UDS HLW pretreated sludge sample was then mixed for 1 hour with the project-approved glass-former chemical (GFC) formulation. This material should be considered representative of the HLW melter-feed stream in the WTP. The melter feed was agitated to suspend and homogenize the solids, and aliquots were drawn at ambient hot-cell temperature. Several of the 20-wt% UDS melter-feed aliquots[a] were diluted with AZ-101 HLW pretreated supernate to two other UDS concentrations (10 wt%, and 15 wt%). The settling behavior of the 10-, 15-, and 20-wt% UDS melter-feed aliquots was measured at ambient hot-cell temperature. The physical properties of these aliquots were also measured at ambient hot cell temperature. Next, the 20-wt% HLW melter-feed sample was allowed to remain undisturbed for a minimum of a 48-hour period. A shear vane was used with a Haake M5 rheometer to determine the melter-feed settled-solids shear strength. The rheological properties of the 10-, 15-, and

(a) In this document, the term "wt% UDS melter feed" refers to the wt% of UDS in the pretreated sludge that was used to prepare a certain melter feed. This value does not represent the actual wt% UDS of the melter-feed slurry.

20-wt% UDS HLW melter feeds were measured with a Haake M5 rheometer with a temperature-controlled water bath at 25°C and 40°C. Additional rheological measurements were performed on the 20-wt% UDS melter-feed sample based on mixing/aging times of 1 day and 1 week. The particle-size distribution was also measured on the 20-wt% UDS melter-feed sample.

Results and Performance Against Objectives

A sample of AZ-101 HLW pretreated sludge was received at an initial UDS concentration of 10.3 wt%. The 10.3-wt% UDS sample was concentrated to 22-wt% UDS via decanting. The shear-strength behavior of the 22-wt% UDS HLW pretreated sludge sample was determined by agitating (i.e., stirring) the sample and allowing it sit undisturbed for various periods of time (referred to as gel time) between measurements. Several resulting shear stress/time curves at various gel times were measured. These data allow for investigation of how the shear strength of sludge rebuilds after being sheared. Even after a 10-minute gel time, a maximum peak could be measured. The shear strength appeared to stabilize after approximately 16 hours at a shear strength of approximately 30 Pa. This dynamic can be seen in Figure S.1 by plotting the shear strength as a function of gel time (10% error in these measurements was assumed and is typical of this technique).

The rebuild behavior of the sludge can be described with a first-order-rate model. This model appears to fit the shear-strength data shown in Figure S.1 well. Using this model, the initial shear-strength parameter (16.8 Pa) should roughly agree with the measured rheological Bingham-yield-stress measurement (14.7 to 18.1 Pa). This model indicates that the shear strength rebuilds immediately from the time that it remains unsheared. The material is expected to reach 95% of its steady-state shear strength (31 Pa) 9 hours from this time.

The sample was diluted to 10- and 15-wt% UDS concentrations. The results from the testing of the AZ-101 HLW Pretreated Sludge at 10-, 15-, 22-wt% UDS concentrations are summarized in Table S.1. Flow curves from these samples indicate that the fluid should be characterized as a Bingham-plastic fluid with the maximum measured rheological parameters occurring at 22-wt% UDS with a Bingham consistency of 11 cP and Bingham yield stress of 11 Pa at 25˚C. At 40˚C, the Bingham-plastic parameters of the 22-wt% UDS pretreated sludge were a Bingham consistency of 7 cP and Bingham yield stress of 10 Pa. The pH of the 22-wt% UDS sample was determined to be 12.1.

Glass-former chemicals were continuously mixed with an AZ-101 20-wt% UDS HLW pretreated-sludge sample. At intervals of 1 hour, 1 day, and 1 week, the rheology and pH of the sample were measured. The results from the tests performed on the melter-feed material are summarized in Table S.1. When glass-former chemicals were added to the AZ-101 pretreated HLW, the pH of the solution dropped from the 12.1 range to a range of 9.9 to 10.4. This is most likely due to the relatively large quantity of soluble carbonate species in the melter-feed formulation.

Even at only 10-wt% UDS, the AZ-101 HLW melter feed exhibits Bingham-plastic rheological behavior. At 10-wt% UDS at 40°C, the low range Bingham-plastic parameters of the melter feed were a Bingham consistency of 4 cP and a Bingham yield stress of 2 Pa. At 20-wt% UDS at 25°C, the high-range Bingham-plastic parameters of the melter feed were a Bingham consistency of 21 cP and a Bingham yield stress of 15 Pa.

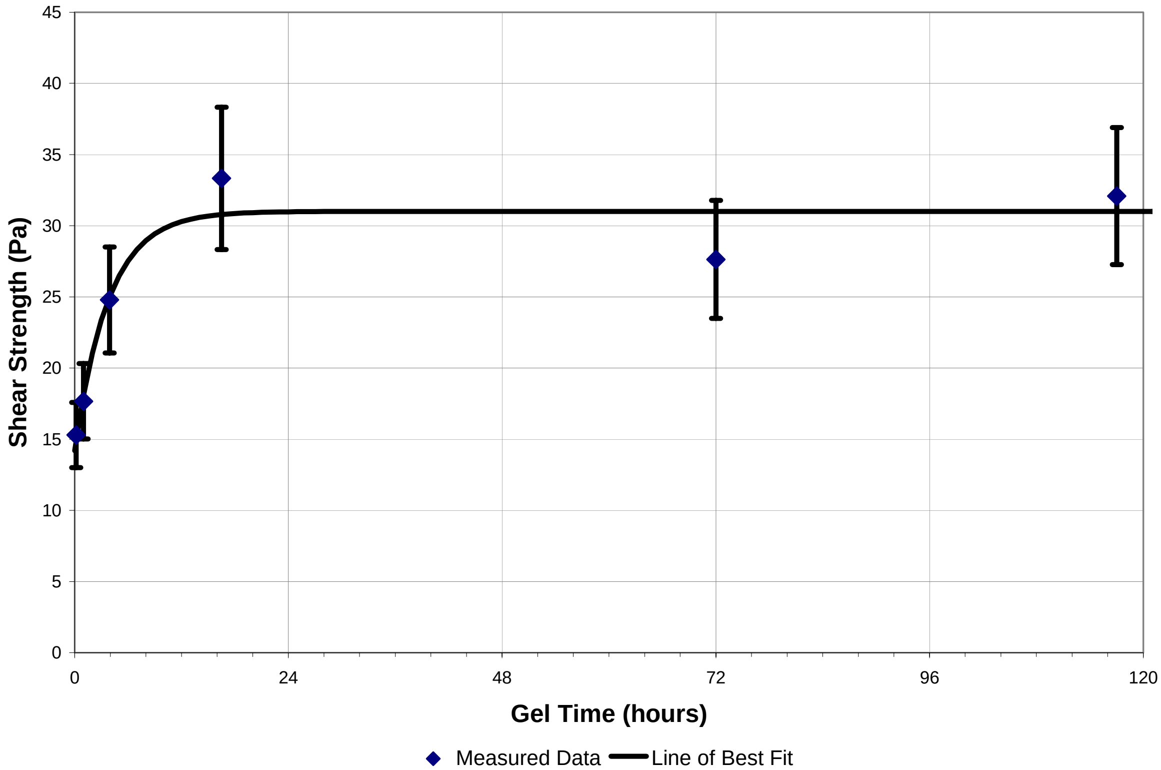


Figure S.1. Summary of the Shear-Strength Rebuild Behavior of AZ-101 Pretreated Sludge

Physical-properties measurements on the AZ-101 HLW melter feed indicate a higher packing efficiency for the 1-week mixed sample. The vol% settled solids increases from 55, 77, and 96% for the 10-, 15-, and 20-wt% UDS melter feeds, respectively. After 1 week of mixing, the vol% settled solids for the 20-wt% UDS sample drops to 89%. The measured wt% UDS increases from 16-, 26-, and 38-wt% UDS for the 10-, 15-, and 20-wt% UDS melter feeds, respectively, after 1 week of mixing. After 1 week of mixing, the quantity of UDS for the 20-wt% UDS sample drops to 33%. Considering subsampling errors in the previous 20-wt% UDS measurements, these values are relatively close. The difference between these values is most likely explained through mass-balance assumption errors when recycling and recovering previous melter-feed rheology samples for the mixing/aging study. This recycling was performed throughout testing due the extremely limited amount of AZ-101 HLW pretreated sludge available (~36 g UDS).

Table S.1. Summary of AZ-101 HLW Physical and Rheological Property Measurements

Physical Property (unless otherwise noted, data presented are for HLW Melter Feed)	Units	10-wt% UDS	15-wt% UDS	20-wt% UDS	20-wt% UDS	20-wt% UDS
Mixing Duration	**n/a**	**1 Hour**	**1 Hour**	**1 Hour**	**1 Day**	**1 Week**
pH (top: melter feed; bottom: pretreated sludge)	n/a	10.0 a	9.9 a	10.3 12.1[b]	10.3 a	10.4 a
Bingham Consistency at 25ºC (top: melter feed; bottom: pretreated sludge)	cP	4.095 <10	10.71 5.2	20.99 10.5[b]	9.9 a	10.64 21.78[c]
Bingham Yield Stress at 25ºC (top: melter feed; bottom: pretreated sludge)	Pa	1.779 0	3.429 2.9	14.7 11.4[b]	5.1 a	3.623 12.59[c]
Bingham Consistency at 40ºC (top: melter feed; bottom: pretreated sludge)	cP	3.845 <10	7.594 3.5	19.31 7.2[b]	9.267 a	9.023 15.14[c]
Bingham Yield Stress at 40ºC (top: melter feed; bottom: pretreated sludge)	Pa	1.871 0	4.910 2.8	18.11 10.3[b]	4.738 a	4.765 11.77[c]
Shear Strength (top: melter feed; bottom: pretreated sludge)	Pa	a a	a a	55 31	a a	23 a
Bulk Density	g/mL	1.183 ± 0.082	1.331 ± 0.092	1.506 ± 0.104	a	1.402 ± 0.010
vol% Settled Solids	%	55.3% ± 5.5%	76.9% ± 7.6%	96.2% ± 9.5%	a	88.9% ± 0.0%
Density of Centrifuged Solids	g/mL	1.370 ± 0.171	1.625 ± 0.202	1.676 ± 0.209	a	1.577 ± 0.017
vol% Centrifuged Solids	%	32.5% ± 2.3%	46.0% ± 3.2%	70.5% ± 5.0%	a	58.1% ± 0.7%
wt% Centrifuged Solids	%	37.6% ± 3.2%	56.2% ± 4.8%	78.4% ± 6.7%	a	65.3% ± 1.0%
Supernatant Density	g/mL	1.063 ± 0.003	1.110 ± 0.003	1.177 ± 0.004	a	1.087 ± 0.014
Density of Settled Solids	g/mL	1.28 ± 0.09	1.39 ± 0.10	1.50 ± 0.11	a	1.42 ± 0.03
wt% Settled Supernatant	%	62.4% ± 16.3%	43.9% ± 11.5%	21.9% ± 5.7%	a	29.7% ± 9.0%
wt% dissolved solids in supernatant	%	8.0% ± 0.2%	10.3% ± 0.3%	10.3% ± 0.3%	a	10.5% ± 0.9%
wt% total solids in Centrifuged Sludge	%	48.0% ± 2.5%	51.1% ± 2.7%	53.5% ± 2.8%	a	55.7% ± 0.3%
wt% Total Solids	%	23.3% ± 1.1%	33.6% ± 1.6%	44.5% ± 2.1%	a	42.1% ± 3.0%
wt% Undissolved Solids	%	16.4% ± 1.5%	25.6% ± 2.4%	37.8% ± 3.5%	a	33.0% ± 0.6%

a—not measured; b— pretreated sludge at 22-wt% UDS; c—melter-feed settled solids.

The settling behavior of the AZ-101 HLW pretreated sludge and melter feed can be characterized as "floccular" settling. This type of settling is characterized by a critical time when the suspended-solids height begins to decrease. This critical time corresponds to the amount of time for flocs to form and begin to settle at a faster rate. The sample of 10-wt% AZ-101 melter feed possessed large GFC particles at a low solids concentration such that the solids began to immediately settle in a "hindered" settling regime. The 22-wt% UDS pretreated sludge and the 20-wt% UDS melter feed mixed for 1 hour did not settle to measurable levels during the 72-hour sedimentation period. However, after 1 week of mixing, the packing efficiency of the sample of 20-wt% UDS melter feed increased such that the settling behavior could be measured. The solid/liquid interface height as a function of settling time for these samples can be seen in Figure S.2.

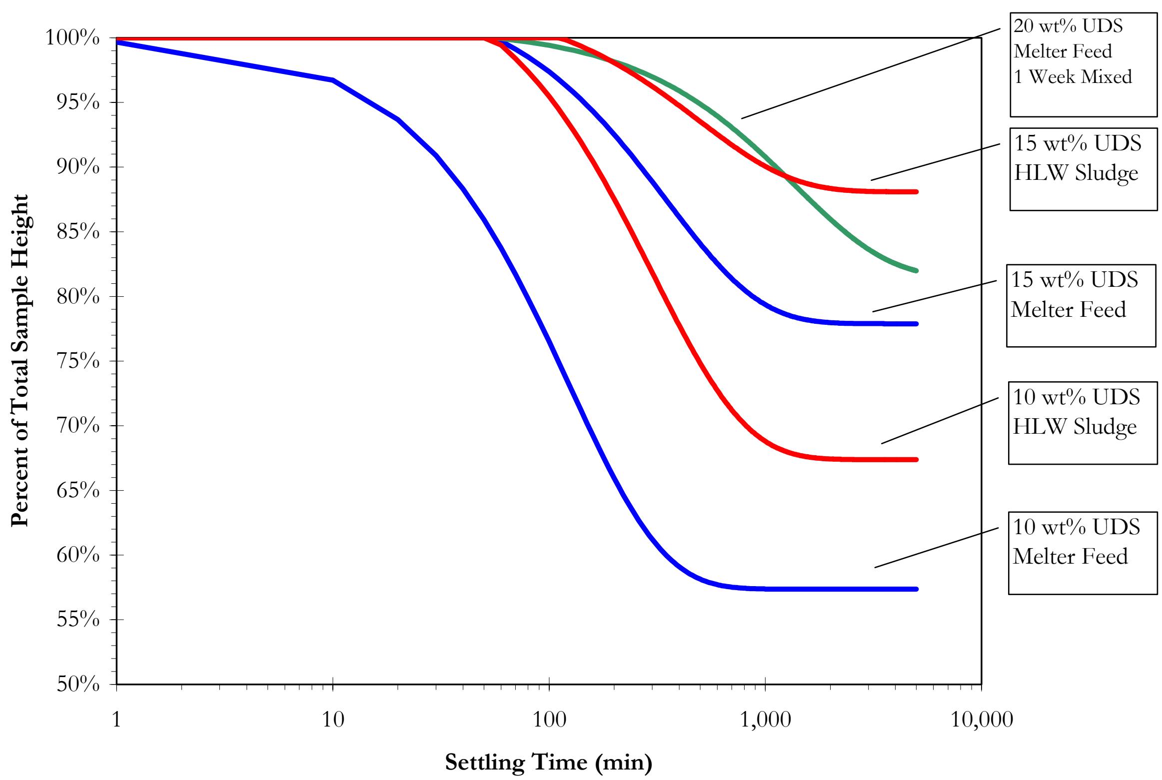


Figure S.2. Summary of AZ-101 Pretreated Sludge and Melter-Feed Settling Behavior

The particle-size distribution of a sample of 20-wt% UDS melter feed was also 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 5 to 10 μm range (see Figure S.3). Approximately 10 vol% of the particles is below 2.1 μm, 50 vol% (i.e., median value) below 7.2 μm, 90 vol% below 23.8 μm, and 95 vol% below 35 μm. With particle sizes below 100 μm, no significant process challenges with respect to particle settling are anticipated. During particle-size measurement, the samples were sonicated to break apart agglomerates of large particles and measure the fundamental particle-size distribution of the suspension. However, bubble entrainment in the measurement cell appeared to bias the resulting particle-size distribution toward larger particle sizes, making these measurements unreliable. Consequently, the unsonicated particle-size result should be considered the primary particle-size distribution because of the high repeatability of particle-size results between subsamples.

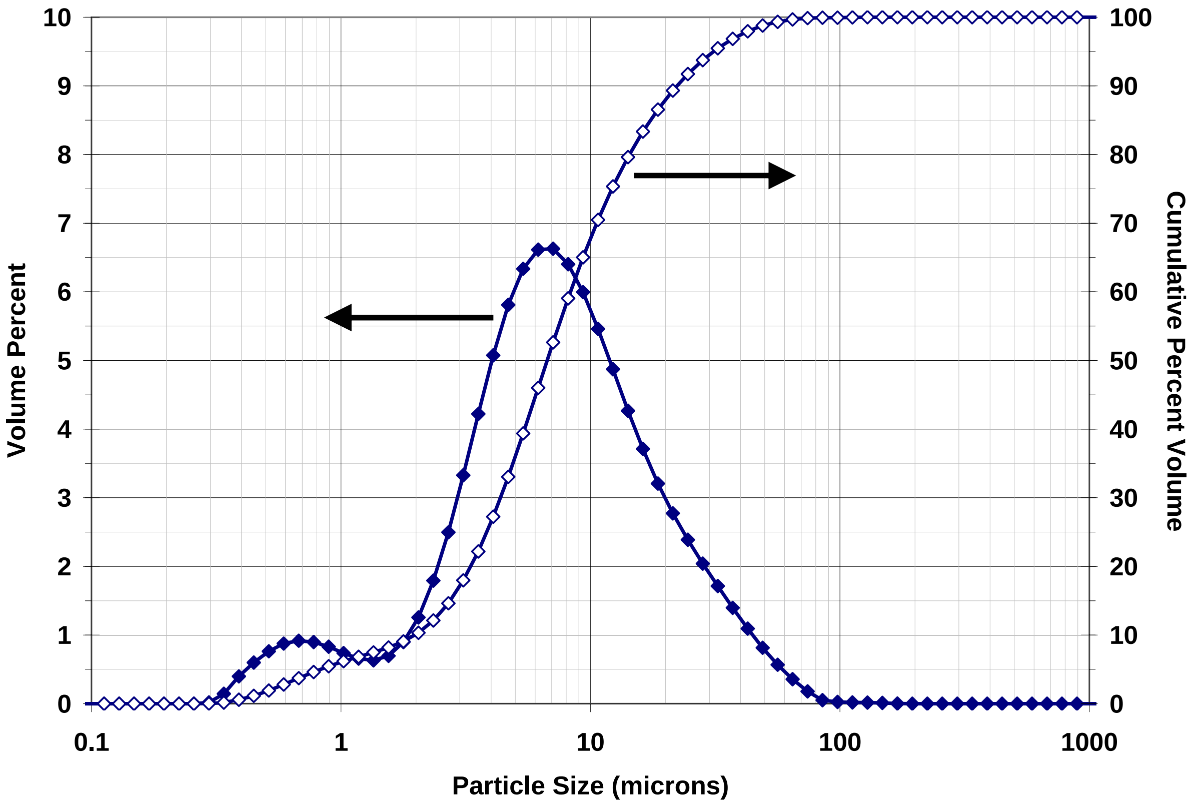


Figure S.3. Summary of the Particle-Size Distribution of AZ-101 Melter Feed

Quality Requirements

Battelle—Pacific Northwest Division (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 in DOE/RW-0333P, Rev. 11, *Quality Assurance Requirements and Description*. A listing of the procedures implementing the DOE/RW-0333P QA requirements is included in Test Plan, TP-RPP-WTP-192 Rev 0, *AZ-101 (Envelope D) Melter Feed Rheology Testing*. 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*.

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-HLW-TSP-RT-02-013 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 1) the reported results are traceable, 2) inferences and conclusions are soundly based, and 3) 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 issue in regard to processing these materials through the WTP:

- Even after settling for several days, neither the AZ-101 HLW pretreated sludge nor the resulting melter feed could reach 25-wt% UDS. The maximum settling solids packing occurs at approximately 22-wt% UDS. This drop in waste loading may impact WTP throughput.

- The HLW pretreated sludge possesses a shear strength that may be difficult to overcome using current pulse jet mixer (PJM) design technology. In a potential plant-upset scenario where the plant loses the capability to agitate the PJM vessels, the HLW pretreated sludge will settle and build a shear strength that must be overcome to resuspend the system. If the PJM vessels do not have the capability to exceed this shear strength, the difficulties will be encountered during a plant restart. Engineering or administrative controls must be in place for the PJM vessels to minimize the potential for this scenario.

Acronyms

BNI	Bechtel National Inc.
GFC	Glass-Former Chemical
HLW	High Level Waste
M&TE	Measuring and Test Equipment
NIST	National Institute of Standards and Technology
PJM	Pulse Jet Mixer
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 accurately measure the physical and rheological properties (in accordance with test plan TP-RPP-WTP-192 Rev 0) on actual AZ-101 pretreated high level waste (HLW) (HLW Envelope D) 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 resulting slurry of washed and leached solids from this cross-flow ultrafiltration process is termed AZ-101 HLW "pretreated sludge" and is the focus of this document.

The AZ-101 HLW pretreated sludge was received at a concentration of 10.3-wt% undissolved solids (UDS). The AZ-101 pretreated HLW was adjusted to various UDS concentrations for physical and rheological property measurements. The purpose of adjusting the solids concentration was to bound the physical and rheological property measurements about a Waste Treatment Plant (WTP) operating point of 20-wt% UDS. The UDS concentrations tested include 10-, 15-, and 22-wt% UDS AZ-101 HLW pretreated sludge.

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 hot cell ambient temperature (nominally 34°C to 38°C). For this work, hot cell ambient is reported as 36°C.

Project-approved glass-former chemicals (GFCs; Hansen and Schumacher 2003) were added to a 20-wt% UDS HLW pretreated sludge sample to produce a HLW "melter feed" stream. Physical and rheological properties of these melter-feed samples were measured. Mixing and aging studies were also conducted on the 20-wt% UDS melter-feed sample.[a] This testing entailed placing a 20-wt% UDS pretreated HLW 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 day and 1 week of mixing.

This report describes the experimental approach and results of the testing. Specifications for this work were provided in Test Specification Number 24590-HLW-TSP-RT-02-013. This report also provides the means of communicating results of testing conducted under test plan TP-RPP-WTP-192.

(a) In this document, the term "wt% UDS melter feed" refers to the wt% of UDS in the pretreated sludge that was used to prepare a certain melter feed. This value does not represent the actual wt% UDS of the melter-feed slurry.

2.0 Quality Requirements

Battelle—Pacific Northwest Division (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 in DOE/RW-0333P, Rev. 11, *Quality Assurance Requirements and Description.* A listing of the procedures implementing the DOE/RW-0333P QA requirements is included in Test Plan, TP-RPP-WTP-192 Rev 0, *AZ-101 (Envelope D) Melter Feed Rheology Testing*. 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*.

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-HLW-TSP-RT-02-013 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 1) the reported results are traceable, 2) inferences and conclusions are soundly based, and 3) the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

3.0 Sample-Preparation Details

This section details preparation of the actual AZ-101 samples used for testing. Section 3.1 describes adjustment steps used to achieve the target UDS concentrations. Section 3.2 describes the addition of GFCs to the pretreated feed to form the melter feed. Unless otherwise stated, all temperatures in this work are reported to ±2°C.

3.1 AZ-101 HLW Pretreated Sludge

The HLW Pretreated Sludge sample was received at a UDS concentration of 10.3 wt%. The 10.3-wt% UDS sample was concentrated to 22-wt% UDS by decanting all of the standing liquid from the fully settled sample. Shear-strength measurements were performed on the 22-wt% UDS sample. The sample was then agitated with an impeller via overhead mixer (see Figure 3.1), and samples were drawn for select physical and rheological properties characterization (see Figure 3.2). The previously removed standing liquid was used to adjust the concentration of the 22-wt% subsamples to 10- and 15-wt% UDS, respectively. Results from these characterization efforts are discussed in the following sections.

22-wt% UDS AZ-101 HLW pretreated sludge | Close-up of 22-wt% UDS HLW pretreated sludge being mixed

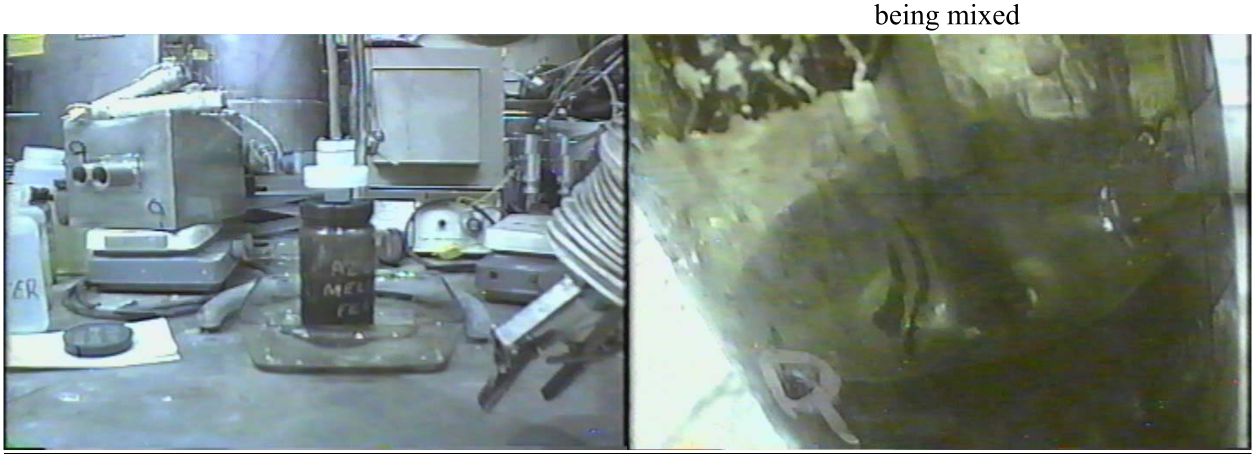


Figure 3.1. Photographs of 22-wt% UDS AZ-101 HLW Pretreated Sludge

10- and 15-wt% UDS AZ-101 HLW pretreated sludge rheology subsamples | Close-up of bubbles rising through AZ-101 HLW pretreated sludge supernate

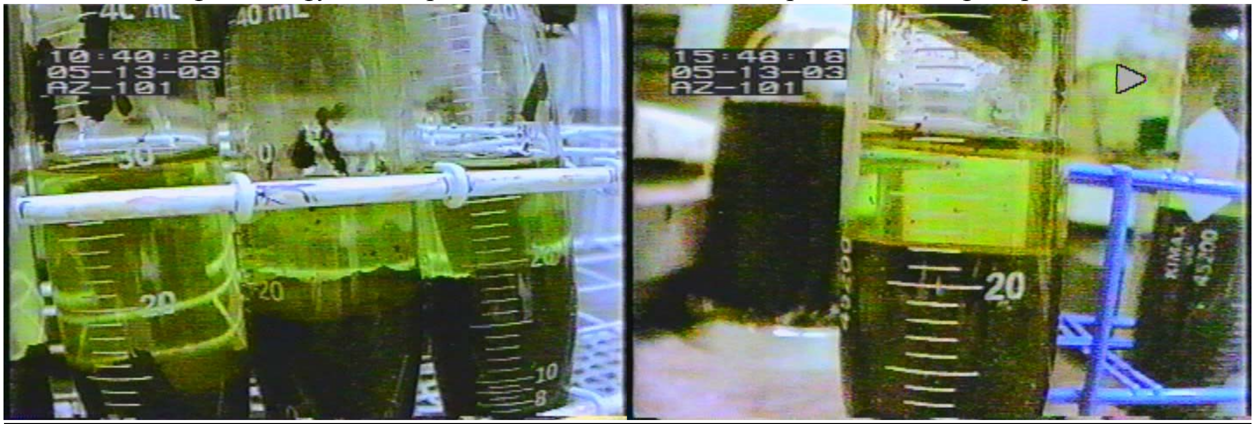


Figure 3.2. Photographs of Rheology Subsamples of AZ-101 HLW Pretreated Sludge

3.2 AZ-101 HLW Melter Feed

After physical and rheological characterization of the HLW pretreated sludge, GFCs were added to the 20-wt% UDS pretreated HLW samples. The purpose of these samples is physical and rheological characterization of the AZ-101 Envelope D HLW melter feed. Glass-former quantities were based on the formulation provided by the Vitreous State Laboratory (VSL) and designated HLW98-95. Table 3.1 lists the composition and type of glass formers added to the AZ-101 pretreated feed sample.

Before adding GFCs, a mixture of dry GFCs with a composition consistent with Table 3.1 was weighed into a vessel at the target-formulation ratio mass (see Table 3.2). The glass-former mixture was 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-192 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 laboratory-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.

$$N^3 = \left(1.96\times10^9 \text{ rpm}^3\cdot\text{cm}^2\right)\cdot\frac{V}{D_i^5} \tag{3.1}$$

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

A 5.0-cm-diameter impeller in a 6.4-cm-diameter glass jar was used for mixing (see Figure 3.3). The impeller was initially maintained at approximately 200 rpm in accordance with Equation 3.1. However, no surface motion was observed at 200 rpm, and the rotational rate was increased to 300 rpm for the duration of the mixing effort to assure adequate mixing. Mixing details are summarized in Table 3.3.

After stirring for 1 hour, samples were removed for physical and rheological testing. Mixing then resumed for a full week for the mixing/aging study (see Table 3.3). Samples were drawn and rheologically characterized after 1 day and 1 week of mixing. Physical properties and rheology results are described in the following sections.

Table 3.1. GFC Formulation HLW98-95 for AZ-101 Envelope D

Mineral	Grade	Company	Percent Mass
Borax 10M Borax $Na_2B_4O_7 \cdot 10H_2O$	Technical Grade	U.S. Borax Valencia, CA www.borax.com	31.3
Sodium Carbonate Na_2CO_3 Anhydrous	Dense Soda Ash	Solvay Minerals Houston TX www.solvayminerals.com	7.3
Lithium Carbonate Li_2CO_3	Technical Grade	Chemettal-Foote Kings Mt NC www.chemetalllithium.com	10.4
Silicon Dioxide SiO_2	SCS-75	U.S. Silica Berkeley Springs WV www.u-s-silica.com	48.7
Zinc Oxide ZnO	Kadox 920	Zinc Corp Amer. Monaca, PA www.horseheadinc.com	2.2
Total	not applicable	not applicable	100

Table 3.2. Quantity of GFCs Added to AZ-101 Envelope D Pretreated HLW Samples

Pretreated Feed UDS Concentration (wt%)	Initial Mass of UDS in Pretreated Sludge (g)	Target Mass of GFCs Added (g)	Actual Mass of GFCs Added (g)	Percent Deviation
20%	37.3	92.75	92.75	0

Table 3.3. Guideline Reporting-Format Mixing Details

Melter-Feed ID: AZ-101 HLW Melter Feed	
Processing Scale (laboratory/bench, pilot, or full): Laboratory	
Activity/Property	**Data or Explanation**
Order of Chemical Additions	Dry glass formers combined then added to waste in mixing vessel
Mixing Time	1 hour, 1 day , 1 week
Impeller Speed	~300 rpm
Impeller Diameter	5.0 cm (2.0 in.)
Tank Diameter	~6.4 cm (~2.5 in.) cylindrical
Number of Baffles	0
Size of Baffles	n/a
Depth of Impeller	sample midpoint using overhead stirrer

Overhead mixer used for GFC addition

Photograph of AZ-101 HLW melter feed after 1 hour of mixing (best image available due to poor lighting in hot cell)

Figure 3.3. Overhead Mixing System Used for Subsampling and GFC Mixing

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. The 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.

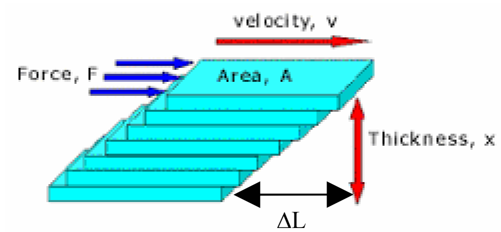


Figure 4.1. Diagram of Fluid Flow Between Stationary and Moving Plates

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

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}.

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).

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

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 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.

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.

Table 4.2. Viscosities of Several Common Newtonian Fluids

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

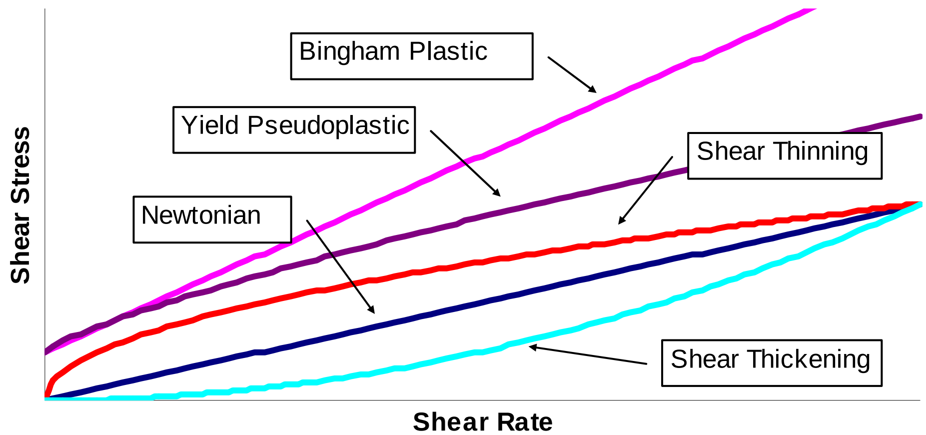


Figure 4.2. Rheograms of Various Fluid Types

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 nonlinear 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 Rheological Characterization Procedure

A Haake M5 rheometer with a temperature-controlled water bath was used for the work described in this report. The M5 system was 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, a Haake SVI sensor system was used.

The testing was conducted as follows. The samples were loaded into the sample container, and the shear rate was increased from 0 to 445 s^{-1} over 2.5 minutes. The sample was held at a shear rate of 445 s^{-1} for 1 minute. Lastly, the shear rate was decreased from 445 to 0 s^{-1} over 2.5 minutes. The test was then immediately repeated with the same sample.

The first ramp cycle shows newly loaded or fresh sample behavior, including breakdown of sample structure through hysteresis, if present. Hysteresis can be seen when the ramp-down curve is in a different location 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.

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.

Brookfield viscosity standard oils (National Institute of Standards and Technology [NIST] traceable) 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. PNWD Rheometer Calibration-Check Results

Date	Brookfield Viscosity Standard Lot No.	Certified Viscosity at 25°C	Measured Viscosity at 25ºC	Percent Deviation
4/7/03	120902	47.4	47.6	0.4%
5/5/03	120902	47.4	48.8	3.0%
6/19/03	21303	103.0	99.3	-3.6%
7/29/03	21303	103.0	102.5	-0.5%

4.2 AZ-101 HLW Pretreated Sludge Rheology

Rheograms from HLW Pretreated Sludge at various UDS concentrations are shown in Figure 4.3. Resulting rheological model fit parameters are summarized in Table 4.4. At 22-wt% UDS, the waste can be categorized as a Bingham plastic. At 25°C, the consistency index is approximately 10 cP while the yield stress is approximately 11 Pa. Increasing the temperature to 40°C drops the consistency index to approximately 7 cP while the yield stress remains relatively unchanged at 10 Pa.

At 15-wt% UDS, the waste can still be categorized as a Bingham plastic. At 25°C, the consistency index is approximately 5 cP while the yield stress drops significantly to 3 Pa. Increasing the temperature to 40°C slightly drops the consistency index to approximately 3.5 cP while the yield stress remains relatively unchanged at 3 Pa.

At 10-wt% UDS, the waste does not appear to possess a yield stress and should be categorized as a Newtonian fluid. The SV1 sensor system is not designed to measure rheological parameters of low-viscosity Newtonian fluids. Therefore, the rheological data generated by this sample with the SVI sensor should be considered an indication of a Newtonian fluid with a viscosity less than 10 cP.

4.3 AZ-101 HLW Melter-Feed Rheology

Rheograms from HLW pretreated sludge at various UDS concentrations are shown in Figure 4.4. Resulting rheological model-fit parameters are summarized in Table 4.5. At 20-wt% UDS, the waste can be categorized as a Bingham plastic. At 25°C, the consistency index is approximately 20 cP while the yield stress is approximately 15 Pa. Increasing the temperature to 40°C drops the consistency index to approximately 19 cP while the yield stress slightly increases to 18 Pa. The slight increase in yield stress is likely due to evaporation of interstitial liquid at 40°C. The small change in rheological parameters due to temperature changes is likely due the increased quantity of UDS in the melter feed from GFC addition. The increased UDS decreases the rheological contribution of the interstitial liquid, which is sensitive to temperature changes.

At 15-wt% UDS, the waste can still be categorized as a Bingham plastic. At 25°C, the consistency index drops to approximately 11 cP while the yield stress drops significantly to 3.5 Pa. Increasing the temperature to 40°C slightly drops the consistency index to approximately 8 cP while the yield stress slightly increases to 5 Pa.

Unlike the HLW pretreated sludge at 10-wt% UDS, which was categorized as Newtonian, the 10-wt% melter feed can be categorized as a Bingham plastic. At both 25°C and 40°C, the waste possesses Bingham-plastic parameters of approximately 5 cP for consistency and approximately 2 Pa for yield stress.

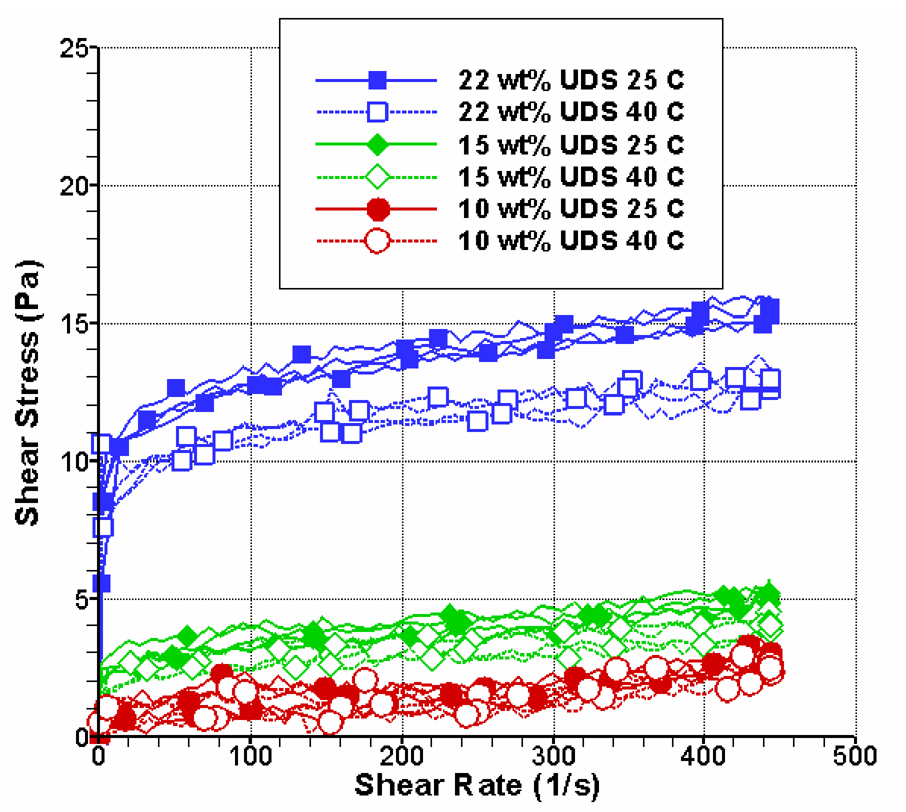


Figure 4.3. Flow Curves of AZ-101 HLW Pretreated Sludge at Various UDS Concentrations and Temperatures

Table 4.4. Rheological Model Fits (10 to 445 s^{-1}) for AZ-101 Pretreated HLW at Various UDS Concentrations and Temperatures

Model/Model Parameter	22-wt% UDS at 25°C	22-wt% UDS at 40°C	15-wt% UDS at 25°C	15-wt% UDS at 40°C	10-wt% UDS at 25°C	10-wt% UDS at 40°C
File Name	**051403_a**	**051403_c**	**051503_a**	**051503_b**	**051503_c**	**051503_d**
Newtonian:						
η – Newtonian viscosity (cP)	n/a	n/a	n/a	n/a	<10	<10
R^2 – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Ostwald (or Power HLW):						
m – the consistency coefficient ($mPa{\cdot}s^{-n}$)	7.06	7.07	1.25	1.52	n/a	n/a
n – the power-law exponent	0.13	0.010	0.22	0.16	n/a	n/a
r– correlation coefficient	0.9892	0.9655	0.9413	0.9205	n/a	n/a
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	11.4	10.3	2.9	2.8	n/a	n/a
η_p – the plastic viscosity (cP)	10.5	7.2	5.2	3.5	n/a	n/a
r – correlation coefficient	0.9644	0.9550	0.9246	0.9378	n/a	n/a
Herschel-Bulkley:						
τ_O^H _ the yield stress (Pa)	8.0	8.6	1.59	2.6	n/a	n/a
k - the Herschel-Bulkley consistency coefficient ($mPa{\cdot}s^{-b}$)	0.999	0.360	0.306	0.0208	n/a	n/a
b - the Hershel-Bulkely power law exponent	0.33	0.42	0.39	0.72	n/a	n/a
r – correlation coefficient	0.9936	0.9755	0.9438	0.9409	n/a	n/a
n/a = not applicable						

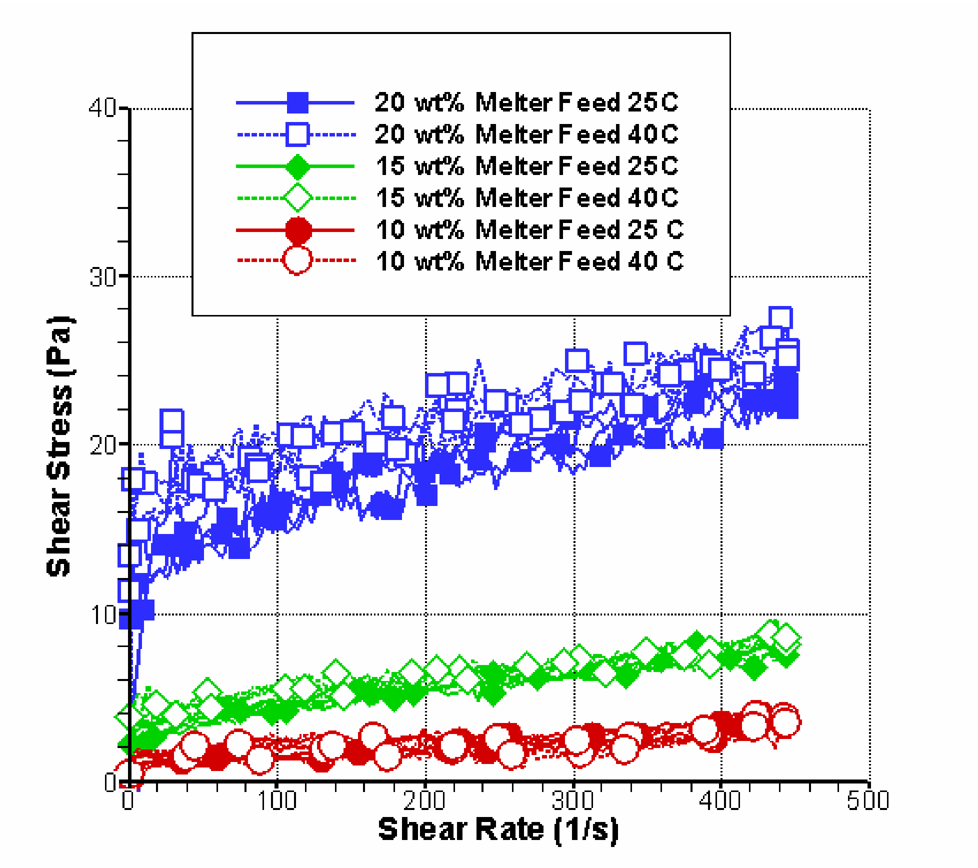


Figure 4.4. Flow Curves of AZ-101 HLW Melter Feed at Various UDS Concentrations and Temperatures

Table 4.5. Rheological Model Fits (10 to 445 s^{-1}) for AZ-101 HLW Melter Feed at Various Concentrations and Temperatures

Model/model Parameter	20-wt% UDS at 25°C	20-wt% UDS at 40°C	15-wt% UDS at 25°C	15-wt% UDS at 40°C	10-wt% UDS at 25°C	10-wt% UDS at 40°C
File UDS me	**062303_a**	**062303_b**	**062403_b**	**062403_c**	**062503_a**	**062503_b**
Newtonian:						
η – Newtonian viscosity (cP)	n/a	n/a	n/a	n/a	n/a	n/a
r – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Ostwald (or Power HLW):						
m – the consistency coefficient (mPa·s^{-n})	7.381	10.93	1.012	2.422	0.6806	0.783
n – the power-law exponent	0.1849	0.1381	0.3323	0.1923	0.2623	0.2385
r – correlation coefficient	0.9448	0.9182	0.9656	0.9545	0.8588	0.7896
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	14.7	18.11	3.429	4.910	1.779	1.871
η_p - the plastic viscosity (cP)	20.99	19.31	10.71	7.594	4.095	3.845
r – correlation coefficient	0.9608	0.9555	0.988	0.9628	0.8827	0.817
Herschel-Bulkley:						
τ_O^H - the yield stress (Pa)	13.19	17.65	3.266	4.144	1.779	1.871
k - the Herschel-Bulkely consistency coefficient (mPa·s^{-b})	0.1497	0.04382	0.01859	0.09422	0.004095	0.003845
b - the Hershel-Bulkely power-law exponent	0.696	0.871	0.913	0.6123	1.00	1.00
r – correlation coefficient	0.9659	0.9562	0.9883	0.972	0.8827	0.817
n/a = not applicable						

4.4 Rheological Effects of Mixing/Aging

This section describes additional rheological measurements performed on 20-wt% AZ-101 melter-feed material that was mixed for a week with selected measurements performed after 1 day and 1 week of mixing. The sample was mixed with the impeller system discussed in Section 3.2 for a period of 1 hour at hot-cell ambient temperature (~36°C). The rheology of this sample was then measured at 25°C and 40°C (see Section 4.3). The sample continued to mix for a period of 1 day. The rheology was again measured at 25°C and 40°C. Finally, the remaining sample continued to mix for a period of 6 additional days (total of 1 week). The rheology was then measured a third time. Figure 4.5 presents the mixing/aging rheograms at 25ºC and 40ºC over 1-hour, 2-day, and 1-week intervals. Deionized water was added to these samples to keep a constant volume while mixing, thus minimizing error due to evaporation. Lastly, the 1-week mixed samples were allowed to settle for 72 hours. The standing liquid was removed, and the rheological properties of the settled-solids layer were measured.

As originally intended, rheological measurements were to be taken after 1 day of mixing at 40°C. Due to water-bath recirculation problems,[a] the 40°C measurement at 1 day of mixing was taken at ambient hot-cell temperature (measured at 36°C). The water-bath recirculation problem was resolved for the remaining mixing/aging measurements.

After 1 day of mixing, the rheological properties of the 20-wt% UDS melter feed drop significantly. This drop can be seen in the rheograms shown in Figure 4.6. The melter feed can be categorized as a Bingham plastic with a consistency 10 cP and a yield stress of 5 Pa (see Table 4.6). These parameters are constant at both 25°C and 40°C and hold with 1 week of mixing. This represents a drop in consistency of 10 cP and a yield stress drop of 10 Pa from the 1-hour mixed samples listed in Table 4.5.

The additional mixing appears to have changed the packing efficiency of the melter-feed samples. Unlike the 1-hour mixed sample, after 72 hours of settling, the 1-week mixed sample had a significant quantity of standing liquid (see Section 7.0). This liquid was removed from the sample, and the rheological properties of the sample were measured. At 25°C, the settled solids appear to behave as a Bingham plastic with a consistency of 22 cP and a yield stress of 13 Pa. At 40°C, the settled solids yield stress slightly drops to 12 Pa while the consistency drops to 15 cP.

(a) This problem has been addressed in corrective action report CAR # 5080.

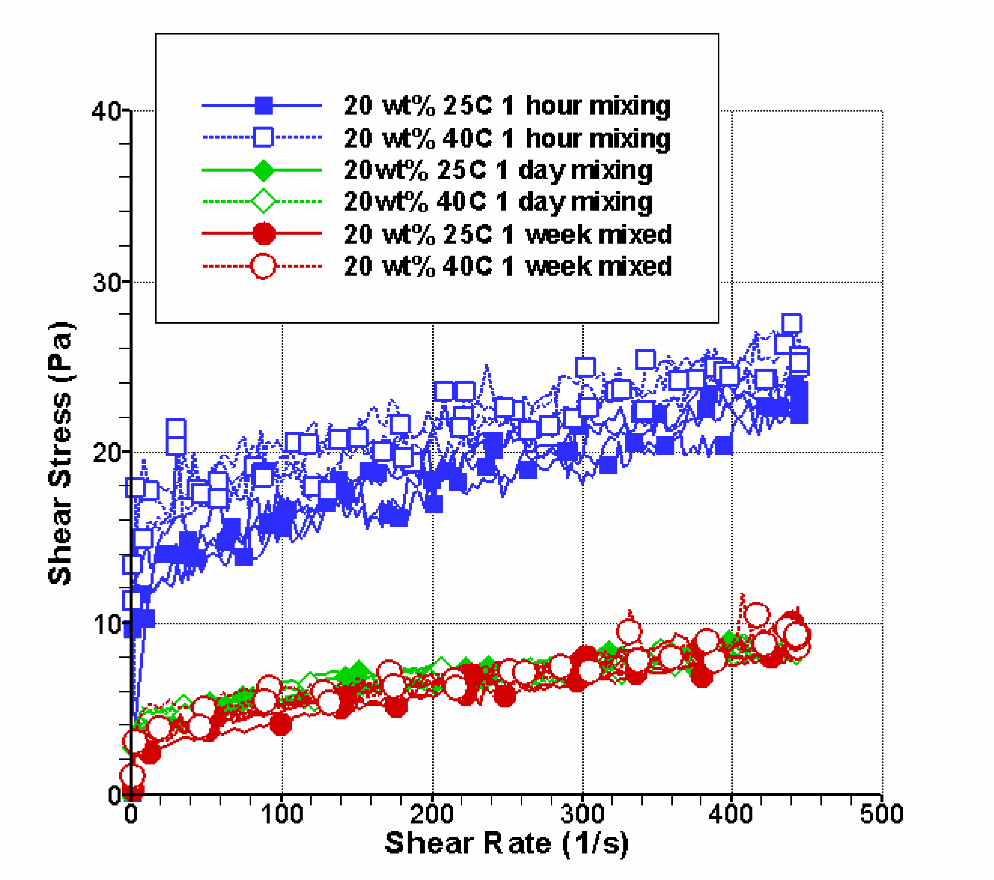


Figure 4.5. Flow Curves of 20-wt% UDS AZ-101 Melter Feed at Various Mixing Durations and Temperatures

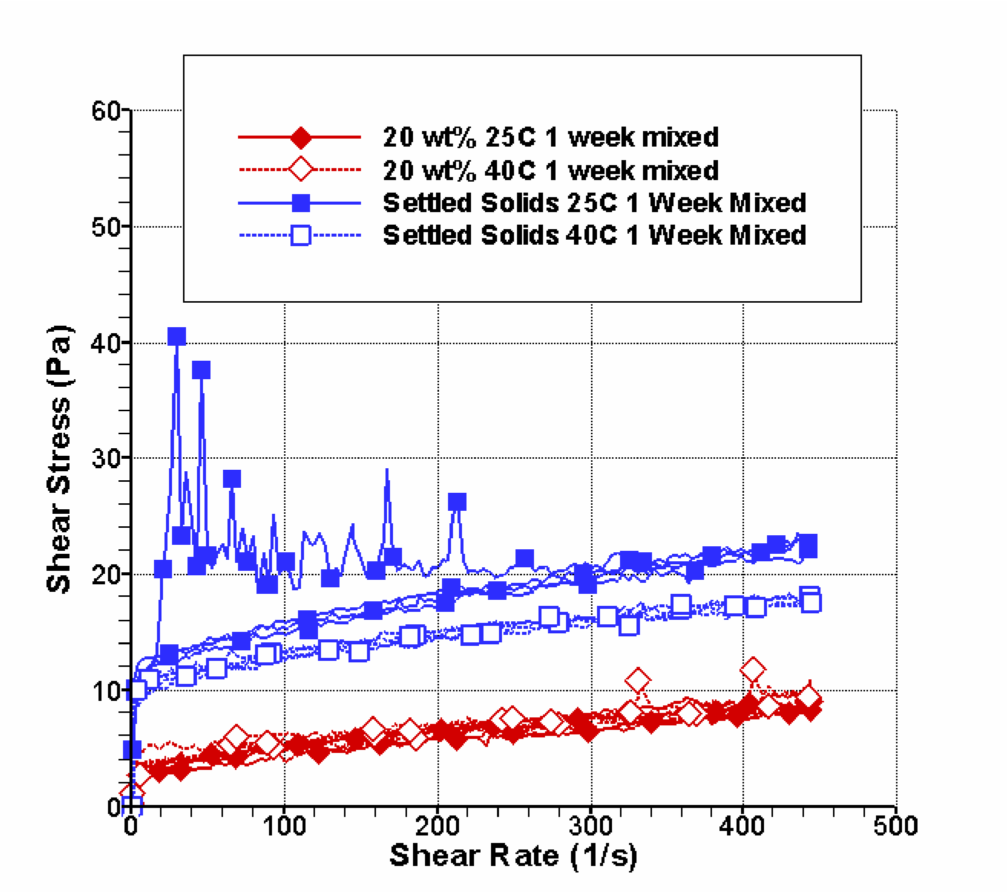


Figure 4.6. Flow Curves of 20-wt% UDS AZ-101 Melter Feed and Settled Solids from the Same Sample at 25°C and 40°C

Table 4.6. Rheological Model Fits (10 to 445 s^{-1}) for 20-wt% UDS AZ-101 HLW Melter Feed at Various Mixing Durations and Temperatures

Model/Model Parameter	1 Day Mixed at 25°C	1 Day Mixed at 36°C	1 Week Mixed at 25°C	1 Week Mixed at 40°C	1 Week Mixed Settled Solids at 25°C	1 Week Mixed Settled Solids at 40°C
File UDS me	**072903-HLRF-C**	**072903-HLRF-D**	**080803-HLRF-A**	**080803-HLRF-B**	**081103-HLRF-A**	**081103-HLRF-B**
Newtonian:						
η – Newtonian viscosity (cP)	n/a	n/a	n/a	n/a	n/a	n/a
r – correlation coefficient	n/a	n/a	n/a	n/a	n/a	n/a
Ostwald (or Power HLW):						
m – the consistency coefficient ($mPa \cdot s^{-n}$)	2.02	1.969	1.126	2.121	6.31	6.345
n – the power law exponent	0.244	0.2369	0.3179	0.2221	0.1959	0.1669
r – correlation coefficient	0.9783	0.9753	0.9531	0.9247	0.9737	0.9727
Bingham Plastic:						
τ_O^B - the Bingham yield stress (Pa)	5.1	4.738	3.623	4.765	12.59	11.77
η_p - the plastic viscosity (cP)	9.9	9.267	10.64	9.023	21.78	15.14
r – correlation coefficient	0.9469	0.9768	0.9741	0.9813	0.9826	0.985
Herschel-Bulkley:						
τ_O^H - the yield stress (Pa)	0.9366	3.71	3.442	4.921	10.24	10.42
k - the Herschel-Bulkely consistency coefficient ($mPa \cdot s^{-b}$)	1.421	0.1312	0.01956	0.004219	0.3303	0.1515
b - the Hershel-Bulkely power law exponent	0.2841	0.5935	0.904	1.121	0.5805	0.6446
r – correlation coefficient	0.9785	0.986	0.9745	0.982	0.9955	0.9919
n/a = not applicable						

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 fluids that exhibit yield stress. 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.

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 factors such as slip flow and inertial effects, 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 this section.

The 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 at 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.

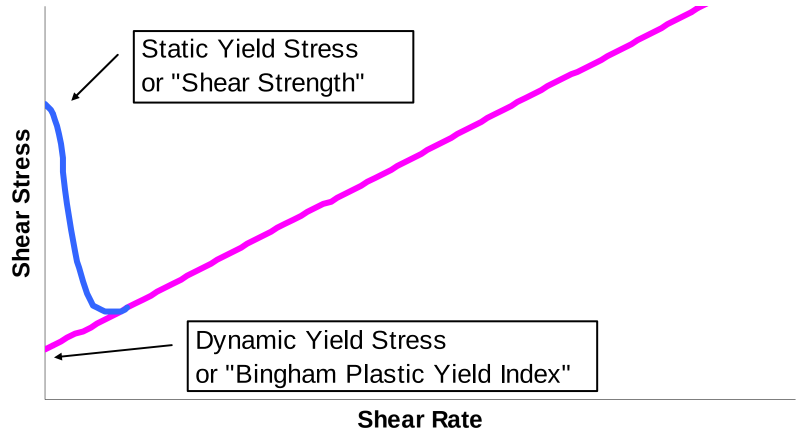


Figure 5.1. Rheogram Illustrating the Concept of Dynamic and Static Yield Stress

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 Shear-Strength Measurement Equipment and Theory

Shear strength can be directly measured 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 minimize wall and end effects (Dzuy and Boger 1985). These geometry requirements were confirmed before material testing.

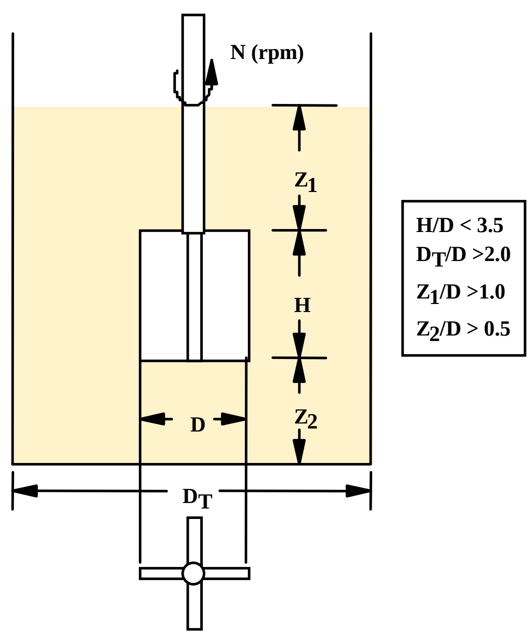


Figure 5.2. Geometrical Requirements of a Shear Vane

A typical stress-time profile is shown in Figure 5.3. The profile shows an initial linear region, followed by a nonlinear 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 nonlinear region represents viscoelastic 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 nonlinear 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.

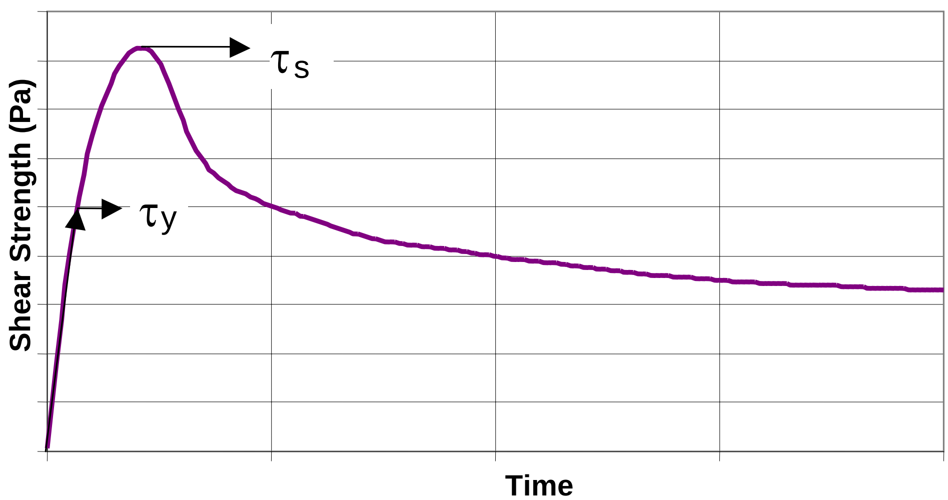


Figure 5.3. Typical Response of a Shear Vane

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

5.2 Shear-Strength System Validation and Calibration

Initially, a viscosity standard was measured with the cup/cylinder geometry on the Haake M5 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. The deviation of the measured viscosity from the certified value was within the allowable 10% (see Table 4.3) and was typical of this particular viscometer model.

5.3 Shear Strength of AZ-101 HLW Pretreated Sludge

With the calibration of the Haake M5 rheometer established, shear-strength measurements were taken on the settled solids from the HLW pretreated sludge samples. The 22-wt% UDS HLW pretreated sludge sample was agitated (i.e., stirred) and allowed to sit undisturbed for various periods of time (referred to as gel time) between measurements. This methodology allows for investigation of how the shear strength of sludge rebuilds after being sheared.

When shear-strength measurements were performed, the shear vanes were immersed in the settled solids according to the geometrical requirements outlined in Figure 5.2. The shear vane used for this report was four bladed with dimensions of D=1.6 cm and 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 at various gel times are shown in Figure 5.4. Even after a 10-minunte gel time, a maximum peak could be measured. The shear strength appeared to stabilize after approximately 16 hours at a shear strength of approximately 30 Pa. This dynamic can be seen in Figure 5.5 by plotting the shear strength as a function of gel time (10% error in these measurements was assumed, which is typical of this technique).

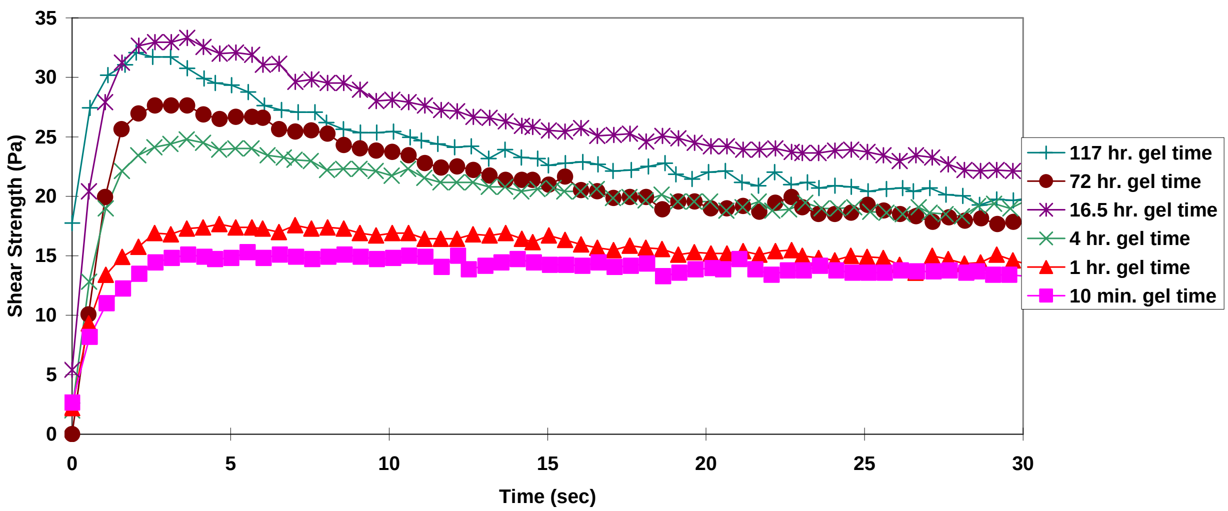


Figure 5.4. Shear Strength Response of 22-wt% UDS AZ-101 HLW Pretreated Sludge

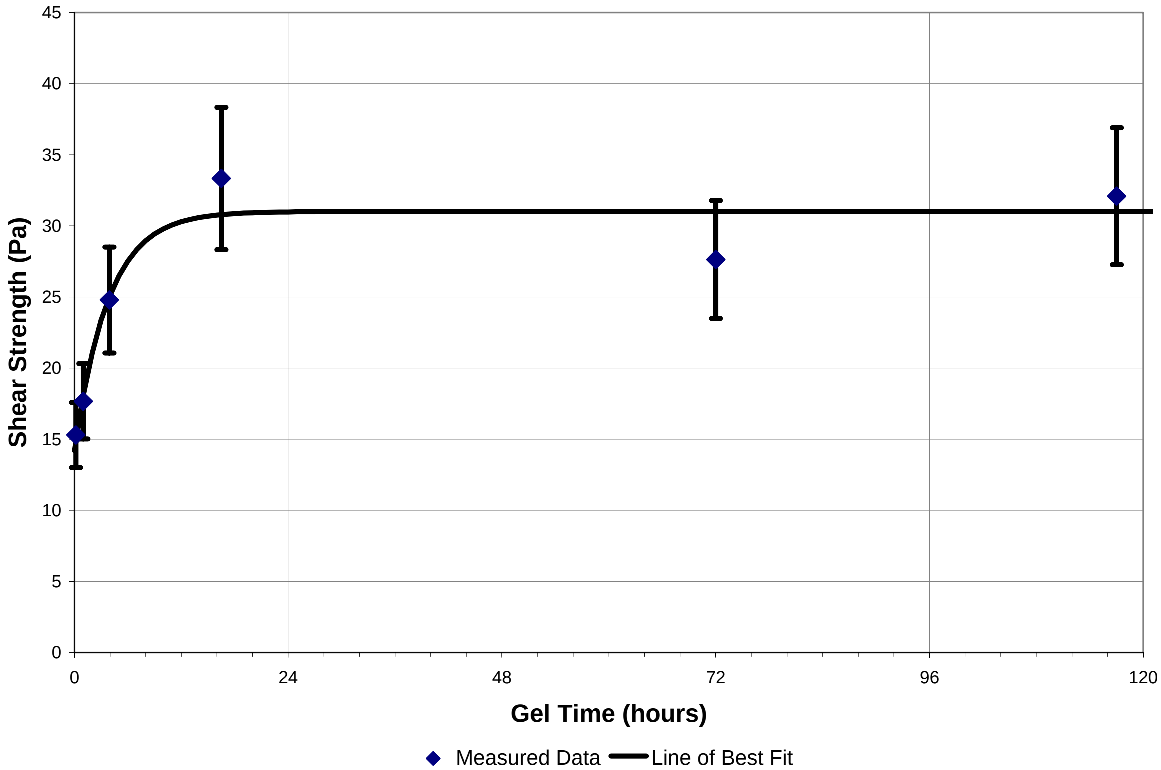


Figure 5.5. Shear Strength as a Function of Gel Time for HLW Pretreated Sludge

Speers et al. (1987) describe this rebuild behavior for several drilling mud slurries with a first-order rate model (see Equation 5.2). This model appears to be a good fit to the shear-strength data shown in Figure 5.5. The model-fit parameters for this model are shown below. Using this model, the initial shear-strength parameter (16.8 Pa) should roughly agree with the measured rheological Bingham-yield-stress measurement (14.7 to 18.1 Pa). This model indicates that the shear strength rebuilds immediately from the time that it remains unsheared. The material is expected to reach 95% of its steady-state shear strength (31 Pa) 9 hours from this time.

$$\tau = A(1-e^{-Bt})+C \tag{5.2}$$

Variable	Description	Value
τ =	shear strength (Pa)	See Figure 5.5 (r^2=0.929)
t =	gel time (hour)	0 to 120 hours
A =	initial (t = 0 hour) shear strength (Pa)	16.8 Pa
B =	time constant ($hour^{-1}$)	0.262 h^{-1}
C =	Difference between initial and steady state shear strength (Pa)	14.2 Pa.

5.4 Shear Strength of AZ-101 Melter Feed

With the calibration of the Haake M5 rheometer established, shear-strength measurements were taken on the settled solids from the 20-wt% UDS melter-feed sample. The shear vanes were immersed in the settled solids according to the geometrical requirements outlined in Figure 5.2. A four-bladed shear was used with dimensions of D=1.6 cm and 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 5.6. The numerical shear-strength values are shown in Table 5.2. These results indicate that the shear strength of the AZ-101 HLW melter feed rises to 55 Pa with the addition of GFCs. However, an additional week of mixing reduced the shear strength of the melter feed to 23 Pa.

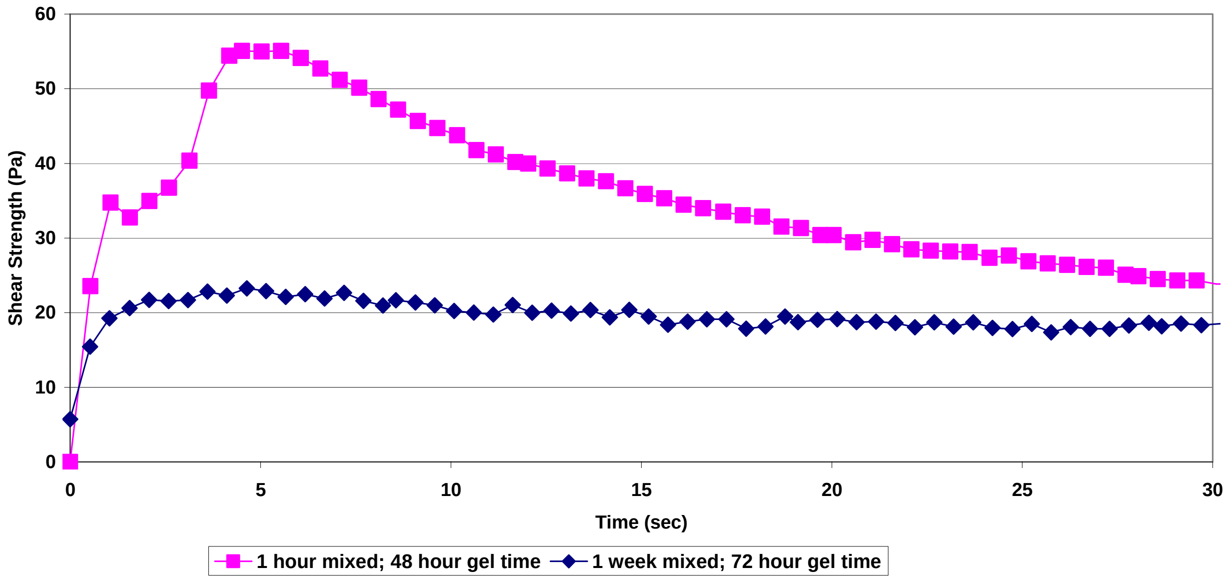


Figure 5.6. Shear-Strength Response of 20-wt% UDS AZ-101 Melter-Feed Settled Solids at Various Mixing Durations

Table 5.2. Summary of 20-wt% UDS AZ-101 Melter-Feed Settled Solids Shear- Strength Data at Various Mixing Durations

Sample	Temp.	Shear Strength (Pa)
1 hour mixed	Hot cell ambient	55
1 week mixed	Hot cell ambient	23

6.0 pH Measurements of AZ-101 HLW Pretreated Sludge and Melter Feed

The pH of the AZ-101 pretreated HLW and melter feeds was measured with a combination glass electrode. The pH for the pretreated HLW was determined to be 12.1 (see Table 6.1). Since the GFCs (see Table 3.1) contain significant amounts of soluble species, such as borax, lithium carbonate, and sodium carbonate, the pH of the resulting melter-feed interstitial liquid dropped significantly. The results of the pH measurement for the melter-feed material were 10.0, 9.9, and 10.3 for three UDS concentrations of 10, 15, and 20 wt%, respectively. During the mixing/aging study, the pH of the samples was also determined to be 10.3 and 10.4 for the 1-day and 1-week mixing durations, respectively, showing no measurable change in pH over the duration of the mixing and aging test. The relatively constant pH range of 9.9 to 10.4 observed throughout the melter-feed study may be due to the significant amount of carbonate added as GFCs, forming a carbonate/bicarbonate buffer solution.

Table 6.1. The pH of the AZ-101 Envelope D Pretreated HLW and Melter Feed

Sample	Mixing Period	pH (at hot cell ambient)
Decanted Supernate from HLW Pretreated Sludge	n/a	12.1
10-wt% UDS Melter Feed	1 hour	10.0
15-wt% UDS Melter Feed	1 hour	9.9
20-wt% UDS Melter Feed	1 hour	10.3
20-wt% UDS Melter Feed	1 day	10.3
20-wt% UDS Melter Feed	1 week	10.4
n/a – not applicable		

7.0 Settling Behavior of AZ-101 HLW Pretreated Sludge and Melter Feed

The settling behavior of the AZ-101 Envelope D pretreated sludges and melter feeds were investigated by agitating ~10 mL samples of 10- and 15-wt% UDS pretreated sludge and 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 40°C.

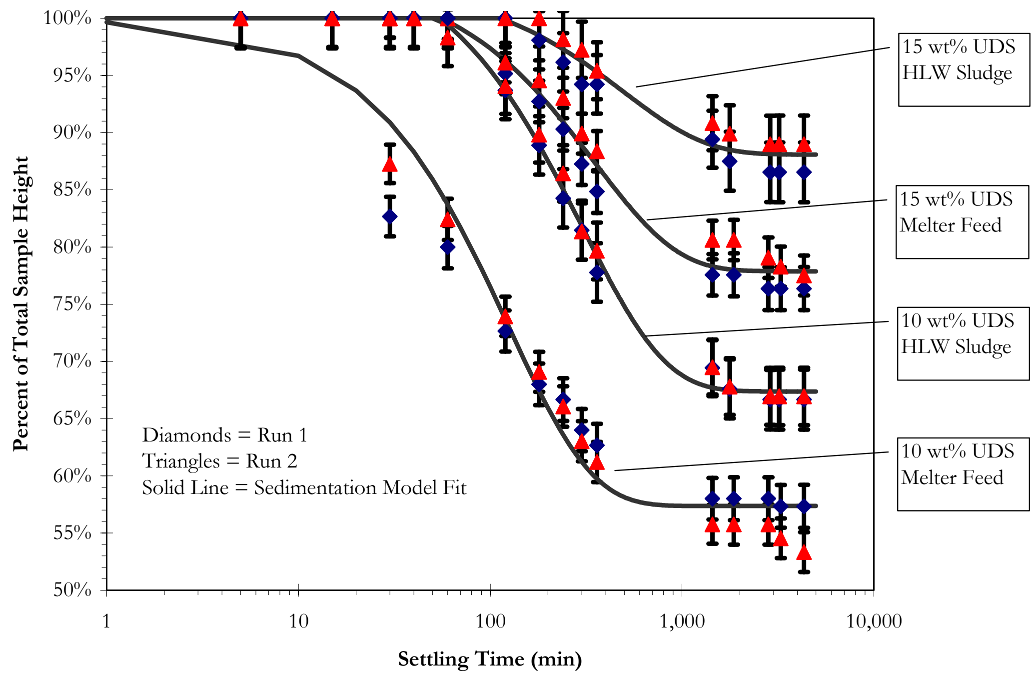
The melter feeds were observed to settle in the "lenticular" settling regime. This regime occurs when agitated solid particulates take time to form flocs and then begin to settle as a mass. This behavior is characterized by the settled-solids layer height remaining fully suspended for a period of time while the flocs form, followed by an inverse sigmoidal height decrease to a final settled-solids volume. Lenticular settling can be modeled through Equation 7.1 (Harris et al. 1975).

$$\frac{h}{h_0} = \begin{cases} 1 & t < t_c \\ 1 + A\left(e^{-B(t-t_c)} - 1\right) & t \geq t_c \end{cases} \qquad (7.1)$$

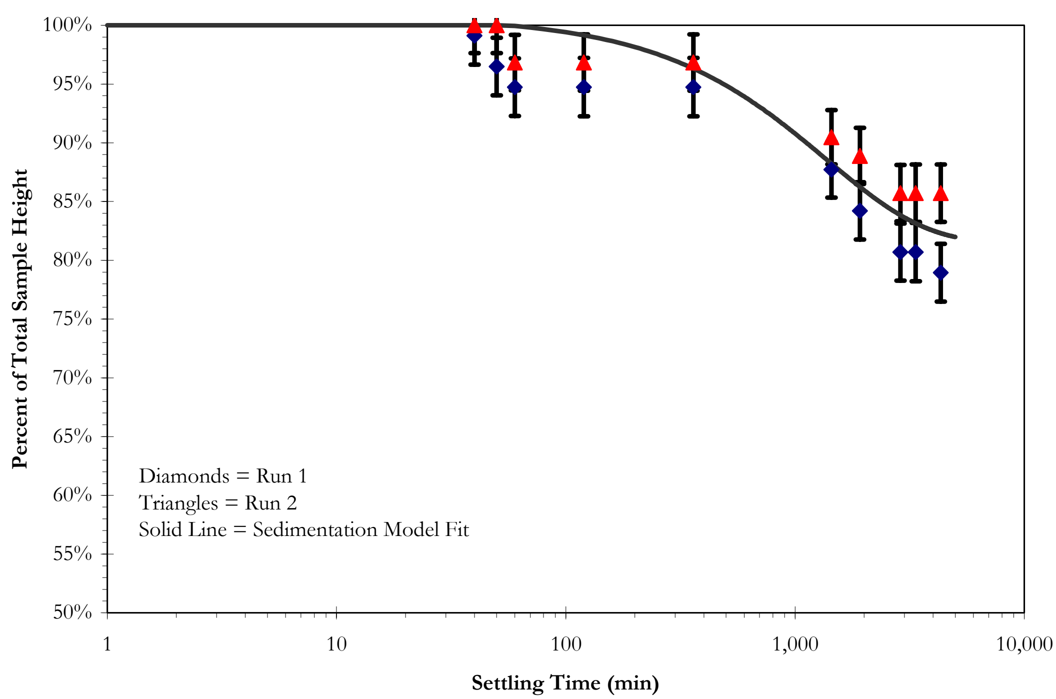
where h is the interface height at time, t, h_0 is the initial interface height, and A and B are fitting parameters. The critical time where the solids-interface height begins to decrease is denoted by t_c.

The settling data are presented graphically in Figure 7.1. As expected, the 15-wt% UDS pretreated sludge settled the slowest. Adding a relatively large quantity of large GFC particles increased the settling rate and packing efficiency of the 15-wt% UDS melter feed. The 10-wt% UDS pretreated sludge sample settled considerably faster than the 15-wt% pretreated sludge. Adding GFCs to the 10-wt% pretreated sludge changed the settling regime from floccular settling to hindered or zone settling. This can be seen by the decrease in the critical time to begin the settling-height decrease in the 10-wt% UDS melter-feed sample.

The 22-wt% UDS pretreated sludge was prepared by decanting nearly all of the standing liquid from the slurry that settled for several days. Due to this preparation method, the 22-wt% UDS pretreated sludge consists of the settled-solids layer, and a settling test on this material is not needed. The 20-wt% UDS melter feed consists of this settled-solids layer with GFCs and a slight increase in the quantity of interstitial liquid. After 3 days of settling for physical-properties testing, this material only slightly settled to 96% of the total sample height (see Section 9.2). Because measurements from 100% to 96% settled volume are within the measurement error of the centrifuge cones, settling data over this range over a several-day period would not be reliable and were not measured. However, the 20-wt% UDS melter feed after 1 week of settling appeared to possess a high packing efficiency and settled to an appreciable level over the 3-day period. The settling behavior of this sample is shown in Figure 7.1. Fitting parameters for the line of best fit described by Equation 6.1 are shown in Table 7.1.



a) dimensionless solid/liquid interface height as a function of settling time for 10- and 15-wt% UDS HLW pretreated sludge and melter feeds



b) dimensionless solid/liquid interface height as a function of settling time for 20-wt% UDS HLW melter feed after 1 week of mixing

Figure 7.1. Sedimentation Curves for AZ-101 HLW Pretreated Sludge and Melter Feeds

Table 7.1. Settling-Model-Fit Parameters of HLW Pretreated Sludge and Melter Feeds

Sample Description	*A*	*B* (min^{-1})	t_c (min)	r^2
10-wt% UDS HLW Sludge	0.326	3.32×10^{-3}	54.8	0.999
10-wt% UDS Melter Feed	0.426	8.01×10^{-3}	0	0.984
15-wt% UDS HLW Sludge	0.119	2.03×10^{-3}	113	0.984
15-wt% UDS Melter Feed	0.221	2.87×10^{-3}	55.8	0.990
20-wt% UDS Melter Feed After 1 Week Mixing	0.185	7.29×10^{-4}	55.8	0.947

8.0 Particle-Size Distribution of AZ-101 HLW Melter Feed

The particle-size distributions (PSDs) of the 20-wt% UDS melter-feed sample that was mixed for 1 hour after GFCs addition is described in this section. A Malvern MS-2000 particle-size analyzer was used to measure the PSD of this sample. Note that the PSD of the AZ-101 pretreated sludge can be found in Geeting et al. (2002).

8.1 Description of Particle-Size Distribution Instrument

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 media. 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.

8.2 Calibration Checks for Particle-Size Distribution Instrument

The performance of the instrument was checked against a National Institute for 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 8.1. To check the functionality of the instrument, a close fit of the D_{50} value is typically required (approximately 10% of the certified range). 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 8.1. Particle-Size Analyzer Calibration Data

49.8 ± 0.8 μm NIST Traceable Particle-Size Standard (Duke Scientific; Lot No. 24608)		Measured Diameter (μm)	Acceptable Range (μm)	Coefficient of Variation Between Five Runs
Malvern MS-2000	D_{10}	46.506	not applicable	0.24%
	D_{50}	49.952	44.1 - 55.7	0.21%
	D_{90}	56.598	not applicable	0.56%

8.3 Particle-Size Distribution Instrument Operating Conditions

The PSD of the 20-wt% UDS 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 PSD by applying shearing forces to agglomerated particles. The shearing forces break apart agglomerates such that the primary PSD 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 six separate samples under all flow/sonication conditions. The suspending medium for the AZ-101 melter-feed particle-size analysis was 0.01 M NaOH. This solution was chosen since it is used during the washing/leaching steps on the HLW pretreated sludge in the cross-flow ultrafiltration unit proceeding GFC addition.

8.4 Particle-Size Distribution 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 8.2. The D_{10}, D_{50}, and D_{90} values are presented along with the associated coefficient of variation between these five subsamples. 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 are nearly achieved with a pump setting of 2500 RPM and sonication level of 0%.

Table 8.2. 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	2.1	15.7%	7.2	10.1%	23.8	4.5%
2500 RPM/ 25% sonication	0.9	13.9%	10.7	21.6%	34.1	4.0%
2500 RPM/ 50% sonication	0.9	35.9%	13.4	8.7%	39.1	10.8%

At a pump setting of 2500 RPM and 0% sonication, the coefficient of variation between the three subsamples is relatively small. These results indicate little difference between the measurements of the five aliquots. The resulting PSD appears consistent with the mesh sizes of the GFCs used in the melter feed. This can be seen in the measured PSD shown in Figure 8.1.

At a pump setting of 2500 RPM and 25% sonication, the coefficient of variation between the three subsamples generally increases, indicating large differences between the measurements taken for each aliquot. These differences can either be due to varying degrees of flocculation, subsampling errors, or bubble formation/entrainment. The presence of a secondary mode at 100 μm, which was not present at the lower sonication level, indicates the presence of bubbles. These PSD runs can be seen in Figure 8.2.

Lastly, at a pump setting of 2500 RPM and 50% sonication, the coefficient of variation between the five subsamples increases significantly above the target ranges discussed above. The presence of secondary modes at and above 100 µm that were not present at lower sonication levels indicates the presence of more bubbles. These PSD runs can be seen in Figure 8.3.

Due to the repeatability between three subsamples, the 2500 RPM and 0% sonication measurements should be considered the fundamental PSD. The average PSD for each sonication level is shown in Figure 8.4. From this figure, one can see that as the level of sonication increases, the quantity of large particles increases. This counter-intuitive behavior is explained by the entrainment of bubbles at higher levels of sonication. Two modes can be seen in the fundamental PSD. One peak is seen at approximately 0.7 µm and another peak at approximately 7 µm. The cumulative PSD is shown in Figure 8.5. This representation of the particle-size measurements indicates that the D_{95} value for the fundamental distribution is approximately 30 µm. The D_{95} value is commonly used as a conservative value of particle size for various engineering calculations.

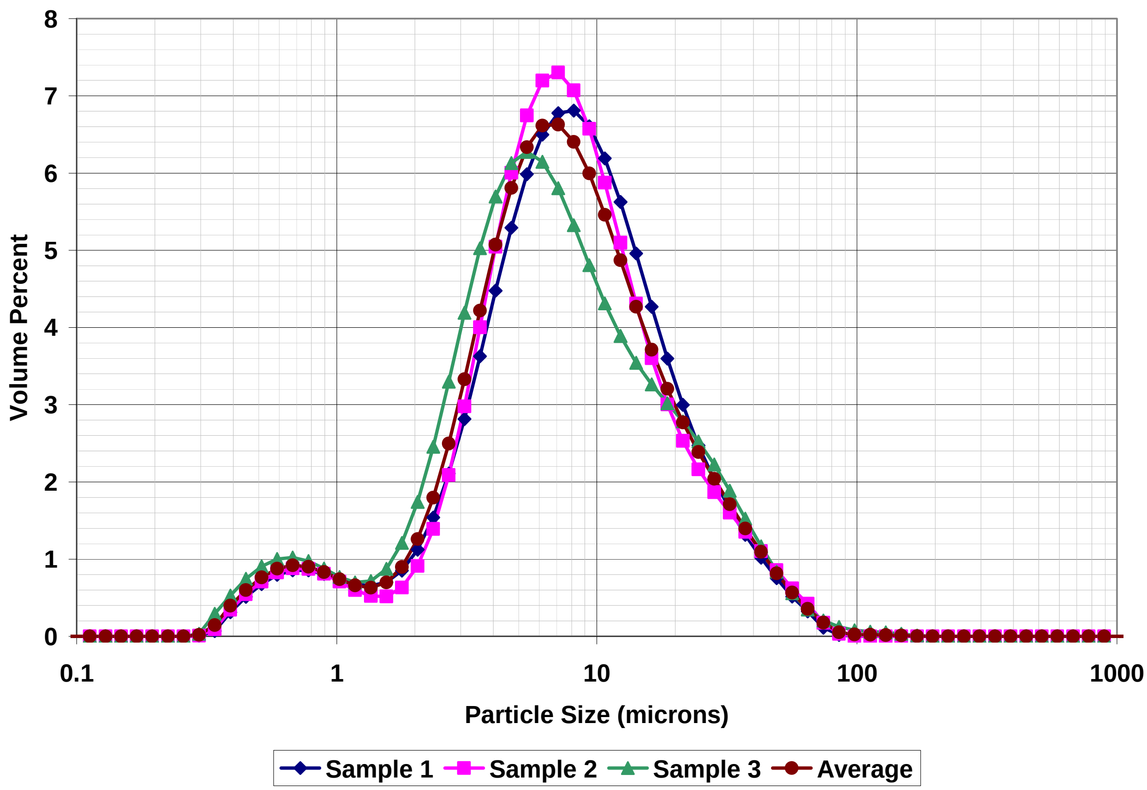


Figure 8.1. PSD of AZ-101 Envelope D Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 0%

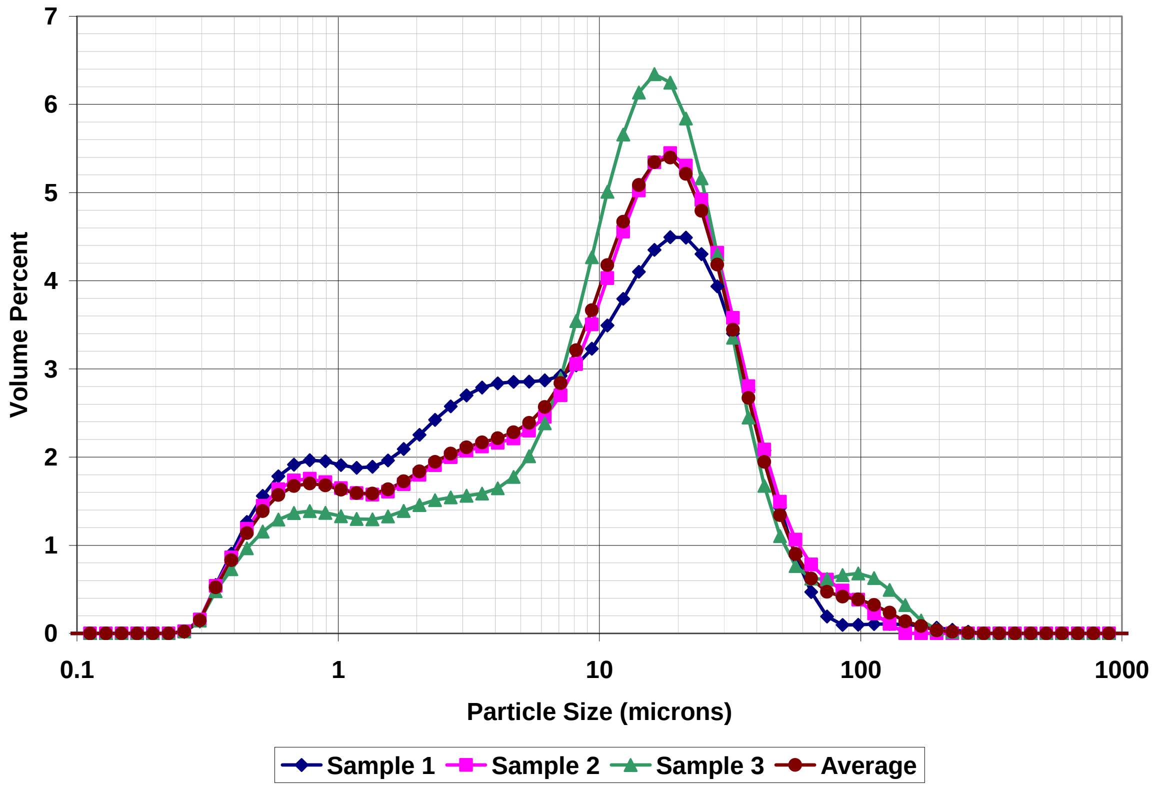


Figure 8.2. PSD of AZ-101 Envelope D Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 25%

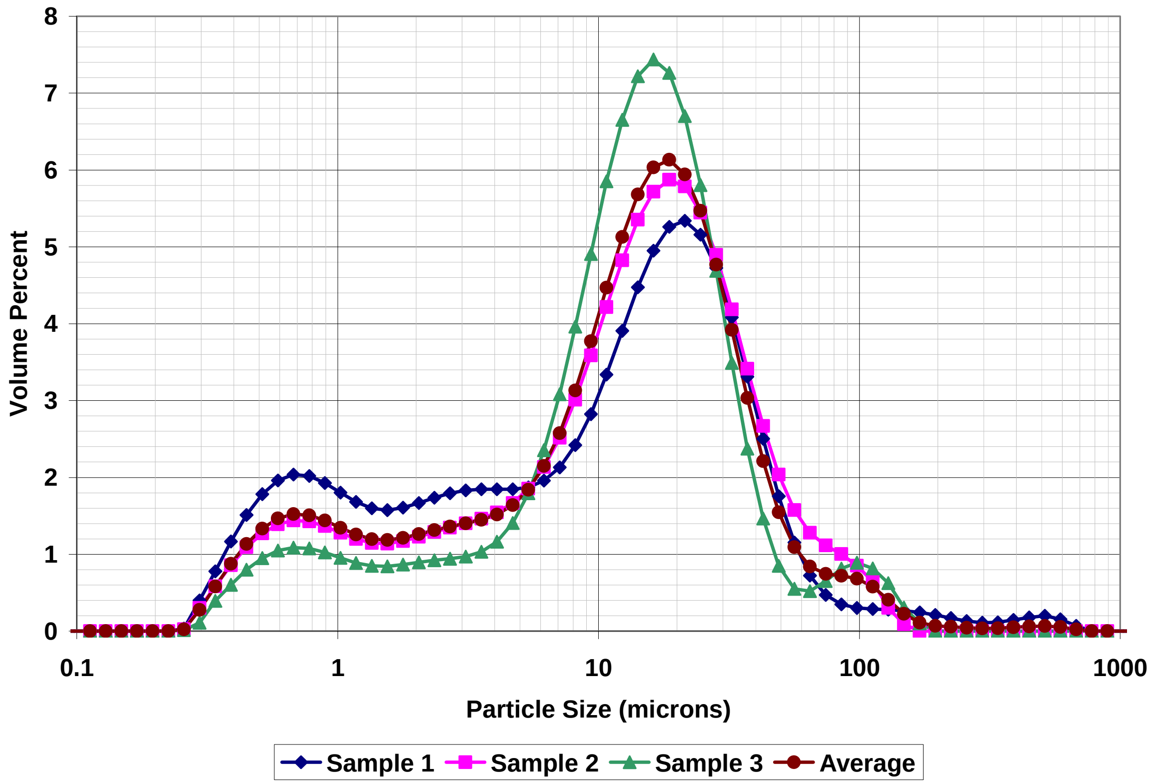


Figure 8.3. PSD of AZ-101 Envelope D Melter Feed at a Pump Setting of 2500 RPM and Sonication Level of 50%

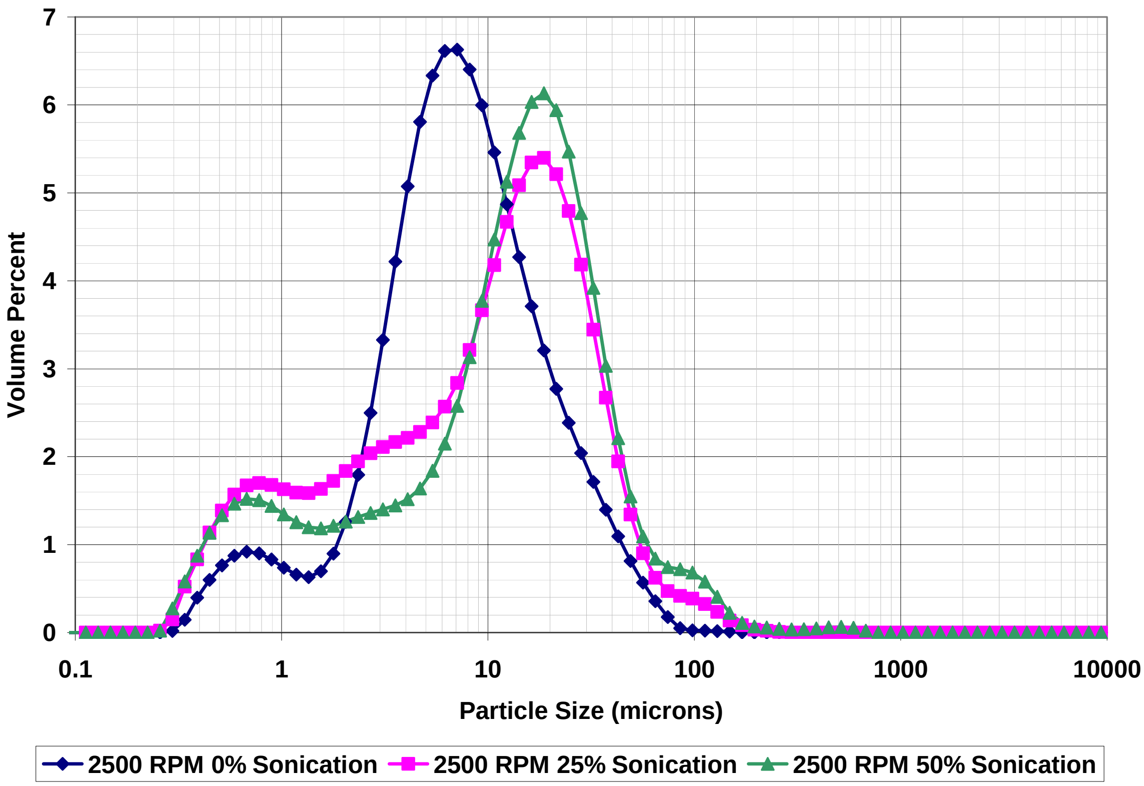


Figure 8.4. Average PSD of AZ-101 Envelope D Melter Feed at a Pump Setting of 2500 RPM and Varying Levels of Sonication

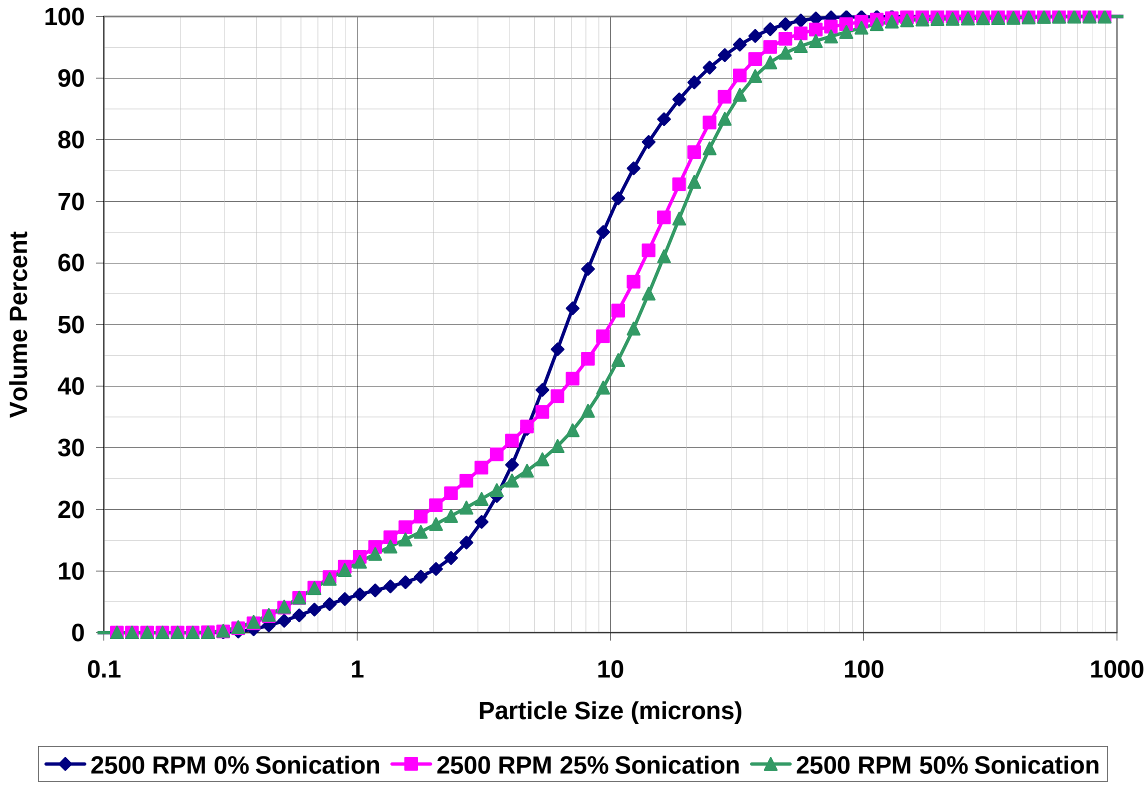


Figure 8.5. Average Cumulative PSD of AZ-101 Envelope D Melter Feed at a Pump Setting of 2500 RPM and Varying Levels of Sonication

9.0 Physical-Properties Testing of AZ-101 HLW Melter Feed

Samples of the AZ-101 pretreated feed and melter feed described in Section 3 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 9.1 of this report provides the general protocol, nomenclature, equations, and definitions from the guidelines document. The physical-properties measurements were performed at ambient hot-cell temperature (~36ºC).

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.

9.1 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 was calculated ($\rho_B=M_B/V_B$). These results can be biased low because of 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. 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_{Mna}. The following equation was used:

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

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.

9.2 Physical Properties of AZ-101 Envelope D Melter Feed

Physical-properties results of the HLW melter feed at each UDS concentration can be found in Table 9.1. Physical-properties measurements were performed at ambient hot-cell temperature (~36°C). The wt% UDS for the 10-, 15-, and 20-wt% UDS melter feeds were 16, 26, and 38%, respectively. The 1 week mixed sample at 20-wt% UDS had a measured UDS concentration of 33%. This difference is likely due to subsampling errors. Due to limited quantities of material for testing, duplicate measurements were taken. Additional errors in the consistency between the 20-wt% UDS melter-feed samples at 1 hour and 1 week may have been introduced through the recycling of 20-wt% 1-hour mixed rheology samples. This recycling was required to accomplish the entire scope of the mixing/aging study with the limited quantity of sample available. The recycled sample was washed from the rheology equipment with deionized water. The excess deionized water was evaporated such that a target mass consistent with 20-wt% UDS was achieved.

Because of limited sample availability, only duplicate samples were measured for physical-properties analysis. Because only duplicate measurements were performed, potential subsampling errors cannot easily be quantified. One subsampling effort was performed on the 20-wt% UDS melter feed. The samples were then diluted an appropriate amount to target values of 10- and 15-wt% UDS. To quantify the subsampling error when drawing these aliquots, the relative mean difference for each physical-property value was calculated. The mean and standard deviation of these values were computed. The error was then estimated by multiplying the average reported value by the sum of the average relative mean difference and twice the standard deviation. The 1-week mixed sample was taken during a separate subsampling activity; therefore, only the relative mean difference was used to compute an estimated error.

Table 9.1. Physical Properties of 10, 15, and 20 wt% UDS AZ-101 Envelope D Melter Feed

Physical Property	Units	10-wt% UDS	15-wt% UDS	20-wt% UDS	20-wt% UDS ; 1 week mixed
Bulk Density	g/mL	1.183 ± 0.082	1.331 ± 0.092	1.506 ± 0.104	1.402 ± 0.010
vol% Settled Solids	%	55.3% ± 5.5%	76.9% ± 7.6%	96.2% ± 9.5%	88.9% ± 0.0%
Density of Centrifuged Solids	g/mL	1.370 ± 0.171	1.625 ± 0.202	1.676 ± 0.209	1.577 ± 0.017
vol% Centrifuged Solids	%	32.5% ± 2.3%	46.0% ± 3.2%	70.5% ± 5.0%	58.1% ± 0.7%
wt% Centrifuged Solids	%	37.6% ± 3.2%	56.2% ± 4.8%	78.4% ± 6.7%	65.3% ± 1.0%
Supernatant Density	g/mL	1.063 ± 0.003	1.110 ± 0.003	1.177 ± 0.004	1.087 ± 0.014
Density of Settled Solids	g/mL	1.28 ± 0.09	1.39 ± 0.10	1.50 ± 0.11	1.42 ± 0.03
wt% Settled Supernatant	%	62.4% ± 16.3%	43.9% ± 11.5%	21.9% ± 5.7%	29.7% ± 9.0%
wt% dissolved solids in supernatant	%	8.0% ± 0.2%	10.3% ± 0.3%	10.3% ± 0.3%	10.5% ± 0.9%
wt% total solids in Centrifuged Sludge	%	48.0% ± 2.5%	51.1% ± 2.7%	53.5% ± 2.8%	55.7% ± 0.3%
wt% Total Solids	%	23.3% ± 1.1%	33.6% ± 1.6%	44.5% ± 2.1%	42.1% ± 3.0%
wt% UDS	%	16.4% ± 1.5%	25.6% ± 2.4%	37.8% ± 3.5%	33.0% ± 0.6%

10.0 Conclusions

A sample of AZ-101 HLW pretreated sludge was received at an initial UDS concentration of 10.3 wt%. The 10.3-wt% UDS sample was concentrated to 22-wt% UDS via decanting. The shear-strength behavior of the 22-wt% UDS HLW pretreated sludge sample was determined by agitating (i.e., stirring) the sample and allowing it sit undisturbed for various periods of time (referred to as gel time) between measurements. Several resulting shear stress/time curves at various gel times were measured. These data allow for investigation of how the shear strength of sludge rebuilds after being sheared. Even after a 10-minute gel time, a maximum peak could be measured. The shear strength appeared to stabilize after approximately 16 hours at a shear strength of approximately 30 Pa.

The rebuild behavior of the sludge can be described with a first-order-rate model. This model appears to fit the shear-strength data shown in Figure S.1 well. Using this model, the initial shear-strength parameter (16.8 Pa) should roughly agree with the measured rheological Bingham-yield-stress measurement (14.7 to 18.1 Pa). This model indicates that the shear strength rebuilds immediately from the time that it remains unsheared. The material is expected to reach 95% of its steady-state shear strength (31 Pa) 9 hours from this time.

The 22-wt% UDS sample was adjusted to 10- and 15-wt% UDS concentrations. Flow curves from these samples indicate that the fluid should be characterized as a Bingham-plastic fluid with the maximum measured rheological parameters occurring at 22-wt% UDS with a Bingham consistency of 11 cP and Bingham yield stress of 11 Pa at 25˚C. At 40˚C, the Bingham-plastic parameters of the 22-wt% UDS pretreated sludge were a Bingham consistency of 7 cP and Bingham yield stress of 10 Pa. The pH of the 22-wt% UDS sample was measured at 12.1.

GFCs were mixed with an AZ-101 20-wt% UDS HLW Pretreated Sludge sample. At intervals of 1 hour, 1 day, and 1 week, the rheology and pH of the sample were measured. When GFCs were added to the AZ-101 pretreated HLW, the pH of the solution dropped from 12.1 to a range of 9.9 to 10.4. This is most likely due to the relatively large quantity of soluble carbonate species in the melter-feed formulation.

Even at only 10-wt% UDS, the AZ-101 HLW melter feed exhibits Bingham-plastic rheological behavior. At 10-wt% UDS at 40°C, the low-range Bingham-plastic parameters of the melter feed were a Bingham consistency of 5 cP and a Bingham yield stress of 2 Pa. At 20-wt% UDS at 25°C, the high range Bingham-plastic parameters of the melter feed were a Bingham consistency of 20 cP and a Bingham yield stress of 15 Pa.

Physical-properties measurements on the AZ-101 HLW melter feed indicate a higher packing efficiency for the 1-week mixed sample. The vol% settled solids increases from 55, 77, and 96% for the 10-, 15-, and 20-wt% UDS melter feeds, respectively. After 1 week of mixing, the vol% settled solids for the 20-wt% UDS sample drops to 89%. The wt% UDS increases from 16-, 26-, and 38-wt% UDS for the 10-, 15-, and 20-wt% UDS melter feeds, respectively. After 1 week of mixing, the quantity of UDS for the 20-wt% UDS sample drops to 33%. Considering subsampling errors in the previous 20-wt% UDS measurements, these values are relatively close. The difference between these values is most likely explained through mass-balance assumption errors when recycling and recovering previous melter-feed rheology samples for the mixing/aging study. This recycling was performed throughout testing due to the extremely limited amount of AZ-101 HLW pretreated sludge available (~36 g UDS).

The settling behavior of the AZ-101 HLW pretreated sludge and melter feed can be characterized as "floccular" settling. This type of settling is characterized by a critical time when the suspended-solids height begins to decrease. This critical time corresponds to the amount of time for flocs to form and begin to settle at a faster rate. The 10-wt% AZ-101 melter-feed sample possessed large GFC particles at a low solids concentration such that the solids began to immediately settle in a "hindered" settling regime. The 22-wt% UDS pretreated sludge and 20-wt% UDS melter feed mixed for 1 hour did not settle to measurable levels during the 72-hour sedimentation period. However, after 1 week of mixing, the packing efficiency of the 20-wt% UDS melter-feed sample increased such that the settling behavior could be measured.

The PSD of a 20-wt% UDS melter-feed sample was also measured. The PSD exhibits two major peaks, one in approximately the 0.5 to 1 μm range and the other in approximately the 5 to 10 μm range. Approximately 10 vol% of the particles are below 2.1 μm, 50 vol% (i.e., median value) below 7.2 μm, 90 vol% below 23.8 μm, and 95 vol% below 35 μm. With particle sizes below 100 μm, no significant process challenges with respect to particle settling are anticipated. During particle-size measurement, the samples were sonicated to break apart agglomerates of large particles and measure the fundamental PSD of the suspension. However, bubble entrainment in the measurement cell appeared to bias the resulting PSD toward larger particle sizes, making these measurements unreliable. Consequently, the unsonicated particle-size result should be considered the primary PSD because of the high repeatability of particle-size results between subsamples.

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Appendix A

Composition of AZ-101 Pretreated HLW Waste and AZ-101 HLW Melter Feed

Appendix A: Composition of AZ-101 Pretreated HLW Waste and AZ-101 HLW Melter Feed

The table below 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 10.9-wt% UDS Pretreated AZ-101 HLW sludge, these compositions have been calculated based on dilution levels and glass-former chemical additions. Secondary waste products were not added to any of the samples reported in this work. Blank spaces in the table are intentional.

Sample	10.9-wt% UDS Pretreated AZ-101 Waste	22-wt% UDS Pretreated AZ-101 Waste	10-wt% UDS Pretreated AZ-101 Waste	15-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS AZ-101 Melter Feed	15-wt% UDS AZ-101 Melter Feed	10-wt% UDS AZ-101 Melter Feed
Bulk Density (g/mL)	1.127					1.51	1.33	1.18
Oxides Loading of Pretreated HLW Sludge or Melter Feed (g ox/L):	113					580	420	280
pH		12.1				10.3	9.9	10.0
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	86	170	79	120	160	106	87	64
Al	13700	27000	13000	19000	24000	16000	14000	10700
As	<34							
B	<6.8					12000	9900	7300
Ba	210	420	190	280	380	250	210	150
Be	<1.4							
Bi	<14							
Ca	1100	2200	1020	1500	2000	1400	1100	820
Cd	2000	4000	1800	2700	3600	2400	2000	1500
Ce	460	920	420	630	840	560	460	340
Co	<6.8							
Cr	330	660	310	460	600	400	330	250
Cs								
Cu	80	160	73	110	150	98	80	59
Dy	<6.8							

Sample	10.9-wt% UDS Pretreated AZ-101 Waste	22-wt% UDS Pretreated AZ-101 Waste	10-wt% UDS Pretreated AZ-101 Waste	15-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS AZ-101 Melter Feed	15-wt% UDS AZ-101 Melter Feed	10-wt% UDS AZ-101 Melter Feed
Eu	<14							
Fe	28000	56000	25000	38000	51000	34000	28000	20000
Hg								
K	270	550	250	380	500	340	280	200
La	800	1600	730	1100	1500	980	800	590
Li	18	35	17	24	32	6400	5300	3900
Mg	160	330	150	230	300	200	160	120
Mn	740	1500	680	1000	1400	910	740	540
Mo	9.0	18	8.8	12	16	11	9	7
Na	7300	10500	9500	9900	10300	30000	26000	22000
Nd	600	1200	550	820	1090	730	600	440
Ni	1300	2700	1200	1900	2500	1700	1400	990
P	620	1200	570	850	1100	760	620	450
Pb	240	490	220	340	450	300	250	180
Pd	320	640	290	430	580	390	320	230
Pr	120	240	110	170	220	150	120	89
Pt								
Rb								
Rh	70	140	64	97	130	86	70	52
Ru	210	430	190	290	390	260	210	160
S								
Sb	<69							
Se	<34							
Si	1800	3600	1700	2500	3300	78000	64000	47000
Sn	410	840	380	570	760	510	420	300
Sr	470	950	430	650	860	580	470	350
Ta	0.9	1.8	0.8	1.2	1.7	1	1	1
Te	<210							
Th	<140							
Ti	24	49	22	34	45	30	24	18
Tl	<69							
U	1700	3300	1500	2300	3000	2000	1700	1200
V	<6.9							
W	<270							
Y	53	106	48	73	97	65	53	39

Sample	10.9-wt% UDS Pretreated AZ-101 Waste	22-wt% UDS Pretreated AZ-101 Waste	10-wt% UDS Pretreated AZ-101 Waste	15-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS AZ-101 Melter Feed	15-wt% UDS AZ-101 Melter Feed	10-wt% UDS AZ-101 Melter Feed
Zn	38	77	35	52	70	5900	4800	3500
Zr	9000	18200	8300	12000	17000	11000	9000	6600
Carbon Analyses								
TIC								
TOC								
Anions								
F	52	104.8	47.7	71.5	95.3	64	52	38
Cl	94	60.9	166.2	122.4	78.5	52	89	133
Br								
NO2	970	1323.8	1281.6	1299.2	1316.8	880	947	1027
NO3	290	0.0	672.9	410.6	117.5	78	299	539
PO4								
SO4	320	260.5	539.6	423.4	307.1	205	308	432
CN								
NH3								
Free OH								
Total OH								
Radioisotopes								
H-3	3.06E-02	6.18E-02	2.81E-02	4.21E-02	5.62E-02	3.75E-02	3.07E-02	2.25E-02
C-14	6.75E-04	1.36E-03	6.20E-04	9.29E-04	1.24E-03	8.27E-04	6.77E-04	4.96E-04
Cr-51								
Fe-59								
Ni-59								
Co-60	1.15E+00	2.33E+00	1.06E+00	1.59E+00	2.12E+00	1.42E+00	1.16E+00	8.49E-01
Ni-63								
Se-79								
Y-88								
Sr-90	8.36E+03	1.69E+04	7.67E+03	1.15E+04	1.53E+04	1.02E+04	8.38E+03	6.15E+03
Sr-90/Y-90								
Nb-94/95								
Tc-99								
Ru-103								

Sample	10.9-wt% UDS Pretreated AZ-101 Waste	22-wt% UDS Pretreated AZ-101 Waste	10-wt% UDS Pretreated AZ-101 Waste	15-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS AZ-101 Melter Feed	15-wt% UDS AZ-101 Melter Feed	10-wt% UDS AZ-101 Melter Feed
Ru-106								
Sn-113								
Sb-125	5.29E+00	1.07E+01	4.86E+00	7.28E+00	9.70E+00	6.48E+00	5.30E+00	3.89E+00
Sn-126	2.88E-02	5.81E-02	2.64E-02	3.96E-02	5.28E-02	3.53E-02	2.88E-02	2.12E-02
Sb\Sn-126								
I-127								
I-129	1.75E-06	3.54E-06	1.61E-06	2.41E-06	3.22E-06	2.15E-06	1.76E-06	1.29E-06
C-133								
Cs-134								
Cs-135								
Cs-137	8.78E+01	1.67E+02	8.72E+01	1.20E+02	1.53E+02	1.03E+02	8.77E+01	6.98E+01
Ce-144								
Sm-151								
Eu-152								
Eu-154	1.38E+01	2.79E+01	1.27E+01	1.90E+01	2.54E+01	1.70E+01	1.39E+01	1.02E+01
Eu-155	1.64E+01	3.32E+01	1.51E+01	2.26E+01	3.02E+01	2.01E+01	1.65E+01	1.21E+01
Pa-231								
U-233	6.21E-04	1.25E-03	5.70E-04	8.54E-04	1.14E-03	7.61E-04	6.22E-04	4.56E-04
U-234	7.37E-04	1.49E-03	6.77E-04	1.01E-03	1.35E-03	9.03E-04	7.39E-04	5.42E-04
U-235	3.08E-05	6.22E-05	2.83E-05	4.24E-05	5.65E-05	3.78E-05	3.09E-05	2.27E-05
U-236	6.84E-05	1.38E-04	6.28E-05	9.41E-05	1.25E-04	8.38E-05	6.86E-05	5.03E-05
U-238	5.51E-04	1.11E-03	5.06E-04	7.58E-04	1.01E-03	6.75E-04	5.52E-04	4.05E-04
Np-237	1.85E-02	3.73E-02	1.70E-02	2.55E-02	3.39E-02	2.27E-02	1.85E-02	1.36E-02
Pu-236								
Pu-238								
Pu-239	1.09E+00	2.20E+00	1.00E+00	1.50E+00	2.00E+00	1.34E+00	1.09E+00	8.03E-01
Pu-240	3.07E-01	6.19E-01	2.82E-01	4.22E-01	5.63E-01	3.76E-01	3.08E-01	2.26E-01
Pu-239/240	1.31E+00	2.65E+00	1.21E+00	1.81E+00	2.41E+00	1.61E+00	1.32E+00	9.65E-01
Pu-241								
Pu-242	7.36E-03	1.48E-02	6.76E-03	1.01E-02	1.35E-02	9.02E-03	7.38E-03	5.41E-03
Pu-241/Am-241								
Am-241	2.71E+01	5.47E+01	2.49E+01	3.73E+01	4.98E+01	3.32E+01	2.72E+01	2.00E+01
Am-241, Am-243								
Am-242								
Am-243								

Sample	10.9-wt% UDS Pretreated AZ-101 Waste	22-wt% UDS Pretreated AZ-101 Waste	10-wt% UDS Pretreated AZ-101 Waste	15-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS Pretreated AZ-101 Waste	20-wt% UDS AZ-101 Melter Feed	15-wt% UDS AZ-101 Melter Feed	10-wt% UDS AZ-101 Melter Feed
Cm-242								
Cm-243								
Cm-244								
Cm-243/244	4.08E-02	8.24E-02	3.75E-02	5.62E-02	7.49E-02	5.00E-02	4.09E-02	3.00E-02
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