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Rheological Studies on Pretreated Feed and Melter Feed from AW-101 and AN-107

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Summary

Rheological and physical properties tests were conducted on actual AN-107 and AW-101 pretreated feed samples prior to the addition of glass formers. Analyses were repeated following the addition of glass formers. The AN-107 and AW-101 pretreated feeds were tested at the target sodium values of nominally 6, 8, and 10 M. The AW-101 melter feeds were tested at these same concentrations, while the AN-107 melter feeds were tested at 5, 6, and 8 M with respect to sodium. These data on actual waste are required to validate and qualify results obtained with simulants.

The AW-101 pretreated feed samples and the AN-107 pretreated feed samples at sodium concentrations of 6M and 8M contained no visible solids following evaporation. The 10 M sodium AN-107 sample contained roughly 1 vol% settled solids following evaporation. After approximately 2 weeks at 1 vol%, solids precipitated overnight from the 10 M Na sample resulting in a settled solids layer occupying roughly 70% of the sample volume. These solids dissolved quickly after dilution to 5 M.

With the exception of the 10 M Na AN-107 sample, the rheograms of both AN-107 and AW-101 samples prior to glass former addition show Newtonian behavior with a linear relation between shear stress and shear rate with no observed yield stress. No thixotropy was observed comparing the increasing and decreasing shear rate curves or between repeat analysis of the same samples. With the exception of some solids in the 10 M AN-107 sample that effected behavior at low shear rates (below ~ 100 s^{-1}), the rheology of the AN-107 and AW-101 feeds were indistinguishable. The viscosities of the 6, 8, and 10 M Na feeds at 500 s^{-1} were 8, 12, and 21 cP respectively at 25°C, and 4, 7, and 12 respectively at 50°C. The 10M Na AN-107 sample displayed Bingham behavior with a thixotropic component.

Rheograms of the AW-101 samples after glass former addition show nearly Newtonian behavior with only a 20-40% drop in viscosity between 33s^{-1} and 500s^{-1}. No thixotropy or yield stresses were observed. The viscosities at 500 s^{-1} of the 6, 8, and 10 M Na feeds were 36, 88, and 230 cP respectively at 25°C, and 16, 46, and 130 cP respectively at 50°C.

After glass former addition, the 5M Na AN-107 melter feed sample showed nearly Newtonian behavior with no thixotropy or yield stresses. The 6 and 8M Na feeds displayed yield pseudoplastic behavior with a thixotropic component. The viscosities at 450-500 s^{-1} of the 5, 6, and 8M feeds were 44, 360, and 1100 cP respectively at 25°C. At 50°C and approximately 275s^{-1} the viscosities were 15, 175 and 1000 cP. The yield stress of the 6 and 8M feeds were 15 and 180 Pa at 25°C, dropping slightly to 12 and 160 at 50°C.

A mixing and aging study was conducted on the 8 M Na AW-101 and AN-107 melter feed following glass former addition. Glass formers were added and the slurries were stirred at a rate consistent with that expected in the River Protection Project Waste Treatment Plant flow sheet. The viscosity of the AW-101 slurry increased from 52 cP at

350 s^{-1} after 1 hour to 67 cP after 1 day.   The viscosity then remained essentially constant as indicated by the 64 cP measurement after 1 week. These measurements were all conducted at 25°C. Sample behavior was nearly Newtonian. No thixotropy or yield stresses were observed. The AN-107 sample viscosity increased at 350s^{-1} from 280 cP after 1 hour to 540 cP after 1 day of mixing. The viscosity after 1 week was 440 cP indicating a possible minor drop during the week although the viscosity at lower shear rates (33s^{-1}) only dropped by ~8% during the week. Rheograms displayed yield pseudoplastic behavior as well as a thixotropic component.

The 8 M Na AW-101 and AN-107 melter feed samples were then allowed to settle for 1 week. No gas retention or gas releases were observed during the study. After one week the settled solids were analyzed for shear stress versus shear rate at 25°C. In the AW-101 sample, two settled solids layers formed. These layers were analyzed separately and both displayed near Bingham behavior with a linear increase in shear stress with shear rate above a yield stress. The yield stress for both layers was 4.6 Pa. Both samples also displayed a thixotropic component with a decreased viscosity and no yield point on the decreasing rate portion of the rheograms.

Only one settled solids layer formed in the AN-107 sample. The 8M Na AN-107 melter feed contained very little standing liquid. Therefore, the rheology of the settled solids was similar to that for the slurry.   After 1 week of settling, the AN-107 settled solids displayed yield pseudoplastic behavior as well as a thixotropic component. The viscosity of the settled solids was only slightly higher than the mixed slurry, and the yield stress of the settled solids was similar to that of the mixed slurry.

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1.0   Introduction

The scope of the present work was to obtain physical and rheological data on actual LAW melter feed samples. The physical and rheological properties of the LAW melter feed are important considerations in the selection of the melter feed preparation flowsheet and processing equipment such as mixers, pumps, piping, and sampling. Measurements on actual waste are required to validate and qualify results obtained with simulants.

Actual samples from tank AW-101 and AN-107 were used in this testing. Multiple samples from each tank were received from Hanford's 222-S laboratory. Using this material, a composite was prepared for each of the tanks. Entrained solids were removed from the AW-101 composite by ultrafiltration. The cesium was then removed by ion exchange. Entrained solids, Sr and transuranics (TRU) were removed from the AN-107 material during the Sr/TRU removal process. Cesium was then removed from the AN-107 material by ion exchange. Applicable reports are listed in Table 1.1.

Table 1.1. Reference Documents for Melter Feed Samples

Activity	Reference Report
AW-101 Entrained Solids Removal	K.P. Brooks, P.R. Bredt, G.R. Golcar, S.A. Hartley, M.W. Urie, J.M. Tingey, K.G. Rappe, L.K. Jagoda, "Ultrafiltration and Characterization of AW-101 Supernatant and Entrained Solids", PNWD-3000, Battelle Memorial Institute, Richland, Washington, October 1999.
AW-101 Cs Removal	D.E. Kurath, D.L. Blanchard, J.R. Bontha, "Small Column Ion Exchange Testing of Superlig 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope A (Tank 241-AW-101)", PNWD-3001, Battelle Memorial Institute, Richland, Washington, June 2000.
AN-107 Entrained Solids and Sr/TRU Removal	R.T. Hallen, P.R. Bredt, K.P. Brooks, L.K. Jagoda, "Combined Entrained Solids and Sr/TRU Removal from AN-107 Diluted Feed", PNWD-3035, Battelle Memorial Institute, Richland, Washington, August 2000.
AN-107 Cs Removal	D.E. Kurath, D.L. Blanchard Jr., J.R. Bontha, "Small Column Ion Exchange Testing of Superlig 644 for Removal of ^{137}Cs from Hanford Tank Waste Envelope C (Tank 241-AN-107)", PNWD-3039, Battelle Memorial Institute, Richland, Washington, June 2000.

Solids concentration, settling rate, density and shear stress versus shear rate were measured on the samples after evaporation to three sodium concentrations (nominally 6, 8, and 10 M) at ambient temperature and at 50°C. The same measurements were conducted on the three mixtures from tank 241-AW-101 after the addition of glass

formers. Measurements were repeated on the AN-107 sample at sodium concentrations of 5, 6, and 8M after addition of glass formers. The 8M Na AW-101 and AN-107 slurries were mixed for 1 week at a shear rate consistent with that expected in the facility. During this mixing, shear stress versus shear rate was measured after 1 hour, 1 day, and 1 week. A shear stress versus shear rate analysis of this slurry was conducted again after 1 week with no mixing.

This report describes the experimental approach and results of the testing. Specifications for this work were provided to Battelle by BNFL under Task Specification Number TS-W375LV-TE00001. This report also provides a means of transmitting to BNFL the completed test plan and analytical data.[1]

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[1] Results presented in this report are based on work conducted under Technical Procedure 29953-010, and Test Plan 29953-46.

2.0   Experimental Approach

2.1   Evaporation and Settling Study

The actual waste samples used in this testing were prepared under conditions similar to those anticipated in the River Protection Project Waste Treatment Plant flow sheet. Both the AW-101 and AN-107 wastes were received for this task following cesium ion exchange. The process flow sheet includes technetium ion exchange for both of these wastes prior to evaporation. However, the technetium ion exchange process does not significantly alter the waste composition. Therefore, the AN-107 samples were not subject to technetium ion exchange prior to performing this work.

The densities of the waste samples were measured at ambient temperature (~23°C). This measurement was conducted by placing a subsample in a graduated glass cylinder of known mass. The density was then calculated by dividing the net mass by the volume. The measured densities were 1.246 g/ml and 1.236 g/ml for the AW-101 and AN-107 samples respectively.

Following the density measurements, each waste was partitioned into three subsamples. Each of the subsamples was then evaporated to one of the target sodium concentrations (6M, 8M, or 10M). The evaporation was conducted in a vacuum oven at ~50°C under approximately 23 inches of Hg vacuum. Three subsamples of each waste were weighed into glass beakers. Using the density of the initial slurries, target weights required to yield the desired sodium concentrations were calculated. Water was then evaporated from the samples. For estimating purposes, it was assumed that for every gram of water evaporated the volume of the samples decreased by one milliliter. Figures 2.1 and 2.2 show the AW-101 and AN-107 samples, respectively, after evaporation.

Following the evaporation step, the samples were placed in glass-graduated cylinders, and the density of each was measured at ambient temperature (~23°C). This volume and mass was then used to calculate the actual sodium concentrations of the evaporated samples. The AW-101 samples were calculated to have Na concentrations of 5.9 M, 7.7 M, and 9.4 M. The AN-107 samples were calculated to have Na concentrations of 5.9 M, 7.9 M, and 9.7 M. The 9.7 M Na AN-107 sample contained approximately 1 vol% settled solids at 23°C. These settled solids were colorless to white in color and consisted of slushy material with some crystal like particles up to approximately 1 mm in size. These solids settled within a few seconds after agitation. None of the other evaporated samples contained visible solids. The densities of the samples were measured at 50°C by placing the sealed graduated cylinders containing the samples in an oven at 50° overnight. The samples were removed from the oven and the volumes were immediately recorded. The samples were allowed to cool before they were reweighed.

Following the density measurements at 50°C, additional solids were observed in the AN-107 10 M Na sample. This observation was made approximately 2 weeks after completion of the evaporation. A photograph of these settled solids is presented in Figure 2.3. It is estimated the sample contains roughly 70 vol% loosely settled solids. Later in the testing, the 10 M Na AN-107 sample was diluted to 5 M. Upon dilution, the solids returned to solution.

Figure 2.1. AW-101 Samples and Glass Formers Prior to Mixing. Samples A, B (B-1 and B-2), and C are 6M, 8M, and 10M Sodium Respectively

Figure 2.2. AN-107 Samples Following 24 hours at 50°C. This Photograph Was Taken Two Weeks After Completion of Evaporation. Note Solids in Sample C That Were Not Observed 2 Days Prior to This Photograph. Samples A, B (B-1 and B-2), and C are 6M, 8M, and 10M Sodium Respectively

Figure 2.3. Close Up of Solids Precipitated Out of 10M AN-107 Sample. While Loosely Packed, Solids Account for Roughly 70% of the Sample Volume

Following the 50°C density measurement on the AW-101 samples, but before the 50°C density measurement on the AN-107 samples, the evaporated samples were stirred using an overhead mixer. While stirring, subsamples were removed for shear stress versus shear rate analyses. Samples were analyzed for shear stress versus shear rate in duplicate at 25°C and 50°C using a Bohlin CS viscometer modified for glovebox operations. Concentric cylinders with a 25-mm-diameter inner cylinder and a "Small Sample Cell" outer cylinder were used as the measuring geometries. The gap for this geometry set is 0.75 mm.

As per our procedure (29953-010), the Test Plan (29953-046), and manufacturers recommendations, we performed a single point calibration check on the instrument every 30 days. This was done with either the 50 cP or 95 cP standard. This calibration check needs to be within 10% of the certified value for standards above 10cP. Rheograms for standards can be found in Appendix A, Figures 1, 15, and 48. The measured viscosity of both the 50 and 95 cP standards were not constant over the entire shear rate range, but remained within the required 10% criteria between approximately 10 and 550 s^{-1}. Since the measured viscosity was not constant over the range, reporting a particular error is not appropriate. The viscosity is the ratio of shear stress to shear rate and the viscosity of the standards were within this acceptance criteria over the 10 s^{-1} to ~550 s^{-1} range. Therefore, this single standard is an effective check of the instruments torque calibration over 3 orders of magnitude. Manufacturer recommendations are only for this single check even if some samples display viscosities above the stress range of the calibration checked provided they are not beyond the maximum torque of the instrument. None of the samples exceeded the maximum torque of the instrument.

Shear stress versus shear rate rheograms were obtained by measuring the shear stress produced at a specific shear rate. The increasing shear rate curve was generated by gradually increasing the shear rate from approximately 0.1 s^{-1} to the maximum achievable shear rate for the given sample, nominally 700 s^{-1}. The decreasing shear rate curve was generated by reducing the shear rate back down to 0.1 s^{-1}. While the instrument is rated to 1100 s^{-1} with this geometry set, these high shear rates are not easily attained with these slurries. At high shear rates, the system tends to over spin producing poor quality data. The shear rate analysis was conducted again with the same sample still in the instrument. If a difference between the first and second run was observed, it would indicate potentially unusual behavior in the samples including (but not limited to) settling of the solids within the instrument, the sample being effected by shearing in the instrument, or water loss through evaporation. In all cases, the first and second runs were virtually identical.

The 8M Na AW-101 sample was divided into 2 equal aliquots. Glass formers were then added to the 6M Na sample, one of the 8M Na AW-101 samples, and the 10M Na AW-101 sample. The second 8M Na AW-101 sample was retained for mixing and aging studies that will be described in Section 2.2 of this report. Glass former quantities were based on the formulation provided by VSL. The VSL formulation was provided for a 4.59 M sodium feed on a mass per liter basis. The quantity of glass formers were first adjusted on a per liter basis to the targeted sodium concentrations (6, 8, and 10 M). The

masses to be added to the 6M Na sample were multiplied by 1.31 (6/4.59=1.31), the masses added to the 8M Na samples were multiplied by 1.74, and the masses added to the 10 M sample were multiplied by 2.18. These adjusted masses on a per liter basis were then multiplied by the volume of sample to calculate how much material to add to each sample. Table 2.1 lists the quantity and type of glass formers added to each of the AW-101 samples.

The 10M AN-107 sample was diluted to 5M with respect to sodium. Upon dilution, the solids formed during the evaporation step dissolved. The 8M Na AN-107 sample was divided into 2 equal aliquots. Glass formers were then added to the 5M Na sample, the 6M Na sample, one of the 8M Na AN-107 samples. The second 8M Na AN-107 sample was retained for mixing and aging studies that will be described in Section 2.2 of this report. Glass former quantities were based on the formulation provided by VSL. The VSL formulation was provided for a 4.8 M sodium feed on a mass per liter basis. The quantity of glass formers were first adjusted on a per liter basis to the targeted sodium concentrations (5, 6, and 8 M). The masses to be added to the 5M Na sample were multiplied by 1.0417 (5/4.8=1.0417), the masses added to the 6M Na samples were multiplied by 1.25, and the masses added to the 8 M sample were multiplied by 1.6667. These adjusted masses on a per liter basis were then multiplied by the volume of sample to calculate how much material to add to each sample. Table 2.2 lists the quantity and type of glass formers added to each of the AN-107 samples.

Prior to addition, the dry glass formers were weighed into a flask and hand mixed using a spatula. The glass former mixture was then slowly added to the samples while the samples were stirred using an overhead mixer. Following the glass former addition, the samples were stirred for an additional hour.

After stirring for one hour, the stir blade was removed and the volume of settled solids was monitored for three days at ambient temperature. After three days, the mass and volume of the bulk samples were recorded and used to calculate the densities of the bulk slurries. Figure 2.4 shows the AW-101 samples during this settling study. The samples were then placed in an oven at 50°C overnight before repeating the settling study at 50°C.

Following the 50°C settling study, shear stress versus shear rate analyses were performed on the samples at 25°C and 50°C as described previously for the evaporated samples. Shear stress versus shear rate analysis were performed on the AW-101 samples using the 25-mm-diameter inner cylinder and a "Small Sample Cell" outer cylinder. The AN-107 samples with glass formers were much more viscous and required use of a 4/40 cone-and-plate measuring geometry on the Bohlin CS10 viscometer.
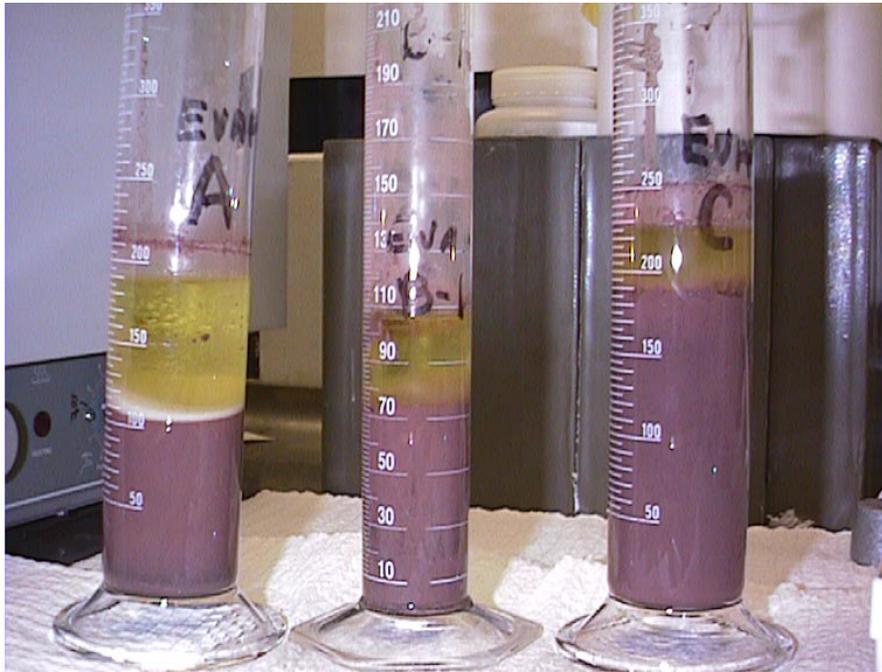
Figure 2.4. AW-101 Samples During 25°C Settling Study Following Glass Former Addition. Samples A, B-1, and C are 6M, 8M, and 10M Sodium Respectively

2.2 Mixing and Aging Study

The second 8M Na AW-101 and AN-107 samples were subjected to a mixing and aging study as specified in the BNFL Task Specification. The 8M Na samples were placed in 250 ml round bottom flasks with a side tube. The samples were stirred using an overhead mixer while the glass formers were added. The flasks were then sealed using a Teflon stirrer bearing and continually stirred for 1 week using a 1-inch (2.54 cm) diameter blade at 480 rpm. The volume of the sample with glass formers was 6.1 in^3 (100 ml). The 480 rpm mixing rate provides the same energy per volume as anticipated in the River Protection Project Waste Treatment Plant. The following equation (provided by BNFL) was used to calculate the proper rotational rate:

$$N^3 = 1.85 \times 10^7 \, V/D_i^5 \hspace{4cm} [1]$$

For this equation, N is the impeller rotational rate in rpm, V is the sample volume in cubic inches and D_i is the impeller diameter in inches.

Samples of the 8M Na slurry were removed from the mixing vessel after 1 hour, 1 day, and 1 week. These samples were immediately analyzed for shear stress versus shear rate at 25°C. These analyses were conducted as described in Section 2.1 for both the evaporated samples and samples with glass formers.

The 8M Na samples were then transferred to 100 ml glass graduated cylinders. The samples were left to settle undisturbed for 1 week. During the settling time, the samples were monitored for any gas retention and releases. Visual observations were supplemented with time-lapse video. No gas bubbles were observed in these samples or any other AW-101 or AN-107 samples during this study.

After one week of settling, the standing liquid was removed, and the settled solids were immediately analyzed for shear stress versus shear rate at 25°C. Given the high solids content of the samples, the Bohlin CS rheometer with the "Small Sample Cell" concentric cylinder geometry could not used.

For the AW-101 sample, a Haake M5 measuring head modified for hot cell operations was used with an SV I measuring geometry. The SV I is a concentric cylinder geometry with a gap of 1.45 mm and a maximum shear rate range of 350 s^{-1}. A 95.5 cP Brookfield viscosity standard was used to check the calibration of the instrument before samples were analyzed. The calibration check was within 10% of the certified value. Upon close inspection, the settled layer in the 8M Na sample was found to consist of a loosely settled layer on top of a firmer higher solids content layer. Both layers were analyzed separately. The shear rate was ramped from approximately 0.1 to 350 s^{-1} generating the increasing shear rate curve, and then back down to 0.1 s^{-1} generating the decreasing curve.

The AN-107 mixing and aging study was conducted using a Bohlin CS viscometer equipped with a 4/40 cone and plate geometry. The 4/40 cone and plate geometry is capable of measuring samples with higher viscosities than the "Small Sample Cell".

Table 2.1. Glass Formers Added to AW-101 Samples

Additive	Grade	Formulation g/L				Start Vol = **142 mL**		Start Vol =146/2 = **73 mL**			Start Vol = **146 mL**	
						Target Wt	Actual Wt	Target Wt	Actual Wt	Actual Wt	Target Wt	Actual Wt
		4.59M	6M	8M	10M	6 M	6 M	8 M	8 M (B-1)	8 M (B-2)	10 M	10 M
Kyanite (Al_2SiO_5)	Raw Kyanite, 325 Mesh	41.74	54.56	72.75	90.94	7.748	7.74	5.311	5.33	5.35	13.277	13.33
Orthoboric Acid (H_3BO_3)	Technical Grade	127.8	166.99	222.66	278.32	23.713	23.70	16.254	16.31	16.32	40.635	40.67
Wollanstonite ($CaSiO_3$)	Powder untreated, NYAN 325 Mesh	32.44	42.41	56.54	70.68	6.022	6.07	4.127	4.21	4.19	10.319	10.35
Red Iron Oxide (Fe_2O_3)	Red Iron Oxide, 325 Mesh (5001)	37.35	48.82	65.10	81.37	6.933	6.97	4.752	4.78	4.79	11.880	11.88
Olivine (Mg_2SiO_4 with some Fe_2SiO_4)	325 Mesh (#180)	22.1	28.89	38.52	48.15	4.102	4.11	2.812	2.81	2.83	7.030	7.04
Ground Silica Sand (SiO_2)	Sil-co-Sil 75, 200 Mesh	262.8	343.58	458.11	572.64	48.789	48.71	33.442	33.45	33.49	83.605	83.63
Rutile (TiO_2)	Premium Grade, Airfloated	14.32	18.72	24.96	31.20	2.658	2.64	1.822	1.85	1.82	4.555	4.55
Zinc Oxide (ZnO)	KADOX-920	21.21	27.73	36.97	46.21	3.937	3.94	2.699	2.71	2.71	6.747	6.76
Zircon Sand ($ZrSiO_4$)	Flour 325 Mesh	31.94	41.75	55.67	69.59	5.929	5.96	4.064	4.12	4.06	10.160	10.15
Sugar	Granular Sugar	51.34	67.11	89.48	111.85	9.530	9.55	6.532	6.61	6.57	16.330	16.43

2.8

Table 2.2. Glass Formers Added to AN-107 Samples

Additive	Grade	Target (g) per liter of feed				Start Vol = 81.0 ml		Start Vol = 109.3 ml		Start Vol = 86.5 ml		Start Vol = 168.0	
						Target Wt	Actual Wt	Target Wt	Actual Wt	Target Wt	Actual Wt	Target Wt	Actual Wt
		4.8M	5M	6M	8M	6 M	**6 M**	6 M	**6 M (B-1)**	8 M	**8 M (B-2)**	5 M	**5M**
Kyanite (Al_2SiO_5)	Raw Kyanite, 325 Mesh	109.07	113.61	136.34	181.78	11.043	11.24	14.906	14.91	15.724	15.72	19.087	19.21
Orthoboric Acid (H_3BO_3)	Technical Grade	187.07	194.86	233.84	311.78	18.941	18.95	25.566	25.59	26.969	26.98	32.737	32.72
Wollanstonite ($CaSiO_3$)	Powder untreated, NYAN 325 Mesh	111.47	116.11	139.34	185.78	11.286	11.29	15.234	15.24	16.070	16.06	19.507	19.51
Red Iron Oxide (Fe_2O_3)	Red Iron Oxide, 325 Mesh (5001)	51.87	54.03	64.84	86.45	5.252	5.27	7.089	7.08	7.478	7.47	9.077	9.09
Lithium Carbonate (Li_2CO_3)	Chemetal Foote Corp. -- Technical Grade	64.75	67.45	80.94	107.92	6.556	6.56	8.849	8.85	9.335	9.34	11.331	11.35
Olivine (Mg_2SiO_4 with some Fe_2SiO_4)	325 Mesh (#180)	32.92	34.29	41.15	54.87	3.333	3.32	4.499	4.50	4.746	4.76	5.761	5.76
Ground Silica Sand (SiO_2)	Sil-co-Sil 75, 200 Mesh	349.7	364.27	437.13	582.83	35.407	35.48	47.792	47.78	50.415	50.40	61.198	61.19
Rutile (TiO_2)	Premium Grade, Airfloated	12.39	12.91	15.49	20.65	1.254	1.25	1.693	1.69	1.786	1.78	2.168	2.18
Zinc Oxide (ZnO)	KADOX-920	31.81	33.14	39.76	53.02	3.221	3.23	4.347	4.33	4.586	4.59	5.567	5.58
Zircon Sand ($ZrSiO_4$)	Flour 325 Mesh	48.54	50.56	60.68	80.90	4.915	4.91	6.634	6.63	6.998	7.01	8.495	8.49
Sugar	Granular Sugar	20.00	20.83	25.00	33.33	2.025	2.02	2.733	2.73	2.883	2.89	3.500	3.51

3.0   Experimental Results

This section details the results of tests conducted on actual AW-101 and AN-107 samples following evaporation to nominal sodium concentrations of 6M, 8M, and 10M. The AW-101 samples were evaporated to 5.9M, 7.7M, and 9.4M. The AN-107 samples were evaporated to 5.9M, 7.9M, and 9.7M. The 9.7M AN-107 sample was later diluted to a sodium concentration of 4.8M. In this section, samples will be referred to according to the nominal sodium concentrations (5M, 6M, 8M, and 10M).

3.1   Density and Settling Study

The densities of the evaporated samples with and without glass formers are provided in Table 3.1. As expected, the densities of the samples prior to glass former addition increase with increasing sample concentration and decreases slightly with temperature. No temperature trend is seen in the AW-101 samples with glass formers. The densities for the AW-101 samples with glass formers increase from 1.59 g/ml at 6M Na to 1.80 g/ml at 8M Na; however, the densities of the 8M and 10M Na samples are similar at roughly 1.80 g/ml.

Table 3.1. Density of AN-107 and AW-101 Samples at 25°C and 50°C With and Without Addition of Glass Formers in g/ml (Error is estimated at ±2% of the Measured Value).

Sample	Without Glass Formers		With Glass Formers	
	25°C	50°C	25°C	50°C
5M AN-107	1.22	NA	1.61	1.59
6M AN-107	1.28	1.26	1.71	1.70
8M AN-107	1.37	1.33	1.79	1.79
10M AN-107	1.44	1.38	NA	NA
6M AW-101	1.31	NM (1.27)	1.59	1.59
8M AW-101	1.37	NM (1.33)	1.80	1.81
10M AW-101	1.44	NM (1.38)	1.77	1.80

NM = not measured due to elimination of 50°C settling study on AW-101 evaporated samples. Values in parentheses are estimated based on sodium concentration.

NA = not available. The density of the 5M AN-107 slurry was not measured at 50°C without glass formers., and glass formers were not added to the 10M AN-107 slurry.

As described in Section 2.1, the AW-101 and AN-107 samples with glass formers were agitated and then allowed to settle at 25°C and 50°C over a 3-day period. The solids settled leaving a clear supernatant above with a distinct interface between the settling solids and the clarified supernatant. Figure 3.1 and 3.2 plots the vol% settled solids (interface height/sample height x 100%) versus time for the AW-101 samples and Figure 3.4 and 3.5 plot the same data for the AN-107 samples. Figures 3.1 and 3.4 uses a semi-log scale while Figure 3.2 and 3.5 are linear.

With the exception of the AW-101 10M Na sample at 25°C, all samples finished settling within the first 24 hours. The AW-101 10M Na sample at 25°C reached a constant value after approximately 45 hours.

Table 3.2 lists the vol% settled solids for the samples. As expected, the data shows the volume percent settled solids increased with sodium concentration and decreased with temperature. For the AW-101 samples at 25°C, the volume percent settled solids increased from 55 to 72 to 83 vol% for the 6, 8, and 10M Na sample respectively. At 50°C, volume percent settled solids increased from 49 to 66 to 72 vol% for the 6, 8, and 10M Na sample respectively. This trend is the result of adding larger mass ratios of insoluble glass formers to the higher concentration samples. The decrease in vol% settled solids with increasing temperature could be the result of one or more soluble species in the precipitate at the lower temperature. This trend could also be the result of a lower viscosity and yield stress leading for greater compaction of the solids at the higher temperature. The AN-107 8M samples did not settle, so the volume percent settled solids it 100 and the data was not plotted in Figures 3.4 and 3.5.

Table 3.2. Volume Percent Settled Solids for the AW-101 and AN-107 Samples with Glass Formers

Sample	25°C	50°C
AN-107 5M	85	74
AN-107 6M	98	93
AN-107 8M	100	100
AW-101 6M	55	49
AW-101 8M	72	66
AW-101 10M	83	72

Figures 3.3 and 3.6 plot the settling rate as a function of time. The settling rate was calculated by dividing the change in settled solids height by time. Minor parallax errors can be magnified by this calculation and result in significant scatter. To minimize scatter, the data plotted in Figures 3.3 and 3.6 have been smoothed using a four point moving average.

Three settling mechanisms are generally observed for this type of sample matrix: free settling, hindered settling, and compression settling. Free settling is settling of discrete particles or flocculated particles without interaction from other particles or the vessel wall. Free settling is denoted by a linear decrease in vol% settled solids over time as the particles fall with fixed velocities. A linear decrease in settling velocity would be seen as a constant or flat portion of a settling rate versus time plot. For flocculating systems, the velocity generally increases as the mass of the particles increase, although particle shape changes can also decrease the settling velocity. Hindered settling occurs when the when particle-particle and particle-wall interactions effect the settling velocities. In an ideal system, hindered settling is denoted by the break from a linear decrease in vol% settled solids with time (i.e. a decrease in the settling rate). Compression settling is the final portion of the vol% settling curve as the system approaches the stable value. Two or even all three of these mechanisms usually occur simultaneously.

All samples in Figure 3.3 show an initially constant settling rate. This region is probably a combination of free as well as some hindered settling. Free settling of the smaller particles is dominating the behavior of the observed solids interface. However, the majority of the solids are at a much higher concentration at the bottom of the column where hindered settling is the dominant mechanism. For the AW-101 6M Na and 8M Na samples, the initial settling rates increase with temperature and decrease with increasing sodium concentration (i.e. 6M Na samples settle faster than 8M Na, and 50°C settle faster than 25°C). The initial settling rate of the 6M Na sample at 50°C was the highest (~0.02 cm/min) followed by the same sample at 25°C (~0.005-0.015 cm/min). The initial settling rate of the 8 M sample at 50°C was between 0.004-0.007 cm/min and at 25°C between 0.001-0.002 cm/min.

This increase in settling rate with increasing temperature and decrease in sodium concentration is probably the result of several factors including a lower supernatant viscosity as well as a decrease in the solids content. Viscosity results to be presented later in this report show that the viscosity of the samples decrease with increasing temperature and increase with higher sodium concentration. The vol% settled solids data in Table 3.2 shows the solids content of the samples decreases with increasing temperature and increases with increasing sodium concentration.

The initial settling rate of the AW-101 10M Na sample at 25°C (~0.004 cm/min) is higher than the same sample at 50°C (~0.001-0.003 cm/min) and is higher than the 8M Na sample at 25°C. The reason for this reverse in the trend observed for the 6 and 8M Na samples is unclear from the available data. It is probably the result of several factors that could include more effective flocculation of fine particulates at higher solids content of the 10M Na sample, competing with a higher concentration of fine soluble particulates that can not be dissolved at the higher temperature with the higher solids loading. This is speculative and more information would be needed if this is to be resolved.

After approximately 4 hours of settling, the settling rate for all of the samples drop dramatically as seen in Figures 3.3 and 3.6. This drop indicates the end of any free settling, and a transition to hindered and compression settling.

The transition from the combination of both hindered and compressive settling to only compression settling as the dominant mechanism is seen at different times for the samples. From Figure 3.1, the AW-101 6 M Na sample at 50°C shows the very slow linear decrease in settled solids volume expected for the compression settling at 6 hours, and the 6M Na at 25°C show the linear decrease starting after 24 hours. With the exception of the 10M Na sample at 25°C, compression settling becomes the dominant mechanism at ~24 hours. Compression settling does not appear to be the dominant settling mechanism for the 10M Na sample at 25°C until after ~60 hour. This late onset for compression settling of the 10M Na sample at 25°C suggests that while the sample is very close to a stable value, the sample may not have reached its final settled height.

Figure 3.1. Volume Percent Settled Solids Versus Time for AW-101 Melter Feed With Glass Formers Using a Semi-Log Scale

3.5

Figure 3.2. Volume Percent Settled Solids Versus Time for AW-101 Melter Feed With Glass Formers Using a Linear Scale

3.6

Figure 3.3. Settling Rates for AW-101 Melter Feed With Glass Formers

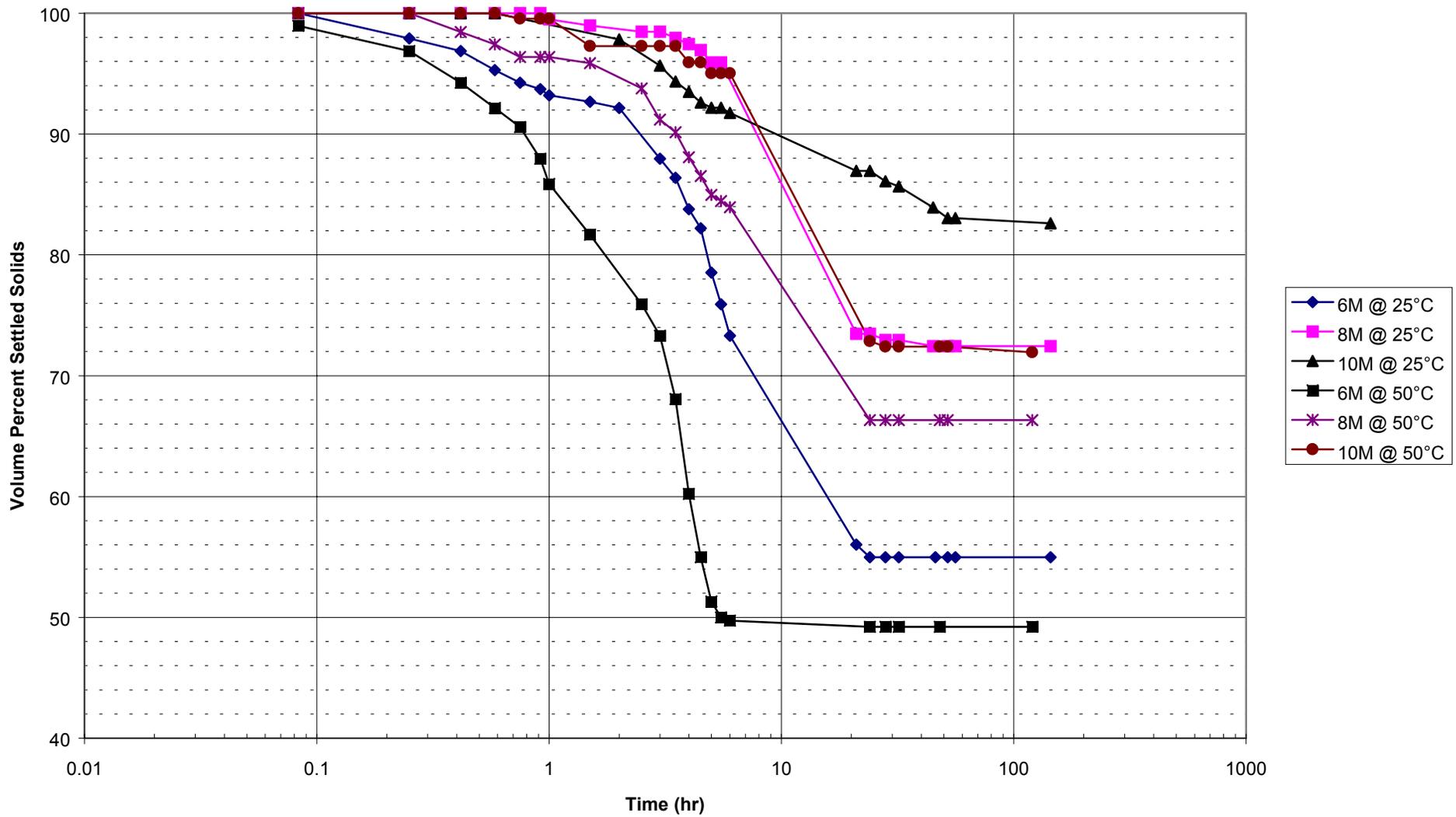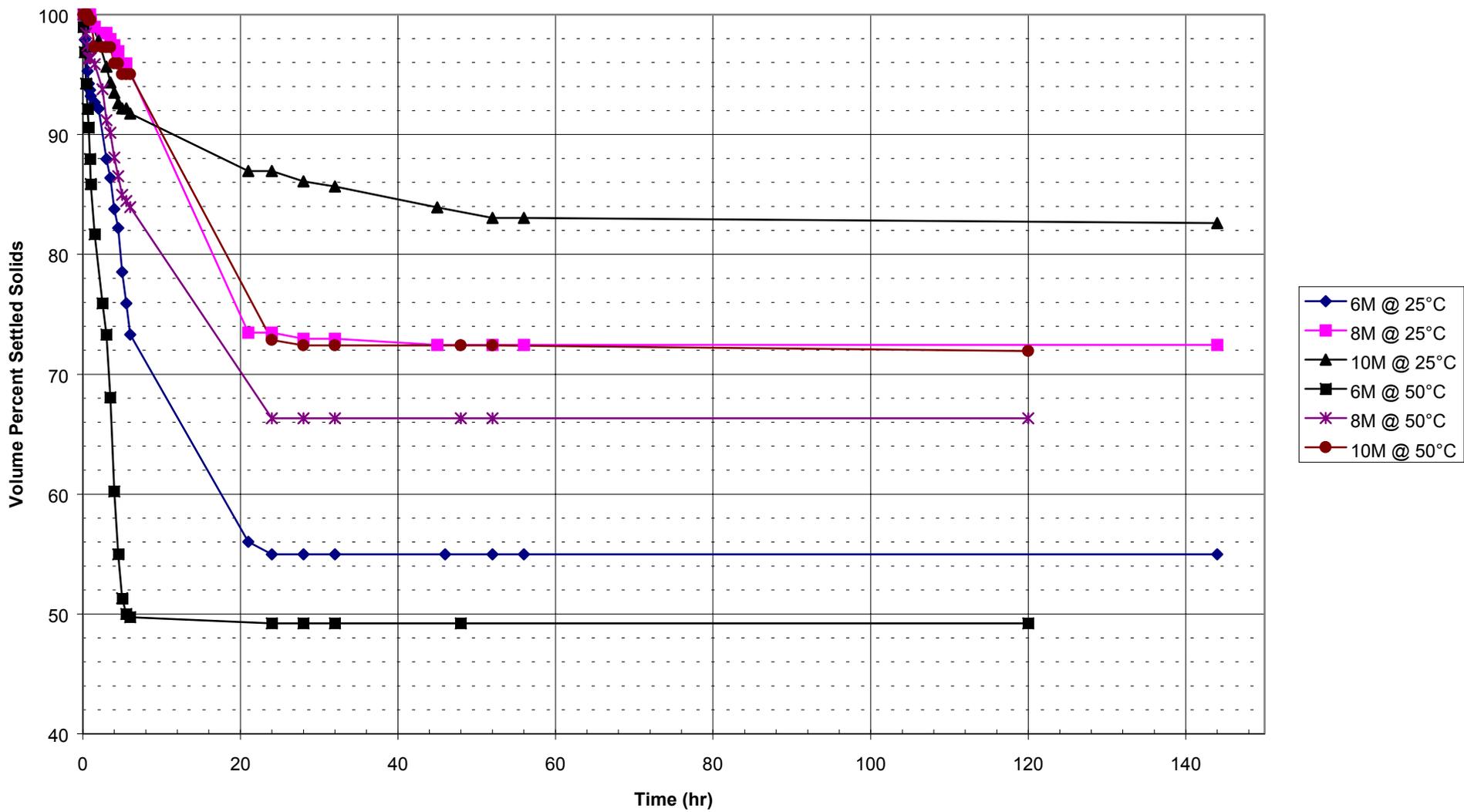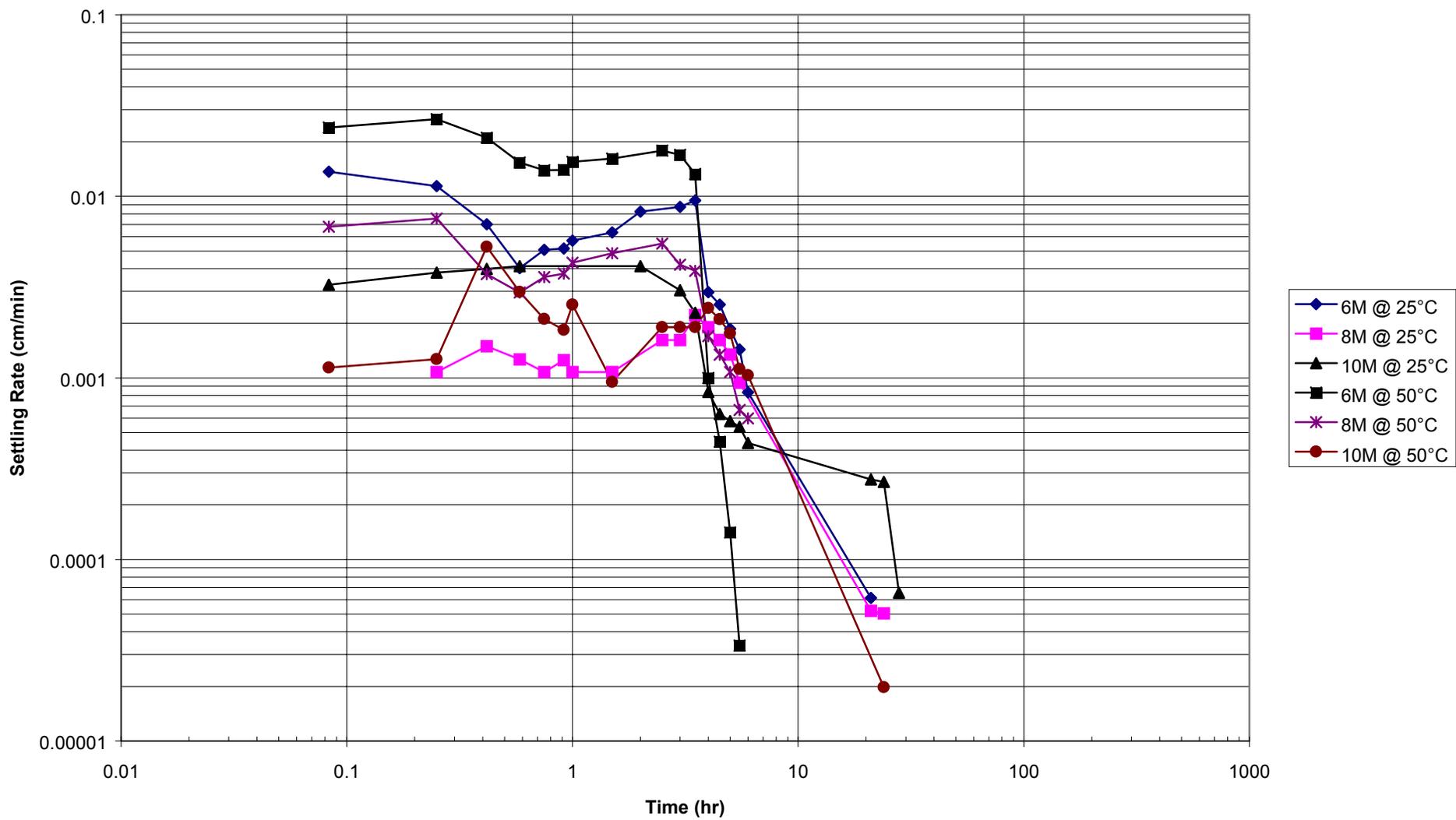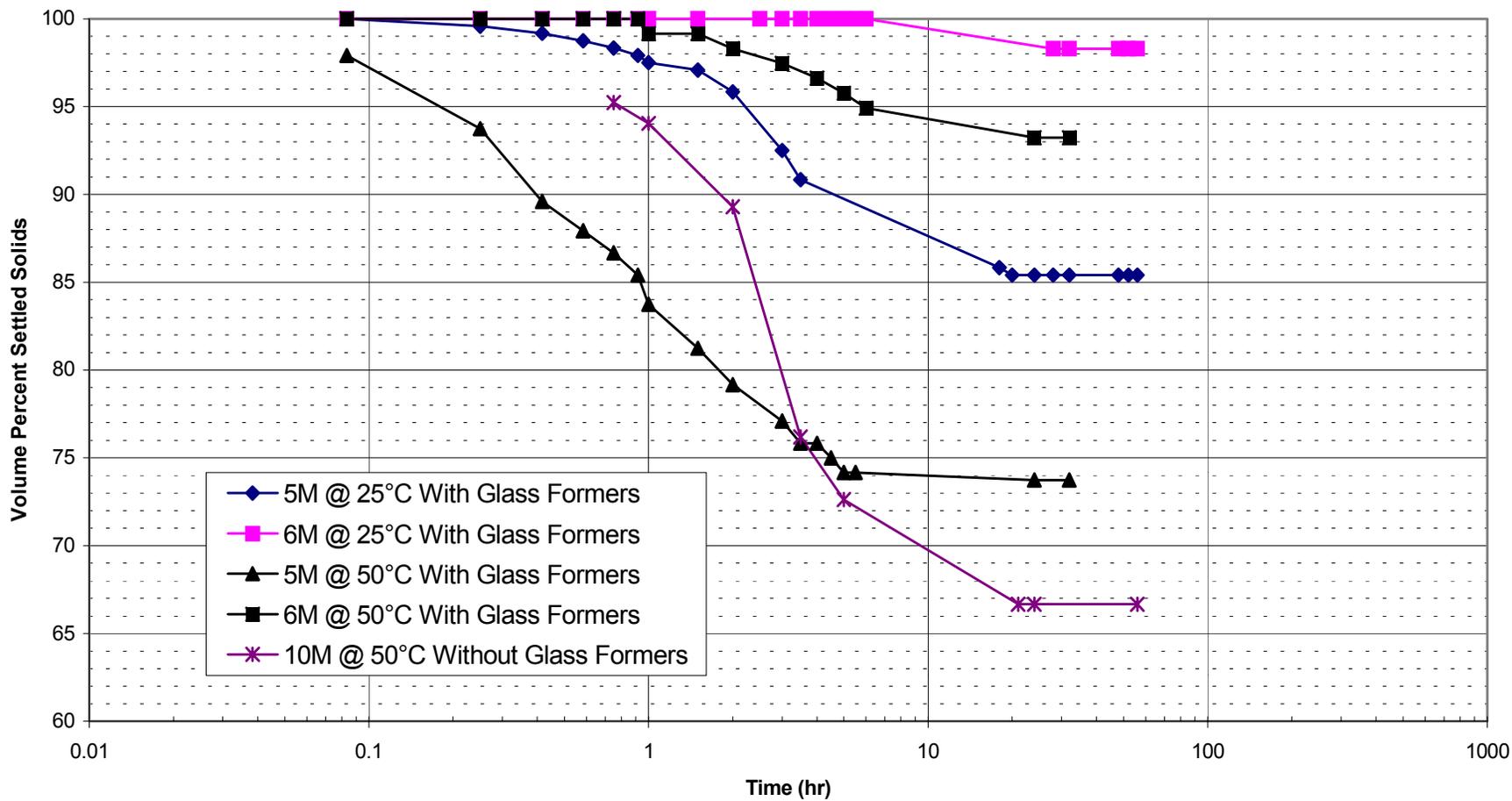Figure 3.4. Volume Percent Settled Solids Versus Time for AN-107 Samples Using a Semi-Log Scale
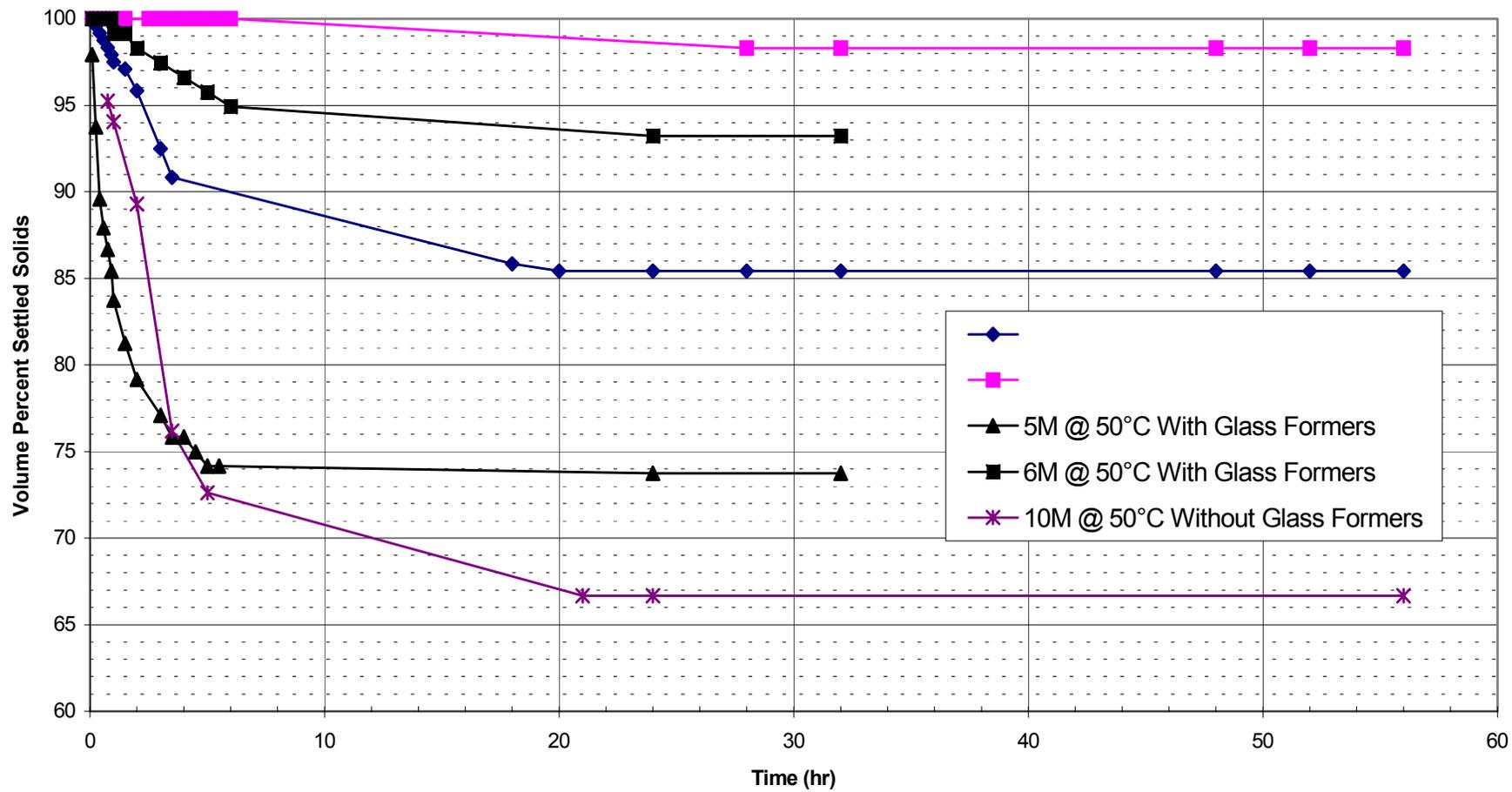
3.8

Figure 3.5. Volume Percent Settled Solids Versus Time for AN-107 Samples Using a Linear Scale
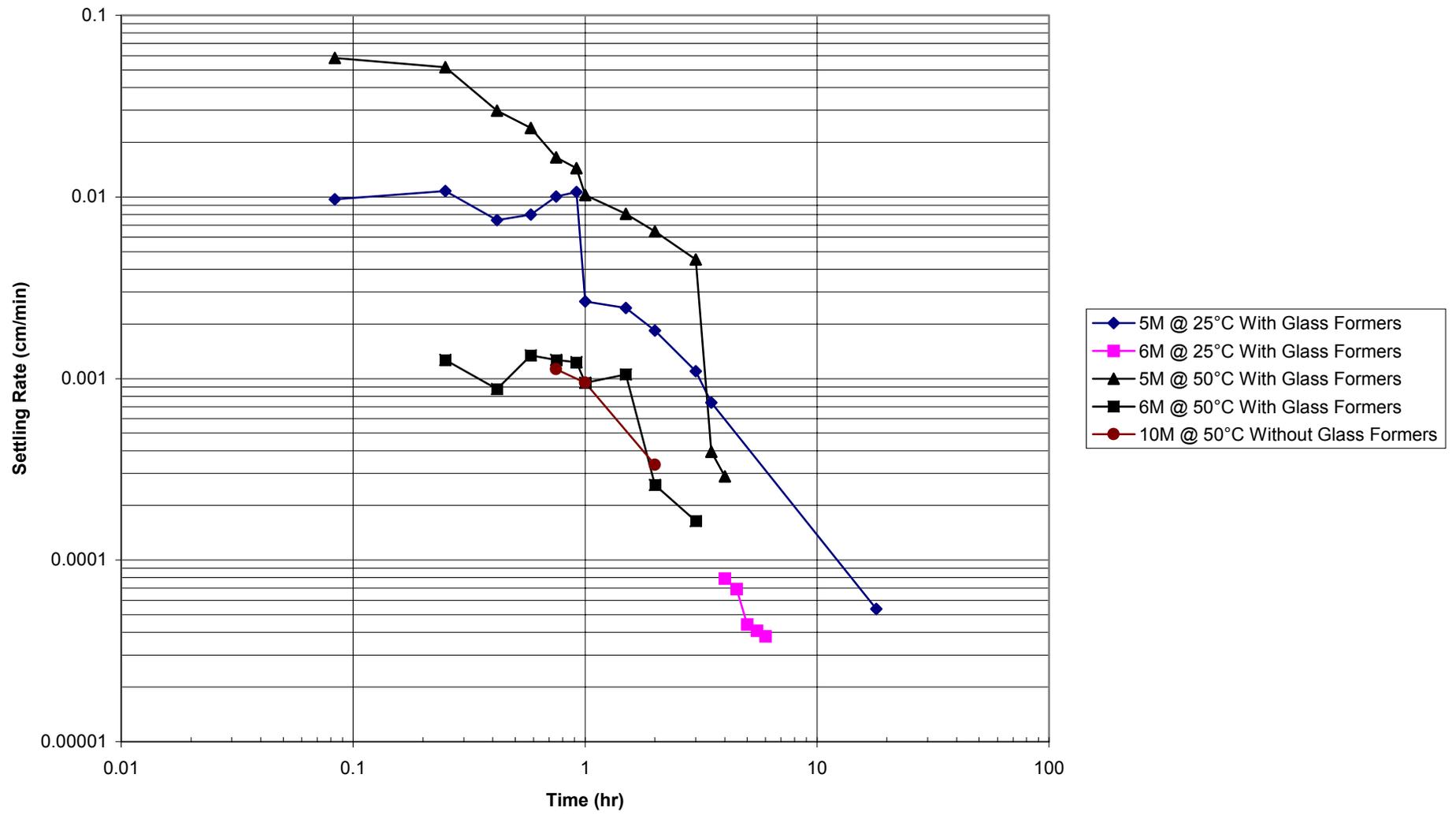
Figure 3.6. Settling Rates for AN-107 Melter Feed

3.2 Rheology

The results of the shear stress versus shear rate analyses are presented in this section. The full set of rheograms, both samples and calibration checks, are included in Appendix A.

3.2.1 Rheology of Evaporated Feed Samples

Shear stress versus shear rate analyses were conducted on the AW-101 evaporated feed samples approximately one month after the evaporation step. The AN-107 sample analyses were conducted approximately 1 week after evaporation. The tabular result for the viscosities at $33s^{-1}$ and $500s^{-1}$ are listed in Table 3.3. These results are the average of duplicate samples. With the exception of the 10M Na AN-107 sample at 25°C, the evaporated samples for both AN-107 and AW-101 displayed a nearly linear relationship between shear stress and shear rate over the shear rate range examined with no detectable yield stress. This is referred to as Newtonian behavior. Since the viscosity is the ratio of the shear stress to the shear rate, the viscosity was nearly constant over the shear rate range examined. As expected, the viscosity of all samples from both tanks increase with sodium concentration and decrease with temperature.

Table 3.3. Viscosity of Evaporated Feed Samples in cP. Values are the Average of Two Duplicate Analyses

	25°C		50°C	
Sample	**$33s^{-1}$**	**$500s^{-1}$**	**$33s^{-1}$**	**$500s^{-1}$**
6M AN-107	9	8	6	4
8M AN-107	14	13	10	8
10M AN-107	56	21	14	11
6M AW-101	8	8	6	4
8M AW-101	13	12	7	6
10M AW-101	22	21	14	12

It should be noted that the results for the AN-107 samples are similar to the AW-101 samples. The only significant difference in the two data sets is the viscosity of the 10M Na samples at $33s^{-1}$. Under these conditions, the AN-107 and AW-101 samples have viscosities of 57 and 22 cP respectively. The higher AN-107 viscosity is probably the result of visible solids in the AN-107 sample (the AW-101 sample was a clear liquid with no solids).

The increasing shear rate curve for the AN-107 10M Na samples were models using the following yield power law:

$$Tau = a + bD^c \qquad [2]$$

where Tau is the shear stress in Pa, and D is the shear rate in s^{-1}. The constants a, b, and c were calculated by a best-fit regression to the data. The results of this fit are presented in

Table 3.4. In the equation, the constant a is the yield stress which is an average of 1.2 Pa for the two duplicates. The divergence of c from unity is a measure of the samples shear thinning (c<1) or thickening (c>1). The duplicate suggests shear thickening, however, this sample also displays a thixotropic component, so c is greater than 1 for the duplicate as a result of the model trying to fit the initial thinning of the material. Therefore, this material is best described as a Bingham plastic with a thixotropic component.

Table 3.4. Yield Power Law Fit for the 10M AN-107 Samples at 25°C

Sample	a (Pa)	b (Pa·s)	c (unitless)	r^2
1	0.62	0.0187	1.00	0.997
2	1.7	0.00824	1.13	0.998

3.2.2   Rheology of Melter Feed with Glass Formers

Shear stress versus shear rate analyses were conducted on the AW-101 melter feed samples approximately two weeks after glass former addition. Analyses of the AN-107 samples were conducted approximately three weeks after glass former addition. These analyses were conducted after the ambient and 50°C settling studies. The tabular result for the viscosities at $33s^{-1}$ and $500s^{-1}$ are listed in Table 3.5.

For the AW-101 sample, the viscosity of the sample decreased slightly with shear rate, approximately 20-40% between $33s^{-1}$ and $500s^{-1}$, this is still a nearly linear relationship between shear stress and shear rate over the shear rate range. In addition, no yield stress was observed. Therefore, the samples with glass formers are still roughly Newtonian in behavior.

The 5M AN-107 sample with glass formers displayed nearly Newtonian behavior with no yield stress and only a slight decrease in viscosity. However, the 6 and 8M AN-107 samples with glass formers have a much higher solids loading compared to the comparable AW-101 samples. As a result, the AN-107 samples do not show the same Newtonian behavior. The AN-107 samples with glass formers displayed a significant decreasing viscosity with increasing shear rate. The 6 and 8M samples also displayed a yield stress. A decreasing viscosity with increasing shear rate above a yield stress is referred to a yield pseudoplastic behavior. The 6 and 8M samples also display a thixotropic component.

As seen in Table 3.5, the viscosities of the samples increase with sodium concentration and decrease with temperature. The sodium trend is expected since the amounts of glass formers added were proportional to the sodium concentration. The glass formers were primarily insoluble in these solutions. Therefore, the higher sodium samples have higher insoluble solids content as well as higher dissolved solids content. Both higher dissolved and insoluble solids result in an increased viscosity. The temperature trend is also expected as the viscosity of most liquids and slurries decrease with increasing temperature.

Table 3.5. Viscosity of Melter Feed Samples with Glass Formers in cP. With the Exception of the AN-107 8M Sample, Values at 25°C are the Average of Duplicate Analyses.

	25°C			50°C		
Sample	**Yield Stress (Pa)**	**33s^{-1}**	**450-500s^{-1}**	**Yield Stress (Pa)**	**33s^{-1}**	**450-500s^{-1}**
AN-107 5M	ND	46	44	ND	27[b]	15[b]
AN-107 6M	15	1100	360	12	510[b]	175[b] (276s^{-1})
AN-107 8M[a]	180	4800	1100	160	5700[b]	1000[b] (276s^{-1})
AW-101 6M	ND	46	36	ND	26	16
AW-101 8M	ND	110	88	ND	60	46
AW-101 10M	ND	260	230	ND	160	130

ND   Not detected
[a] Due to thixotrotropic behavior only the increasing shear rate curve data was used.
[b] Due to sample drying only data from the first sample was used.

3.3   Mixing and Aging Study

As described in Section 2.2, an 8M Na AW-101 and an 8M Na AN-107 subsample were used for mixing and aging studies. Glass formers were added and the slurries were stirred for 1 week. Subsamples were removed after 1 hour, 1 day and 1 week and immediately analyzed for shear stress versus shear rate at 25°C. The samples were then left undisturbed for 1 week. The standing liquid was then decanted and the settled solids were analyzed for shear stress versus shear rate at 25°C. A "Small Sample Cell" concentric cylinder geometry on the Bohlin CS was used with the AW-101 mixing study subsamples. The AW-101 settled solids were too viscous for the "Small Sample Cell", so the settled solids were measured using a Haake M5 viscometer with an SVI concentric cylinder geometry.

The AN-107 mixing and aging study was conducted using a Bohlin CS viscometer equipped with a 4/40 cone and plate geometry. The 4/40 cone and plate geometry is capable of measuring samples with higher viscosities than the "Small Sample Cell".

The results are presented in tabular form in Table 3.6 at 33s^{-1} and 350s^{-1}. The rheograms show an increase in viscosity for some duplicate runs. The increase in viscosity is probably the result of sample evaporation between analyses. Therefore, only results for the initial runs are presented.

The 8M Na mixing study samples displayed the same rheological behavior observed previously. The viscosity of the AW-101 sample decreased only slightly with shear rate, approximately 10-15% between 33s^{-1} and 500s^{-1}. This is a linear relationship between shear stress and shear rate over the shear rate range. In addition, no yield stress was observed. The AN-107 samples displayed yield pseudoplastic behavior as well as a thixotropic component.

3.13

Table 3.6. Viscosity of 8M Na Melter Feed Samples with Glass Formers During Mixing and Aging Study. Analyses Conducted at 25°C Using a Haake M5 Viscometer with an SVI Concentric Cylinder Geometry. Values are in cP

Sample[a]	Yield Stress (Pa)	Increasing Curve @ 33s^{-1}	Decreasing Curve @ 33s^{-1}	350 s^{-1}
AN-107 After 1 Hour of Mixing	20	1100	610	280
After 1 Day of Mixing	10	1300	980	540
After 1 Week of Mixing	15	1200	900	440
Settled Solids	20	1900	1400	570
AW-101 After 1 Hour of Mixing	NO	59	NA	52
After 1 Day of Mixing	NO	77	NA	67
After 1 Week of Mixing	NO	76	NA	64
Loosely Settled Solids	4.8	270	180	130
Tightly Settled Solids	5.3	360	260	220

[a] Due to sample drying between analyses, mixing results are for initial samples only.
NO, Yield stresses were not observed
NA, Viscosity of increasing and decreasing rate curves are similar

The results in Table 3.6 show a 30% increase in viscosity over the first day of mixing for the AW-101, but no change after the first day. The viscosity at 350s^{-1} after 1 hour was 52 cP and increased to 67 cP after 1 day. However, after 1 week the viscosity did not increase again and was measured at 64 cP.

The changes in viscosity for the AN-107 samples were similar to the AW-101 samples. The AN-107 sample viscosity increased at 350s^{-1} from 280 cP after 1 hour to 540 cP after 1 day of mixing. The viscosity after 1 week was 440 cP indicating a possible minor drop during the week although the viscosity at lower shear rates (33s^{-1}) only dropped by ~8% during the week.

The samples were then transferred to a 100-ml graduated cylinder and allowed to settle for one week. No gas retention or releases were observed during this work. After one week, the standing liquid was removed and the settled solids were analyzed for shear stress versus shear rate at 25°C. During the AW-101 sample collection, it was noted that the settled solids had formed in two distinct layers. The upper layer appeared to be more soupy and containing finer solids. This upper layer was referred to as the loosely settled solids layer. The lower layer was pastier and appeared to contain more solids that had less interstitial liquid. Both layers were analyzed separately. The AN-107 sample contained only one layer.

As seen in Table 3.6, the viscosity of the loosely settled AW-101 solids decreased from 270 cP at 33 s^{-1} to 130 cP at 350 s^{-1}. The tightly settled solids decreased from 360 to 220 cP over the same range. This is still a roughly linear relationship between shear stress and shear rate. To quantify the sample behavior, the increasing shear rate curves were modeled using a yield power law as described in Section 3.2.2. The result of this fit is presented in Table 3.7. Both samples displayed average yield stresses of 4.6 Pa. The average value of c was 0.976 for both samples indicating a nearly linear relationship between shear stress and shear rate. This is defined as Bingham behavior. These samples display a thixotropic component as seen in the lack of a yield point on the decreasing rate portion of the rheogram, and the slightly lower viscosity.

The 8M Na AN-107 sample with glass formers contained very little standing liquid as noted Figure 3.4. Therefore, the rheology of the settled solids is similar to that for the slurry. The AN-107 settled solids displayed yield pseudoplastic behavior as well as a thixotropic component. As seen in Table 3.6, the viscosity of the settled solids is only slightly higher than the mixed slurry, and the yield stress of the settled solids is similar to that of the mixed slurry.

Table 3.7. Yield Power Law Fit for the 8M AW-101 Settled Solids following Glass Former Addition. Analyses Were Conducted at 25°C

Sample	a (Pa)	b (Pa·s)	c (unitless)
Loosely Settled 1	5.2	0.183	0.929
Loosely Settled 2	4.0	0.110	1.019
Tightly Settled 1	5.7	0.223	0.983
Tightly Settled 2	3.5	0.240	0.969

4.0   Conclusions

The following conclusions were made based on the rheological and physical properties of the AN-107 and AW-101 evaporator and melter feeds. These conclusions have been divided into categories for clarity.

Evaporation

- Evaporation of the pretreated AW-101 feed to sodium concentrations of 6, 8, and 10 M resulted in clear yellow solutions with no visible solids.

- Evaporation of the pretreated AN-107 feed to 6 and 8 M Na resulted in darkened brown solution with no visible solids.

- The 10 M Na AN-107 sample contained only ~1vol% solids immediately following evaporation. After approximately 2 weeks with only 1 vol% solids, additional solids precipitated overnight from solution forming a settled solids layer representing roughly 70 percent of the sample volume.

Rheology of Evaporated Feeds

- With the exception of the 10 M Na AN-107 sample at shear rates below ~100 s^{-1}, the rheology of the AN-107 and AW-101 feeds were indistinguishable at similar sodium concentrations. The viscosities of the 6, 8, and 10 M Na feeds at 500 s^{-1} were 8, 12, and 21 cP respectively at 25°C, and 4, 7, and 12 respectively at 50°C.

- The 6, 8, and 10 M Na AW-101 feeds as well 6, and 8 M Na AN-107 feeds exhibited Newtonian behavior with no thixotropy.

- The 10 M Na AN-107 feed at 25°C exhibited Bingham behavior with yield stress of approximately 1 Pa, and a thixotropic component.

AW-101 Melter Feed Settling and Rheology

- For the 6 M Na and 8 M Na samples, the initial settling rates increase with temperature and decrease with increasing sodium concentration (i.e., 6 M Na samples settle faster than 8 M Na, and 50°C settle faster than same sample at 25°C).

- The initial settling rate of the 10 M Na sample at 25°C is higher than the same sample at 50°C and is higher than the 8 M Na sample at 25°C. The reason for this reverse in the trend observed for the 6 and 8 M Na samples is unclear from the available data. It is probably the result of several factors that could include more effective flocculation of fine particulates at higher solids content of the 10 M Na sample, competing with a higher concentration of fine soluble particulates that cannot be dissolved at the higher

temperature with the higher solids loading. This is speculative and more information would be needed if this is to be resolved.

- The AW-101 melter feed samples show nearly Newtonian behavior with no thixotropy or yield stresses observed. The viscosities at 500 s^{-1} of the 6, 8, and 10 M feeds were 36, 88, and 230 cP respectively at 25°C, and 16, 46, and 130 cP respectively at 50°C.

AN-107 Melter Feed Settling and Rheology

- The initial settling rates for all three sodium concentrations increase with temperature and decrease with increasing sodium concentration (i.e., 5 M Na samples settle faster than 6 M Na, and 50°C settle faster than same sample at 25°C).

- The 5M Na AN-107 melter feed sample showed nearly Newtonian behavior with no thixotropy or yield stresses. The 6 and 8M Na feeds displayed yield pseudoplastic behavior with a thixotropic component. The viscosities at 450-500 s^{-1} of the 5, 6, and 8M feeds were 44, 360, and 1100 cP respectively at 25°C. At 50°C and approximately 275s^{-1} the viscosities were 15, 175 and 1000 cP. The yield stress of the 6 and 8M feeds were 15 and 180 Pa at 25°C, dropping slightly to 12 and 160 at 50°C.

8M Na AW-101 Melter Feed Mixing and Aging

- The viscosity (at 500 s^{-1} and 25°C) of the slurry increased from 52 cP after 1 hour of mixing to 67 cP after 1 day. The viscosity then remained essentially constant at 65 cP after 1 week of mixing. For comparison, the viscosity of the 8 M Na melter feed sample that was used in settling studies was 88 cP at 500 s^{-1} and 25°C. This other sample was analyzed approximately 3 weeks after glass former addition with only occasional stirring. This suggests that a combination of additional aging and lack of mixing could result in an additional increase in viscosity.

- Rheograms of slurry samples analyzed after 1 hour, 1 day, and 1 week show nearly Newtonian behavior with no thixotropy or yield stresses.

- No gas retention or releases were observed during 1 week of settling.

- After 1 week of settling, 2 settled solids layers formed. The upper layer appeared to have a lower solids content while the lower layer had a thicker consistency.

- Rheograms of the two separate settled solid layers exhibit Bingham behavior with a similar yield point of 4.6 Pa. Both layers displayed a thixotropic component.

- The AN-107 sample viscosity increased at $350s^{-1}$ from 280 cP after 1 hour to 540 cP after 1 day of mixing. The viscosity after 1 week was 440 cP indicating a possible minor drop during the week although the viscosity at lower shear rates ($33s^{-1}$) only dropped by ~8% during the week.

- Rheograms of slurry samples analyzed after 1 hour, 1 day, and 1 week displayed yield pseudoplastic behavior as well as a thixotropic component.

- No gas retention or releases were observed during 1 week of settling.

- The 8M Na AN-107 sample with glass formers contained very little standing liquid. Therefore, the rheology of the settled solids is similar to that for the slurry. After 1 week of settling, the AN-107 settled solids displayed yield pseudoplastic behavior as well as a thixotropic component. The viscosity of the settled solids is only slightly higher than the mixed slurry, and the yield stress of the settled solids is similar to that of the mixed slurry.