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Continuously Stirred Tank Reactor Parameters That Affect Sludge Batch 6 Simulant Properties

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EXECUTIVE SUMMARY

Significant differences in the physical properties of simulated wastes are observed depending on the preparation route selected. The preferred method for making simulant is by using a continuously stirred tank reactor (CSTR). There are several parameters that control the physical properties of the simulant. This work focuses on determining the effect of varying the parameters of pH, temperature, flow rate, and mixing speed during the simulant preparation for the purpose of making a simulant that is more prototypical of Savannah River Site sludge that is transferred to the Defense Waste Processing Facility (DWPF) for processing.

A matrix was developed to establish the ranges of the parameters being investigated. Temperature was varied from 22-70 ºC, pH from 9-14, flow rate 30-250 ml/min, and mixing speed 350-1000 rpm. A series of 10 batches was made in the continuous stirred tank reactor (CSTR) using a sludge batch 6 composition. These batches were analyzed to determine the changes in particle size, rheology, and foaming. Data was analyzed using JMP statistical software to determine the aggregate effect of varying the parameters.

By varying the parameters stated above for the precipitation process, the following effects and correlations were observed for the ten batches prepared:

Particle Size

- Mean particle size ranged from 3-38μm and was consistent with previous simulants.
- Changes in pH, flow rate, and mixing speed are statistically significant with respect to particle size.
- The effect of flow rate and mixing speed are linear while that of pH is quadratic. Results indicated that a lower pH produces smaller particles.

Rheology

- Increasing wt.% insoluble solids increases yield stress, as expected.
- Changes in pH, flow rate, temperature, and mixing speed are statistically significant with respect to yield stress.
- The effect of the tested parameters is linear.
- By varying the parameters tested, it appears that simulant yield stress could be adjusted to targeted value.

Foaming

- Increasing mixing speed had a slight effect on increasing simulant foaming.
- Changes in pH, flow rate, and temperature had no effect on foaming.

Recommendations

The work performed for this study looked at four parametric effects for simulant SB6A. This resulted in 10 distinct batches for analysis. This was the least number of batches that could be prepared and still have the statistical ability to determine the individual effects of these parameters on the physical properties of simulant particle size, rheology, and foaming. For a more accurate correlation of the influence of these parameters, an additional 10 batches would need to be prepared and tested. SRNL is currently partnering with foam experts at the Illinois Institute of Technology (IIT). IIT will perform a study on simulants provided to them by SRNL. Their recommendations will be incorporated into a future test program.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
AD	Analytical Development
CSTR	Continuous Stirred Tank Reactor
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
PSAL	Process Science Analytical Laboratory
SB	Sludge Batch
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

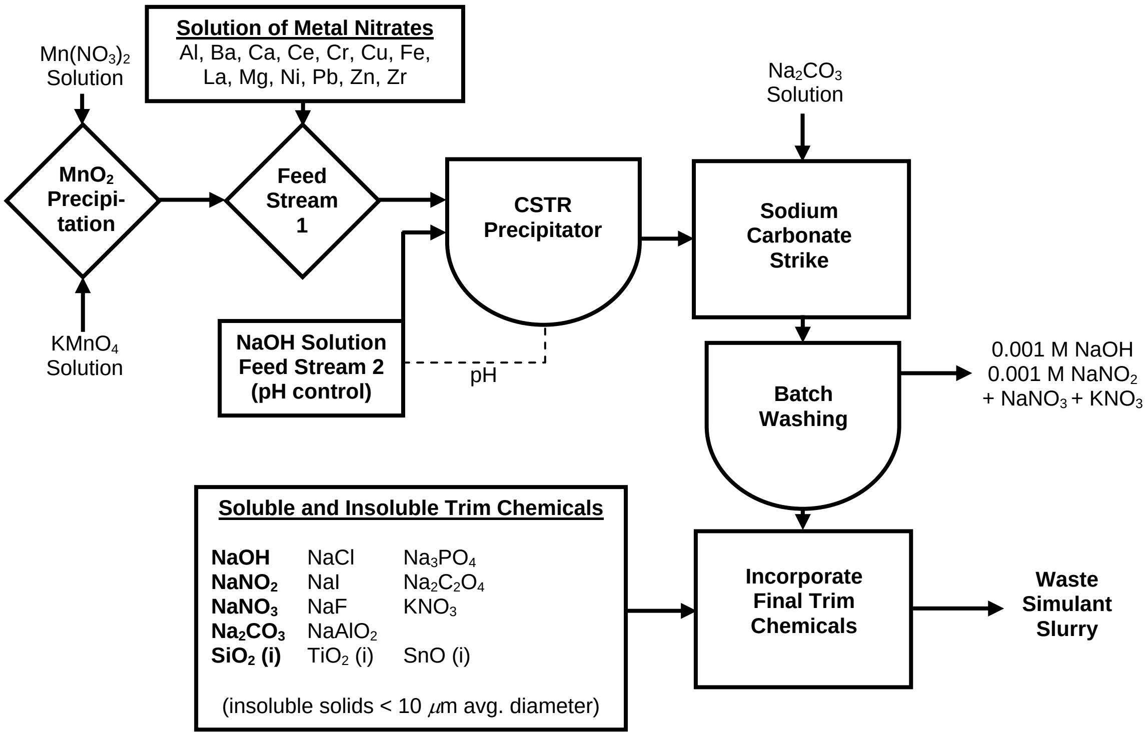
1.0 Introduction

The High Level Radioactive Waste (HLW) Sludge in Savannah River Site (SRS) waste tanks was produced over a period of over 60 years by neutralizing the acidic waste produced in the F and H Separations Canyons with sodium hydroxide. The HLW slurries have been stored at free hydroxide concentrations above 1 M to minimize the corrosion of the carbon steel waste tanks. Sodium nitrite is periodically added as a corrosion inhibitor. The resulting waste has been subjected to supernate evaporation to minimize the volume of the stored waste. In addition, some of the waste tanks experienced high temperatures so some of the waste has been at elevated temperatures. Because the waste is radioactive, the waste is transforming through the decay of shorter lived radioactive species and the radiation damage that the decay releases. The goal of the Savannah River National Laboratory (SRNL) simulant development program is to develop a method to produce a sludge simulant that matches both the chemical and physical characteristics of the HLW without the time, temperature profile, chemical or radiation exposure of that of the real waste.

Several different approaches have been taken historically toward preparing simulated waste slurries [1-2]. All of the approaches used in the past dozen years involve some precipitation of the species using similar chemistry to that which formed the radioactive waste solids in the tank farm. All of the approaches add certain chemical species as commercially available insoluble solid compounds. The number of species introduced in this manner, however, has varied widely. All of the simulant preparation approaches make the simulated aqueous phase by adding the appropriate ratios of various sodium salts. The simulant preparation sequence generally starts with an acidic pH and ends up with a caustic pH (typically in the 10-12 range).

The current method for making sludge simulant involves the use of a temperature controlled continuously stirred tank reactor (CSTR). Precipitated MnO_2 is combined with metal nitrates and fed into the CSTR. The metals are precipitated by a caustic NaOH stream. The rates at which these streams are added allows for pH adjustment of the mixture. A graphical representation of this process is given in Figure 1. In using the CSTR method for developing simulant, there are various parameters that can be adjusted in order to effectuate a physical change in the resulting simulant: pH, temperature, mixing speed, and flow rate. How will changing these parameters affect the physical properties of the sludge simulant? The ability to determine which parameter affects a particular property could allow one to develop a simulant that would better match the physical characteristics of HLW sludge.

Figure 1: Graphical representation of simulant development process using CSTR.



2.0 Experimental Procedure

2.1 SB6-A Simulant Basis

The simulant used in these experiments was Sludge Batch 6-A (SB6-A). The characterization and methods with which this sludge simulant was precipitated, washed and trimmed has been previously reported[3].

The simulant basis for insoluble solids was taken from "Sludge Batch 6 Projected Batch and Blend Compositions", LWO-LWP-2009-00001 (Table 1). The simulant basis for the supernate was "Flowsheet for Aluminum Removal from Sludge Batch 6", SRNL-STI-2008-00389 (Table 2). Note that no surrogate was used for uranium. All other elements, with the exception of sodium, were re-normalized.

Table 1: Basis for the SB6-A Insoluble Solids

FEED DENSITY (INPUT)		1.12	G/ML
Insoluble Solids wt %		11.96	
Insoluble Solids, mass/Liter		133.95	g/L
Total Solids wt%		17.31	
Total Solids, mass/Liter		193.87	g/L
Element	**Total Solids Wt %**	**Oxides**	**Wt % Oxides**
Al	12.92	Al_2O_3	24.41
Ba	0.21	BaO	0.23
Ca	1.88	CaO	2.63
Ce	0.18	Ce_2O_3	0.21
Cr	0.30	Cr_2O_3	0.44
Cu	0.09	CuO	0.11
Fe	16.21	Fe_2O_3	23.18
K	0.04	K_2O	0.05
La	0.09	La_2O_3	0.11
Mg	1.33	MgO	2.21
Mn	6.16	MnO_2	9.75
Na	18.61	Na_2O	25.09
Ni	3.52	NiO	4.48
Pb	0.14	PbO	0.15
Si	0.52	SiO_2	1.11
Th	1.26	ThO_2	1.43
Ti	0.02	TiO_2	0.03
U	4.67	U_2O_3	5.14
Zn	0.13	ZnO	0.16
Zr	0.37	ZrO_2	0.50

Table 2: Basis for the SB6-A Supernate

SUPERNATE TARGET INPUTS	
Liquid Volume (gal)	281,000
SpG, kg/L	1.035
Na^{+}, M	1.01
NO_2^{-}, M	0.34
NO_3^{-}, M	0.18
OH^{-}, M	0.29
Cl^{-}, M	0.00409
SO_4^{-2}, M	0.019
F^{-}, M	0.00069
CO_3^{-2}, M	0.05
AlO^{2-}, M	0.05
C_2O_4-^{2,} M	0.0041
PO_4^{-3}, M	0.00046
K^{+}, M	0.0032

2.2 Parametric Study

A matrix detailing the parameter values was created and is represented in Table 3. The matrix was initially set up into two blocks. Completion of block 1 will provide the data needed to determine if continuation with Block 2 is justified. This study focuses solely on block 1. pH will be examined over the range of 9-14, flow rate from 20-360 mL/min, temperature 22-85 C, and mixing 100-1000 rpm[i].

Table 3: Matrix presenting parameters of runs 1-10

run	*block*	*targeted pH*	*measured pH*	*flow rate (ml/min)*	*temperature (ºC)*	*mixing speed (rpm)*
1	1	11.5	13.2	140	46	550
2	1	14	14.2	250	22	1000
3	1	14	14.0	30	22	350
4	1	9	9.0	250	22	350
5	1	9	9.4	30	22	1000
6	1	14	14.0	250	70	350
7	1	9	11.5	250	70	1000
8	1	14	14.3	30	70	1000
9	1	9	11.2	30	70	350
10	1	11.5	13.8	140	46	550

[i] It was determined after the first run that a mixing speed of 100 rpm was insufficient to produce a well-mixed simulant within the CSTR, therefore, the lower mixing limit was increased to 350 rpm.

The matrix was set up with the assumption that changes in particle size would be linear with respect to the parameters being changed. Upon completion of Block 1, the data was to be evaluated to determine if linearity exits. If not, additional runs would be included to determine the mathematical relationship (i.e. linear, logarithmic, quadratic, etc.).

Each run had a different set of parameters, except for the first and last runs of the block which were identical for both blocks. For changes to temperature, the feed pumps were stopped until the new temperature was reached. For all parametric changes, in order to ensure that the system had time to equilibrate to the new changes, each run discarded seven volume turnovers of the CSTR. This is similar to exponential decay. Each volume turnover represents a half-life. After the seventh turnover, it is estimated that only 0.781 percentage remains of the simulant based on the previous parameters. The eighth volume was collected for analysis. The "discarded" seven volume turnovers from all ten runs were collected into one drum for use in other programs.

A run plan was drafted that provided details on the chemical composition of the simulant. Ten separate batches were made at a volume of ten liters. It was determined that having separate batches would help ensure good mixing and homogeneity of the feed. Details of the CSTR run plan have been previously published [5].

2.3 Sample Analysis

2.3.1 *Elemental analysis*

Samples of each finished simulant were analyzed at the Process Science Analytical Laboratory (PSAL) to determine the elemental chemical composition. The slurry composition was determined as follows. Duplicate samples were calcined at 1100 °C, and then the solids were dissolved using either a Na_2O_2/NaOH fusion or a lithium tetraborate/lithium nitrate fusion. The preparations were then analyzed using a Varian Vista Axial Inductively Coupled Plasma Atomic Emission Spectrometer (AXICP-AES) to measure the cations present.

2.3.2 *Anions*

Slurry samples for anion analyses were prepared by PSAL using weighted dilutions and were analyzed using a Dionics DX500 Ion Chromatograph (IC). Weighted dilutions involved diluting a known mass of slurry with a known mass of de-ionized water. The resulting slurry was filtered. The solid free liquid was further diluted as necessary with de-ionized water to obtain IC readings within the calibration range of the instrument.

2.3.3 *Wt% solids*

A slurry sample of known mass was introduced and dried at about 110 °C. The mass loss was used to determine the wt% total solids of the slurry. A slurry sample was also filtered or centrifuged to remove 99.9% of the insoluble solids. A known mass of filtrate was introduced and dried at about 110 °C. The mass loss was used to determine the wt% total solids of the supernate, or the "wt% dissolved solids". The two values were combined algebraically to calculate the wt% insoluble solids of the slurry and the wt% soluble solids of the slurry. Solids analyses were performed in duplicate using two separate aliquots of sample for each measurement.

2.3.4 *Particle size*

Particle size analysis was obtained by submitting samples to Analytical Development for analysis. Samples were analyzed with a Microtrac S3500 Tri-laser Particle Size Analyzer. This instrument uses angular light scattering techniques to measure the particle size distribution. Preparation of the samples for analysis by the Microtrac consists of dilution of the slurry with water. The particle size distribution can be expressed in terms of a volume distribution, number distribution or area distribution. In this report, the graphical display of particle size data will use the particle diameter and number distributions. The calculated mean of the volume, number and area distributions will also be reported. It should be noted that the mean for a volume distribution is weighted toward the larger particles while the mean for the number distribution is weighted toward the smallest particles. The calculated specific surface area in $meters^2/cm^3$ is based on an assumption of smooth, solid spherical particles and does not reflect porosity or topology of the particles.

2.3.5 *Rheology*

Slurry rheology measurements were performed using a Haake RS600 rheometer at 25 °C. The rheometer uses a Searle type measuring system, where both speed and torque are measured at the rotating shaft. The rheometer was operated in the controlled rate mode for all of the data reported in this report. A few measurements were also made in the controlled stress mode when additional clarification of a rheology result was needed. The measuring geometries used were the cylindrical sensor and cup (Z41 Ti) for the less viscous slurries and the cone and plate (35 mm Ti/4 degree) for the slurries that were too thick for loading into the cylindrical geometry.

Flow curves were obtained by linearly varying the shear rate from 0 to 500 $seconds^{-1}$ over a given time period. The program details for the flow curves are listed in Table 4 and Table 5 for the cylindrical and cone geometries respectively. The measured shear stresses for the down flow curves were fitted to the Bingham Plastic rheology model over the shear rate range of 50 to 500 $seconds^{-1}$. Within this report, up curves are reported.

Table 4: Cylindrical geometry rheology program

PROGRAM SECTION	SHEAR RATE (SEC^{-1})	TIME (MIN)
Up Curve	0 to 500	5
Hold Period	500	2
Down Curve	500 to 0	5

Table 5: Cone and Plate rheology program

PROGRAM SECTION	SHEAR RATE (SEC^{-1})	TIME (MIN)
Initial Hold	0	2
1st Up Curve	0 to 500	5
1st Hold	500	2
1st Down Curve	500 to 0	5
Hold	0	2
2nd Up Curve	0 to 500	5
2nd Hold	500	2
2nd Down Curve	500 to 0	5

3.0 Results and Discussion

3.1 Simulant Composition

Samples from runs 1A[i]-10 were analyzed for chemical composition. As can be seen in Table 6, compositional variation appears to be greatest for aluminum and sodium for runs 2, 3, 6, 8, and 10. These runs correspond to ones that tested the effect of higher pH. One of the known effects of higher pH is metal dissolution. Run 5 was used as a final target, as all other runs could be normalized relative to it. Aluminum to iron ratios were kept constant for all runs. In order to normalize the compositions, chemical trim additions were made (Table 7) in order to achieve the final composition reported in Table 8.

Table 6: Elemental wt.% composition of runs 1A-10.

Run	Al	Ba	Ca	Ce	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	S	Si	Zn	Zr
1A	14.41	0.32	2.77	0.24	0.35	0.14	22.55	0.08	1.94	12.21	1.32	4.96	0.16	0.04	0.03	0.20	0.71
2	4.33	0.16	4.01	0.35	0.35	0.19	31.70	0.01	2.83	12.47	0.56	7.16	0.05	0.04	0.04	0.28	0.32
3	4.54	0.21	3.80	0.33	0.32	0.18	30.10	0.06	3.51	13.19	1.04	6.72	0.02	0.03	0.03	0.26	0.23
4	17.98	0.21	2.43	0.25	0.39	0.13	22.28	0.04	1.94	9.03	0.64	4.85	0.16	0.03	0.03	0.19	0.23
5	18.17	0.17	2.47	0.26	0.41	0.14	23.45	0.04	2.09	7.39	0.52	5.23	0.15	0.02	0.03	0.21	0.15
6	4.49	0.34	3.99	0.34	0.38	0.19	31.30	0.03	2.81	12.49	1.03	7.09	0.03	0.03	0.03	0.27	0.28
7	16.95	0.25	2.82	0.24	0.39	0.14	22.96	0.05	2.01	9.38	0.50	5.06	0.14	0.17	0.03	0.20	0.15
8	2.98	0.28	3.84	0.33	0.23	0.18	30.33	0.04	2.69	14.48	1.38	6.78	0.03	0.04	0.07	0.25	0.31
9	16.44	0.19	2.75	0.24	0.40	0.13	22.32	0.06	1.94	10.60	0.51	4.94	0.15	0.03	0.03	0.19	0.30
10	5.87	0.34	3.68	0.32	0.39	0.16	28.63	0.04	2.54	12.98	1.71	6.36	0.03	0.04	0.02	0.25	0.29

Table 7: Chemical trim addition made to runs 1A-10.

Chemical		1A	2	3	4	5	6	7	8	9	10
Boehmite	**AlOOH**	4.84	17.85	19.07	0.00	0.00	19.73	1.16	14.98	1.33	19.15
Silica	**SiO2**	1.48	1.16	1.27	1.55	1.37	1.31	1.32	0.90	1.45	1.41
Titania	**TiO2**	0.50	0.39	0.43	0.53	0.46	0.44	0.45	0.31	0.49	0.47
Sodium Nitrite	**NaNO2**	12.58	10.42	11.15	13.74	12.19	11.42	11.72	7.97	12.86	11.88
Sodium Nitrate	**NaNO3**	7.93	6.56	7.03	8.66	7.68	7.20	7.38	5.02	8.10	7.48
Sodium Sulfate	**Na2SO4**	1.35	1.12	1.19	1.47	1.31	1.22	1.25	0.85	1.38	1.27
Sodium Hydroxide	**NaOH**	6.68	5.53	5.92	7.30	6.48	6.07	6.22	4.23	6.83	6.31
Sodium Carbonate	**Na2CO3**	2.74	2.27	2.43	2.99	2.65	2.49	2.55	1.73	2.80	2.58
Sodium Chloride	**NaCl**	0.15	0.13	0.14	0.17	0.15	0.14	0.14	0.10	0.16	0.15

[i] The first run is labeled 1A, as it had to be repeated due to solids settling in the precipitator feed line. The simulant from Run 1 was discarded and not reported in any of the analytical results.

Table 8: Final composition of runs 1A-10.

	1A	2	3	4	5	6	7	8	9	10
Fe	14.67	14.79	14.59	15.04	15.52	14.82	15.12	14.46	14.83	14.63
Al	11.92	12.04	11.87	12.72	12.64	12.06	12.31	11.76	12.07	11.88
Mn	7.94	5.82	6.39	6.10	4.89	5.91	6.18	6.90	7.04	6.63
Ni	3.23	3.34	3.26	3.27	3.46	3.36	3.33	3.23	3.29	3.25
Ca	1.81	1.87	1.84	1.64	1.63	1.89	1.85	1.83	1.83	1.88
Mg	1.26	1.32	1.70	1.31	1.38	1.33	1.33	1.28	1.29	1.30
Na	12.22	12.32	12.15	12.53	12.93	12.35	12.59	12.05	12.36	12.19
Cr	0.23	0.17	0.16	0.26	0.27	0.18	0.26	0.11	0.26	0.20
Ce	0.16	0.16	0.16	0.17	0.17	0.16	0.16	0.16	0.16	0.16
Zn	0.13	0.13	0.13	0.13	0.14	0.13	0.13	0.12	0.13	0.13
Ba	0.21	0.07	0.10	0.14	0.11	0.16	0.16	0.13	0.13	0.17
Pb	0.10	0.02	0.01	0.11	0.10	0.01	0.09	0.01	0.10	0.01
Zr	0.46	0.15	0.11	0.16	0.10	0.13	0.10	0.15	0.20	0.15
Cu	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.09	0.09	0.08
K	0.05	0.00	0.03	0.03	0.03	0.02	0.03	0.02	0.04	0.02
Si	0.65	0.66	0.64	0.67	0.69	0.66	0.67	0.64	0.66	0.65
S	0.02	0.02	0.02	0.02	0.02	0.02	0.11	0.02	0.02	0.02
Ti	0.28	0.28	0.27	0.28	0.29	0.28	0.28	0.27	0.28	0.28

3.2 Particle size

The CSTR parameters were set up in such a way as to ensure the formation of a range of particle sizes. It was assumed that particle size would be a major contributing factor to the settling rate and rheology of the simulant. Therefore, being able to directly control the particle size of the simulant would allow better control of the rheological properties of the simulant. The results of the particle size analysis, performed by AD, can be seen in Table 9. Runs 5 and 7 showed a bimodal particle size distribution. It is not certain which parameter changes, if any, result in the bimodal distribution. One physical interpretation is that they represent the product of a nonhomogeneous precipitating system [9].

Table 9: Results of particle size analysis

Run	Volume Mean Diameter (µm)
1A	22.3
2	31.9
3	31.5
4	22.9
5	3.1, 24.8
6	38.2
7	3.8. 17.1
8	24.6
9	11.1
10	31.5

Particle size distributions were consistent with that which has been seen in previous studies [1, 6]. A representation of a typical distribution seen for this set of experiments is presented in Figure 2. Particle sizes based on mean volume diameters for batches 1A – 10 are presented in Figure 3. Distributions for all runs are located in Appendix A, Exhibit A-1.

Figure 2: Mean volume distribution for SB6A batch 1A.

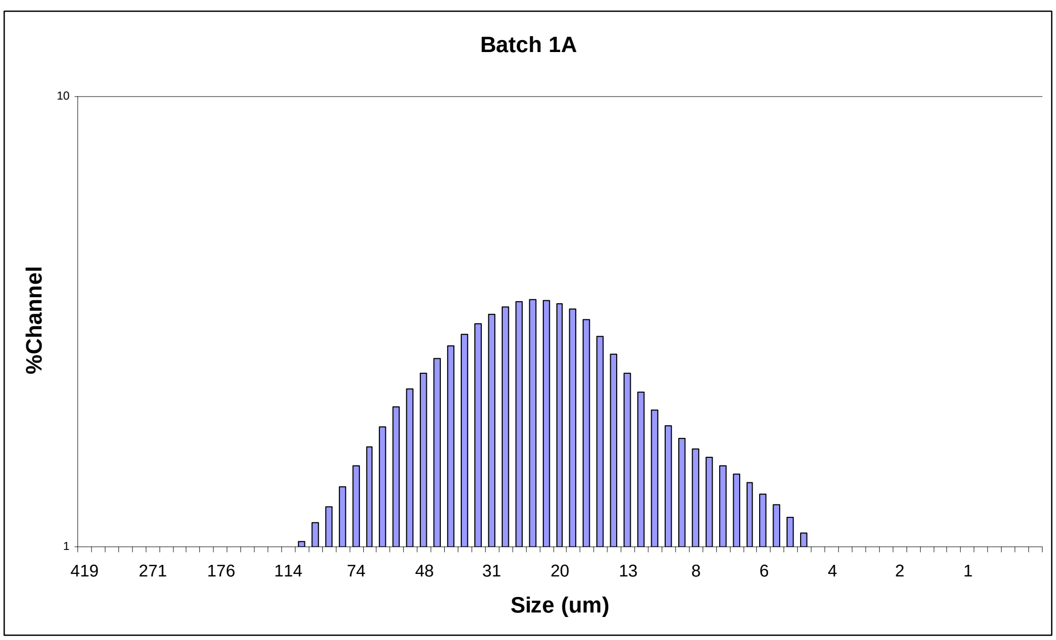
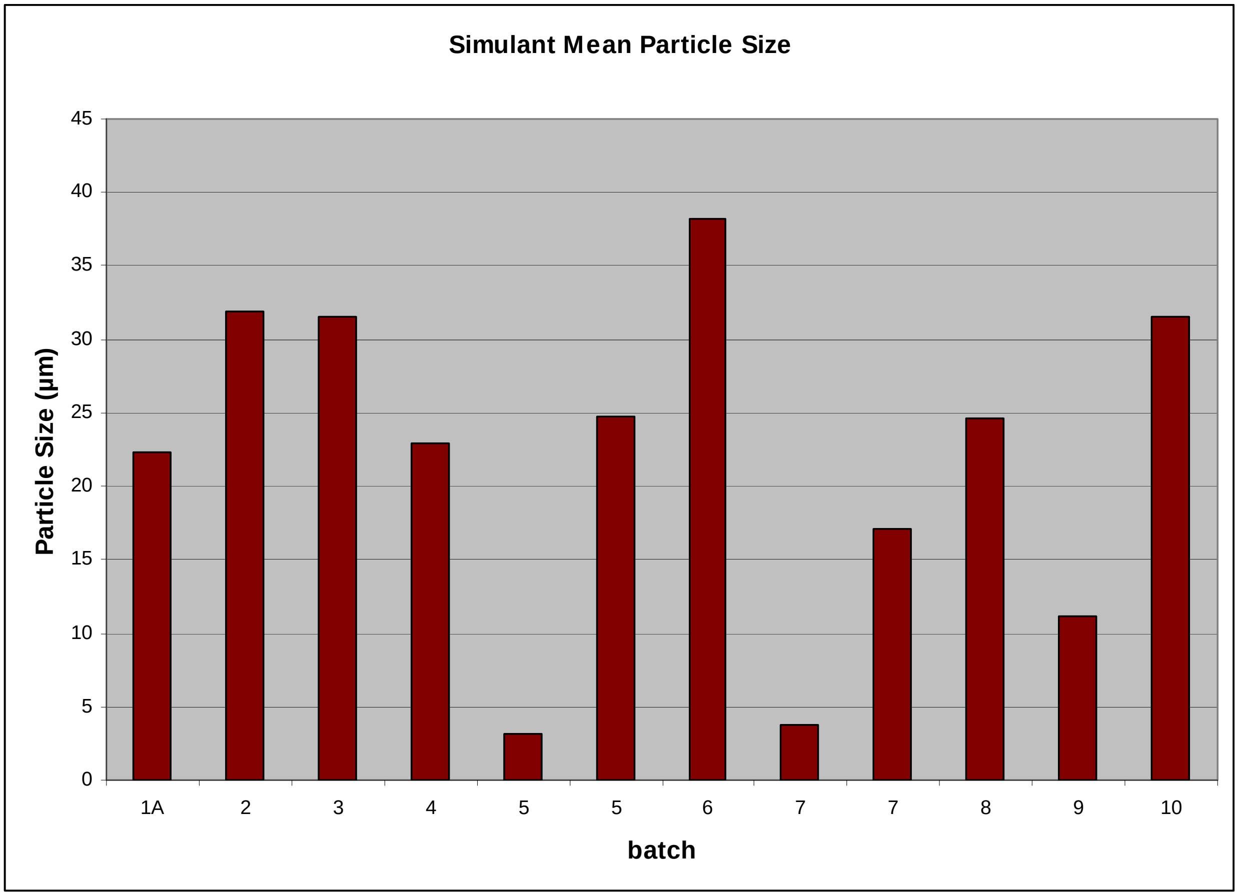
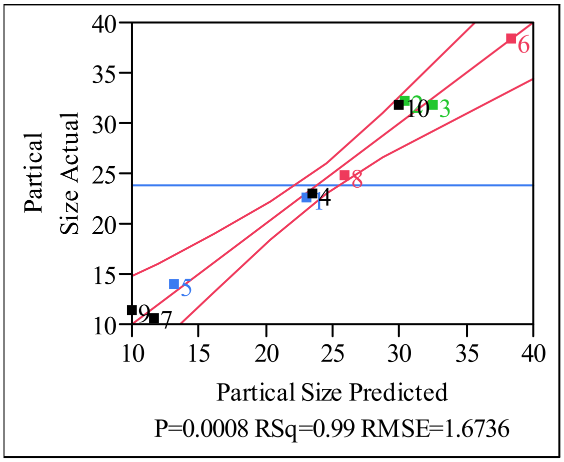


Figure 3: Mean particle size for SB6A simulant batches.



An analysis of the parametric factors affecting particle size was performed using JMP statistical software [7]. The results of that analysis indicate that pH, flow rate, and mixing speed were factors that contributed, to some degree, to the simulant particle size. Of the parameters tested, temperature seemed to have smallest, or no impact. The analytical output provided equations that show the relative effect of each contributing parametric factor and the degree of accuracy with which one could predictably target desired particle sizes (Figure 4).

Figure 4: JMP software analysis of parametric effect on particle size.



Summary of Fit

RSquare	0.986562
RSquare Adj	0.969764
Root Mean Square Error	1.67363
Mean of Response	23.83
Observations (or Sum Wgts)	10

Analysis of Variance

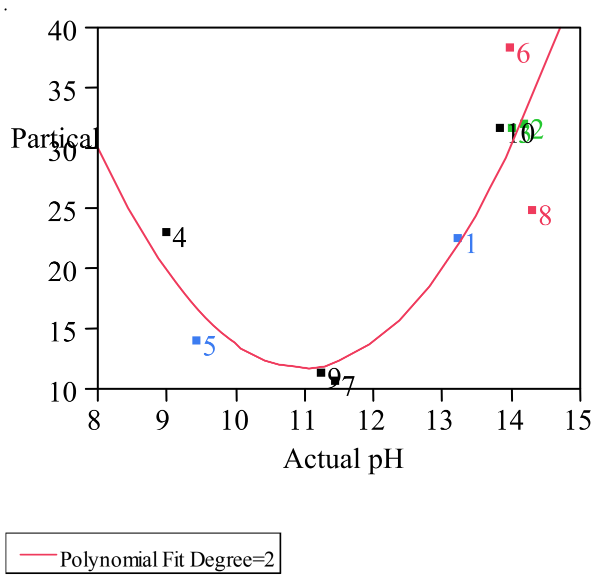
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	822.55185	164.510	58.7320
Error	4	11.20415	2.801	**Prob > F**
C. Total	9	833.75600		0.0008

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-61.19439	5.983634	-10.23	0.0005
Actual pH	6.4095057	0.416364	15.39	0.0001
flow rate (ml/min)	0.0288282	0.005556	5.19	0.0066
mixing speed (rpm)	-0.011146	0.001809	-6.16	0.0035
(Actual pH-12.463)*(Actual pH-12.463)	2.2513661	0.227186	9.91	0.0006
(Actual pH-12.463)*(mixing speed (rpm)-650)	-0.003204	0.00094	-3.41	0.0271

As can be seen in Figure 4, the data show a good fit for predicted versus actual particle size with an R^2 value of 0.99. Parametric estimates shows the degree to which each contributing parameter affects the particle size. Of those parameters, it appears as though pH has the largest effect. When one looks solely at the effect of pH, the quadratic presented in Figure 5 is seen which shows the dependence of pH on simulant particle size.

Figure 5: JMP software analysis of the effect of pH on simulant particle size.



Polynomial Fit Degree=2
Partical Size = -59.25008 + 6.0550294*Actual pH + 2.0454203*(Actual pH-12.463)^2

Summary of Fit

RSquare	0.766863
RSquare Adj	0.700253
Root Mean Square Error	5.269579
Mean of Response	23.83
Observations (or Sum Wgts)	10

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	639.37676	319.688	11.5126
Error	7	194.37924	27.768	**Prob > F**
C. Total	9	833.75600		0.0061

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-59.25008	17.96978	-3.30	0.0132
Actual pH	6.0550294	1.277852	4.74	0.0021
(Actual pH-12.463)^2	2.0454203	0.686074	2.98	0.0205

3.3 Simulant Settling

SB6A simulant batches 1 – 10 were allowed to settle over a period of several days. Photos of the degree of settling are presented in Figure 6 and Figure 7. From visual inspection of the settled simulants, it can be seen that the more settled batches (6, 8, 3, 2) were obtained at high pH, while the less settled batches (4, 10, 5, 9, 1, 7) were from lower pHs. Ideally, one would expect to see a more settled simulant resulting for those containing larger particle sizes. This was not consistent with the tested simulant batches in this study.

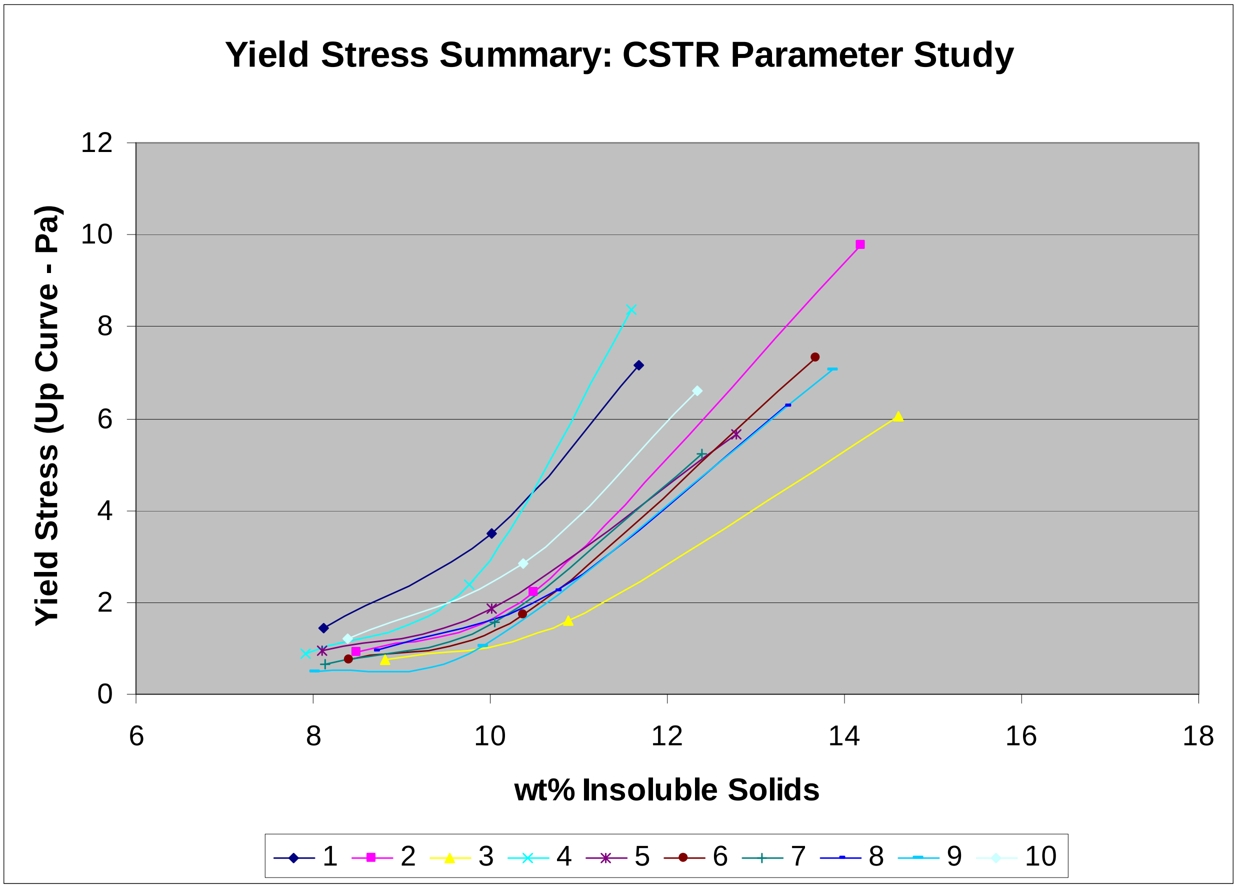
Figure 6: Degree of settling for SB6A batches 1-5.

Figure 7: Degree of settling for SB6A batches 6-10.

3.4 Rheology

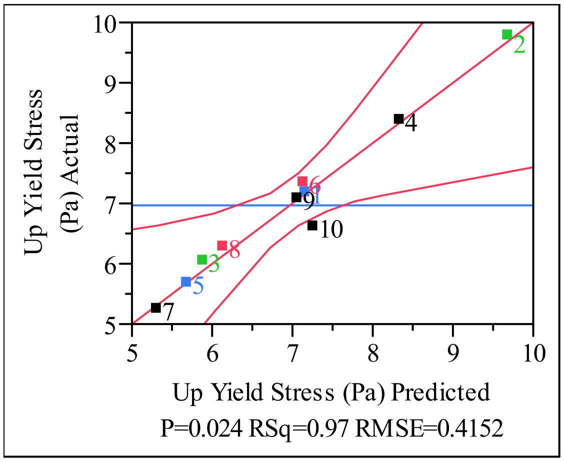
The rheology of the SB6A simulant batches was measured using a rotational Haake rheometer at three different wt.% insoluble solids (Figure 8). The observed trend was expected, seeing an increase in yield stress with increasing levels of insoluble solids [8].

Figure 8: Yield stress summary of SB6A simulant batches 1-10, relative to wt.% insoluble solids



When yield stress is examined with respect to the effect of varying the parametric values, it is seen that pH, flow rate, temperature and mixing speed all have a linear effect (Figure 9). The data show a strong correlation between the predicted and actual yield stress with an R^2 value of 0.97, with the exception of batch 10. For all of the batches, the up curve yield stresses were higher than the down curve yield stresses. Summary and detailed rheology data is found in Appendix A, Exhibit A-2.

Figure 9: JMP software analysis of parametric effect on rheology



Summary of Fit

RSquare	0.968091
RSquare Adj	0.904274
Root Mean Square Error	0.415199
Mean of Response	6.953
Observations (or Sum Wgts)	10

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	15.690639	2.61511	15.1697
Error	3	0.517171	0.17239	**Prob > F**
C. Total	9	16.207810		0.0240

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	5.530639	0.926903	5.97	0.0094
Actual pH	0.1608891	0.070377	2.29	0.1063
flow rate (ml/min)	0.0065354	0.001335	4.90	0.0163
temperature (ºC)	-0.022687	0.006341	-3.58	0.0373
mixing speed (rpm)	-0.000699	0.000445	-1.57	0.2146
(flow rate (ml/min)-140)*(temperature (ºC)-46)	-0.000342	5.561e-5	-6.16	0.0086
(temperature (ºC)-46)*(mixing speed (rpm)-650)	-6.224e-5	1.882e-5	-3.31	0.0455

3.5 Foaming

Part of the simulant development program involves testing the effect of differing sludge simulant formulation parameters on foaming behavior. Procedure ITS-0142 was used with a supplemental R&D Direction, SRNL-L3100-2009-00211. For each test, an antifoam test apparatus was charged with 300 mL of sludge. Antifoam was available but was not needed. The boilup rate was 0.8 g/min with a hot plate setting of 450°C during the initial heat-up phase and 400°C at steady state; the sludge boiled at 100 - 101°C. The boiling was conducted under reflux conditions for 60 to 80 minutes before shutdown. Mercury was not present in the sludges. The extent of foaming on the 10 simulants is documented in Table 10 The plots of the average and maximum foam heights (normalized by mass), reveals only a very weak positive dependence of foam height with mixing speed during precipitation. For Figure 11; the slope is approximately 0.04 mL/rpm. Figure 12 through Figure 14 reveal no dependence on pH, flow rate, and temperature. Since foaming was mild, foaming rises of 30 to 90 mL (avg and peak values, respectively), antifoam was not needed. There was no correlation of foam height relative to particle size (Figure 10).

Figure 10: Foaming height versus particle size distribution

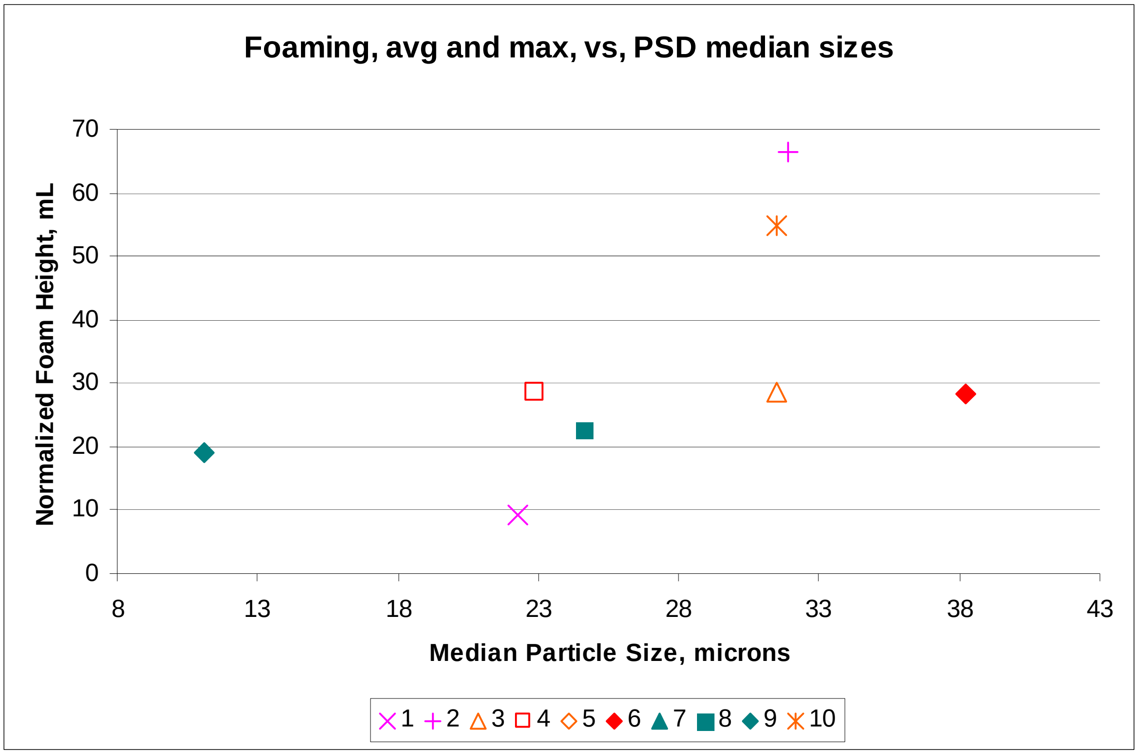


Table 10: CSTR sludge formulation parameters

Run[a]	mass, g	Cold hgt start[b]	Total hgt avg/max	Foam hgt avg/max[c]
1A[d]	320.4	310 mL	320/380 mL	10/70
2[e]	316.4	310 mL	380/400 mL	70/90
3[e]	315.9	310 mL	340/340 mL	30/30
4[f]	316.2	310 mL	340/360 mL	30/50
5[e]	316.0	310 mL	360/380 mL	50/70
6[e,f]	319.6	310 mL	340/380 mL	30/70
7[d,g]	323.7	310 mL	380/400 mL	70/90
8[d,g]	264.6	280 mL	300/340 mL	20/60
9[d,h]	314.6	320 mL	340/400 mL	20/80
10[i]	274.1	300 mL	350/380 mL	50/80

Where,

a) caustic boiling from 60 to 80 minutes, T = 101°C, 250 rpm stirring, fill to ~ 300 mL in 4 L rig

b) height of vortex using mixer at 250 rpm, room temperature

c) difference of total height (with foam) and cold, non-foam sludge yields only the foam height

d) small and large bubbles, on sides and near shaft, respectively

e) small bubbles (mostly), on sides and near shaft, respectively

f) frothy across the entire surface

g) small amount of whitish foam

h) tan color around the shaft at 78°C (during the heating phase, as opposed to cooling/shutdown)

i) small and large bubbles mostly on side

Figure 11: Foaming height (average and maximum) vs. mixing speed

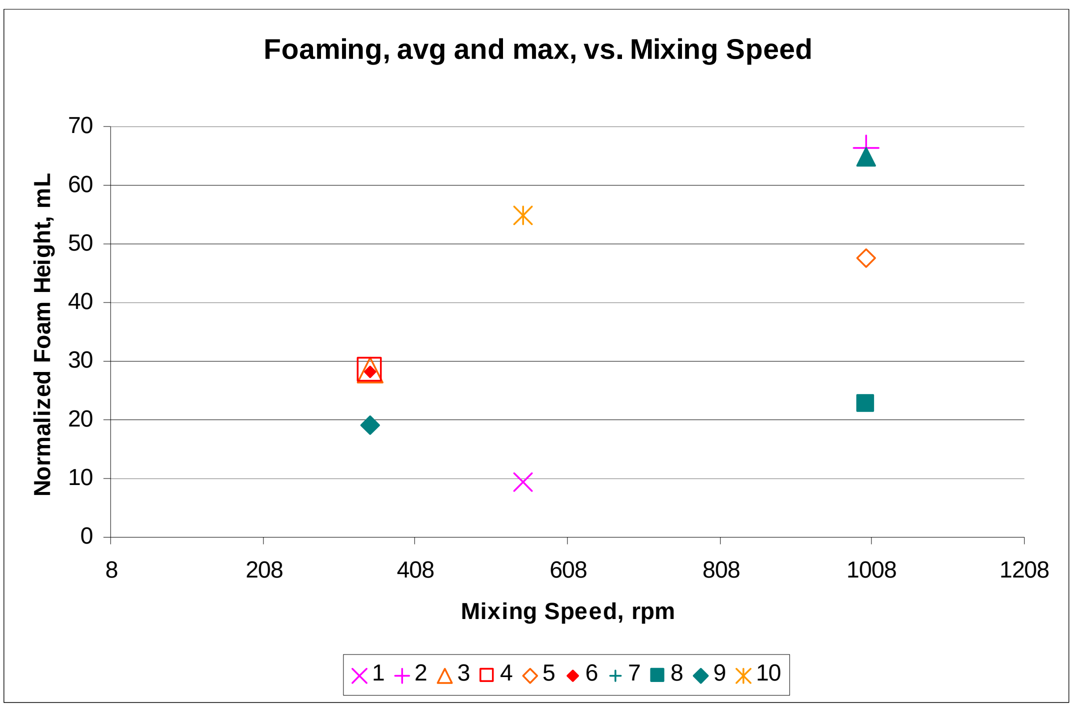


Figure 12: Foaming height (average and maximum) vs. pH

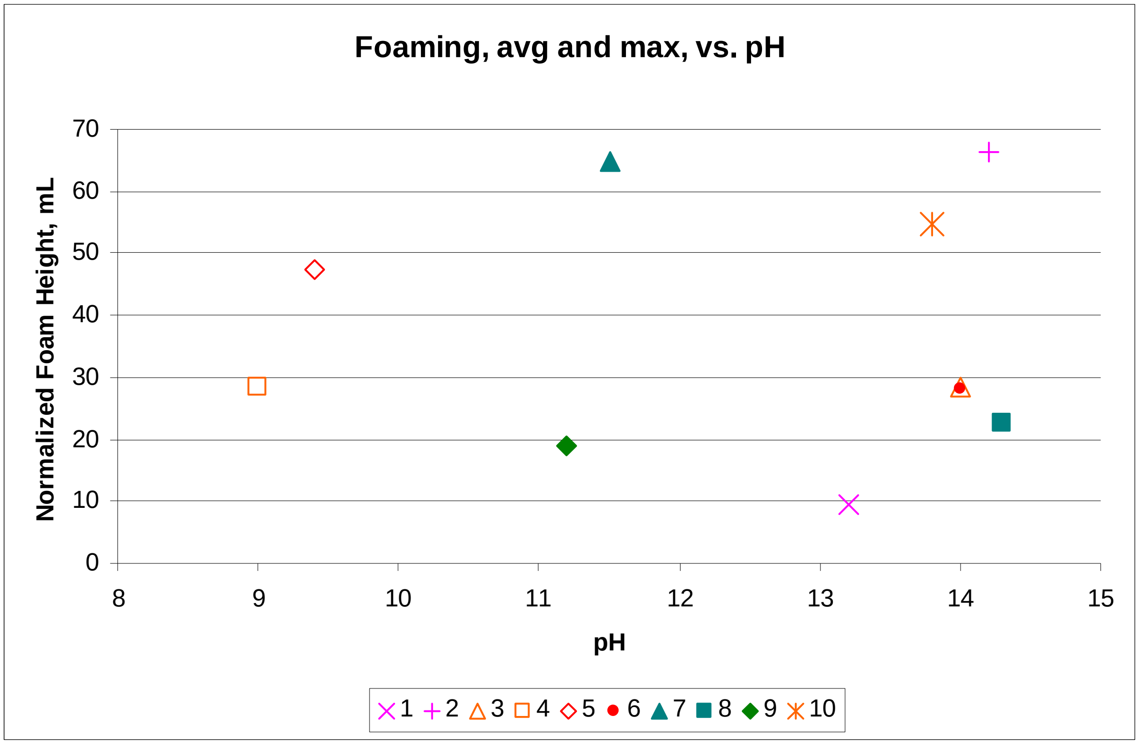


Figure 13: Foaming height (average and maximum) vs. flow rate

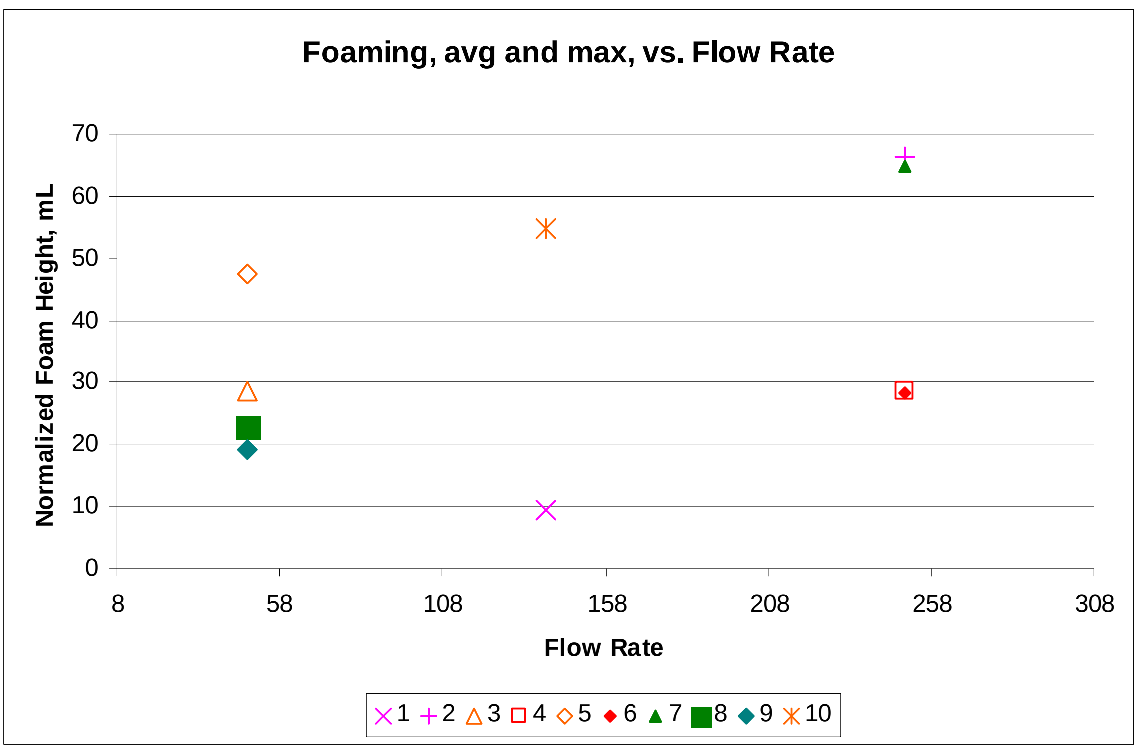
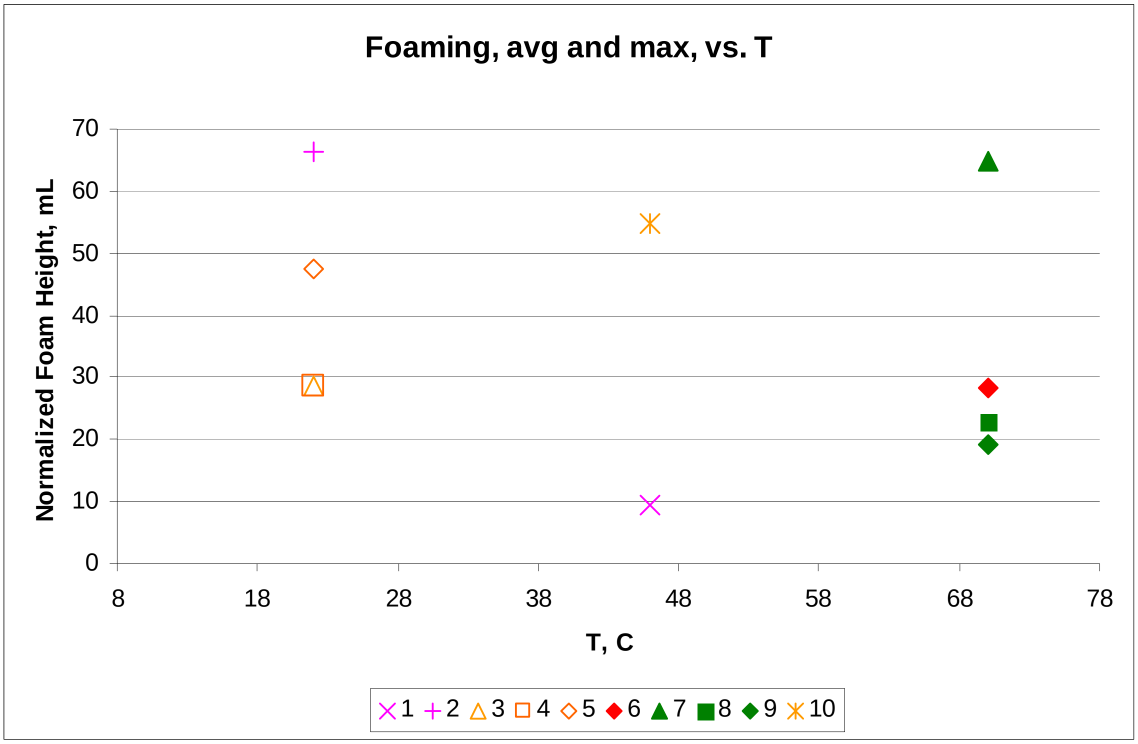


Figure 14: Foaming height (average and maximum) vs. temperature



4.0 Conclusions

Historically, it has been seen that significant differences in the physical properties of simulated wastes are observed depending on the preparation route selected. The focus of this research was to look at which parameters would have an effect on the simulant properties of particle size, rheology, and foaming using the CSTR preparation method in order to make a sludge simulant that is more prototypical of Savannah River Site sludge. Each of these properties has an important impact on DWPF waste processing, and as such there is a need to be able to correctly simulate these properties of actual waste sludge.

By changing the values for pH, temperature, flow rate, and mixing for sludge slurry precipitations the following observations were made:

<u>Particle Size</u>

- Mean particle size ranged from 3-38μm and was consistent with previous simulants.
- Changes in pH, flow rate, and mixing speed are statistically significant with respect to particle size.
- The effect of flow rate and mixing speed are linear while that of pH is quadratic. Results indicated that a lower pH produces smaller particles.

<u>Rheology</u>

- Increasing wt.% insoluble solids increases yield stress, as expected.
- Changes in pH, flow rate, temperature, and mixing speed are statistically significant with respect to yield stress.
- The effects of the tested parameters are linear.
- By varying the parameters tested, it appears that simulant yield stress could be adjusted to a targeted value.

<u>Foaming</u>

- Increasing mixing speed had a slight effect on increasing simulant foaming.
- Changes in pH, flow rate, and temperature had no effect on foaming.

5.0 Recommendations

The work performed for this study looked at four parametric effects for simulant SB6A. This resulted in 10 distinct batches for analysis. This was the least number of batches that could be prepared and still have the statistical ability to determine the individual effects of these parameters, if any, on the physical properties of simulant particle size, rheology, and foaming. For a more accurate correlation of the influence of these parameters, 10 additional batches would need to be prepared and tested. The results presented in this report are only for the simulant tested, SB6A. It is not known what effect, if any, differences in sludge composition will have on the results of this parametric study. Additional testing of sludge batches of varying composition would identify compositional effects on the physical properties investigated.

Although conclusions can be drawn that several parameters had an effect on the physical properties of the tested simulant (i.e. the effect of pH on particle size), none of the parameters tested led to a simulant that foamed consistent with sludge foaming under caustic boiling, as seen with the real sludge. SRNL is currently partnering with foam experts at the Illinois Institute of

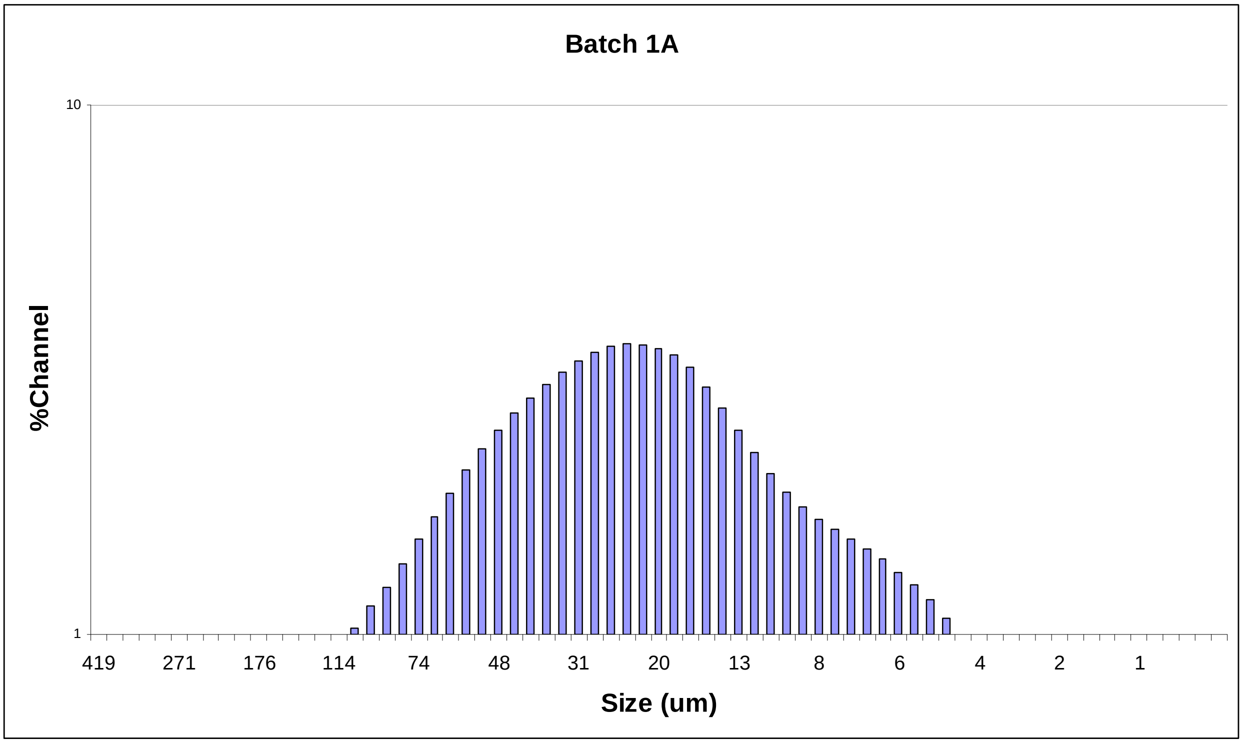
Technology (IIT). IIT will perform a study on simulants provided to them by SRNL. Their recommendations will be incorporated into a future test program.

6.0 References

1. R.E. Eibling, "Impact of Simulant Production Methods on the Physical Properties of DWPF Sludge Batch 3 Simulant", WSRC-TR-2004-00578.
2. D.C. Koopman, "Rheology Improvements During Preparation of 40-Inch Heel Case Simulants for Sludge Batch 4", WSRC-STI-2006-00067.
3. J.D. Newell, "SB6-A Simulant Development", SRNL-3100-2009-00069.
4. D.D. Larsen, "Sludge Batch 6 Projected Batch and Blend Compositions", LWO-LWP-2009-00001.
5. J.D. Newell, "Run Plan for Continuously Stirred Tank Reactor (CSTR) Parametric Study", SRNL-L3100-2009-00147.
6. D.P. Lambert, "Impact of Simulant Production Methods on SRAT Product", WSRC-TR-2005-00294.
7. JMP™, Version 7.0.2, SAS Institute Inc., Cary, NC, 1989-2007.
8. R.E. Eibling, "Impact of Irradiation and Thermal Aging on DWPF Simulated Sludge Properties", WSRC-TR-2005-00543.
9. D.C. Koopman, "Impact of Preparation Methods and Scale Factors on Sludge Batch 4 Simulant Properties, WSRC-STI-2006-00088.

Appendix A

Exhibit A-1: Mean volume distributions for batches 1A-10



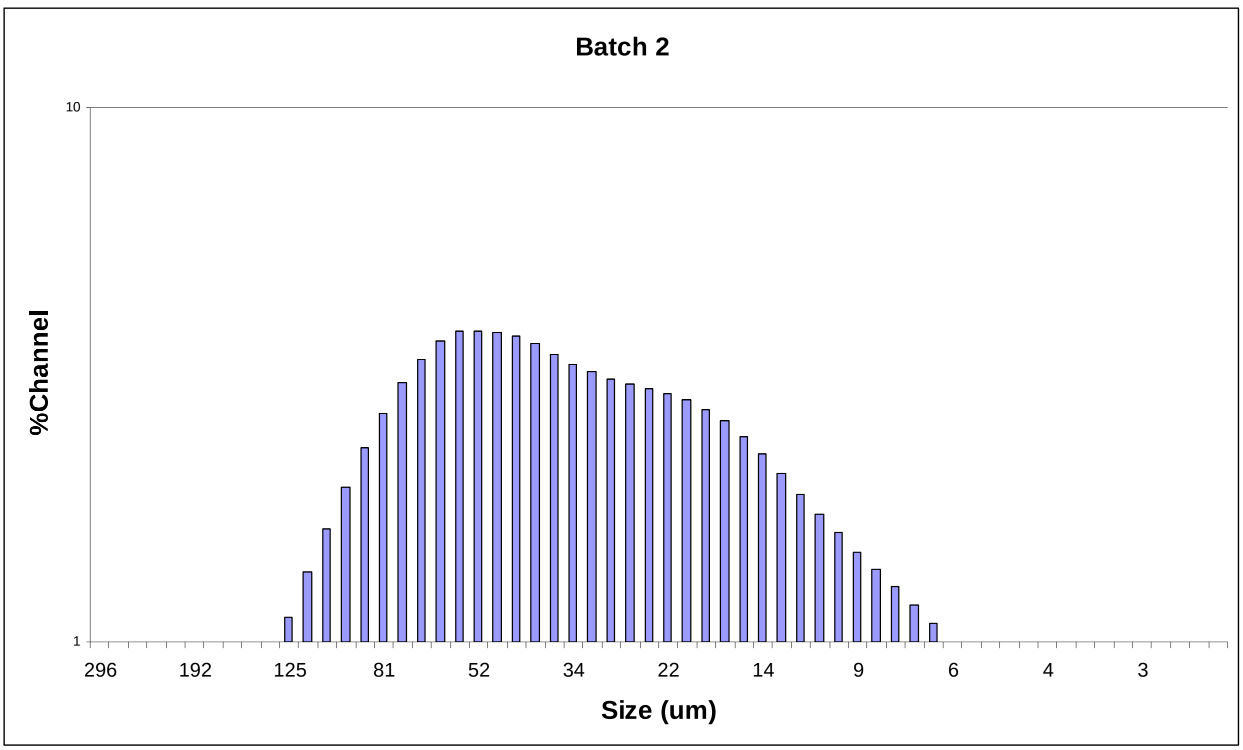
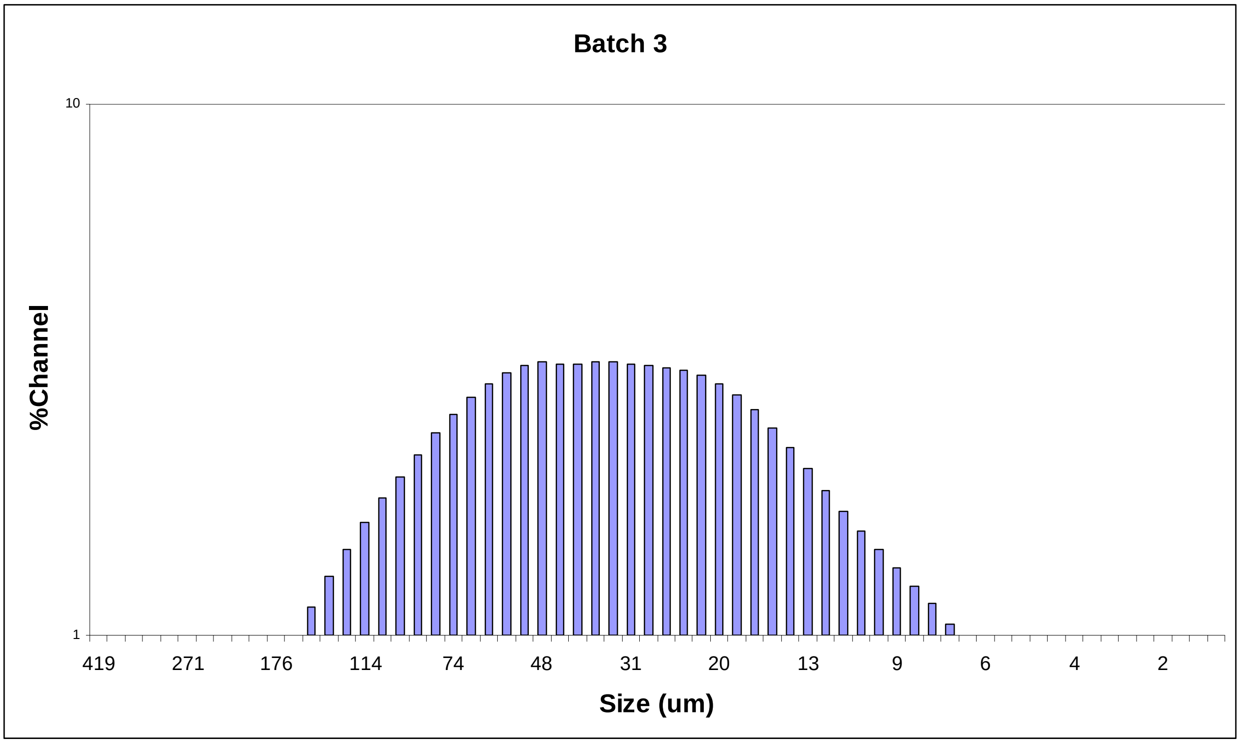


Exhibit A-1: Mean volume distributions for batches 1A-10 (cont.)



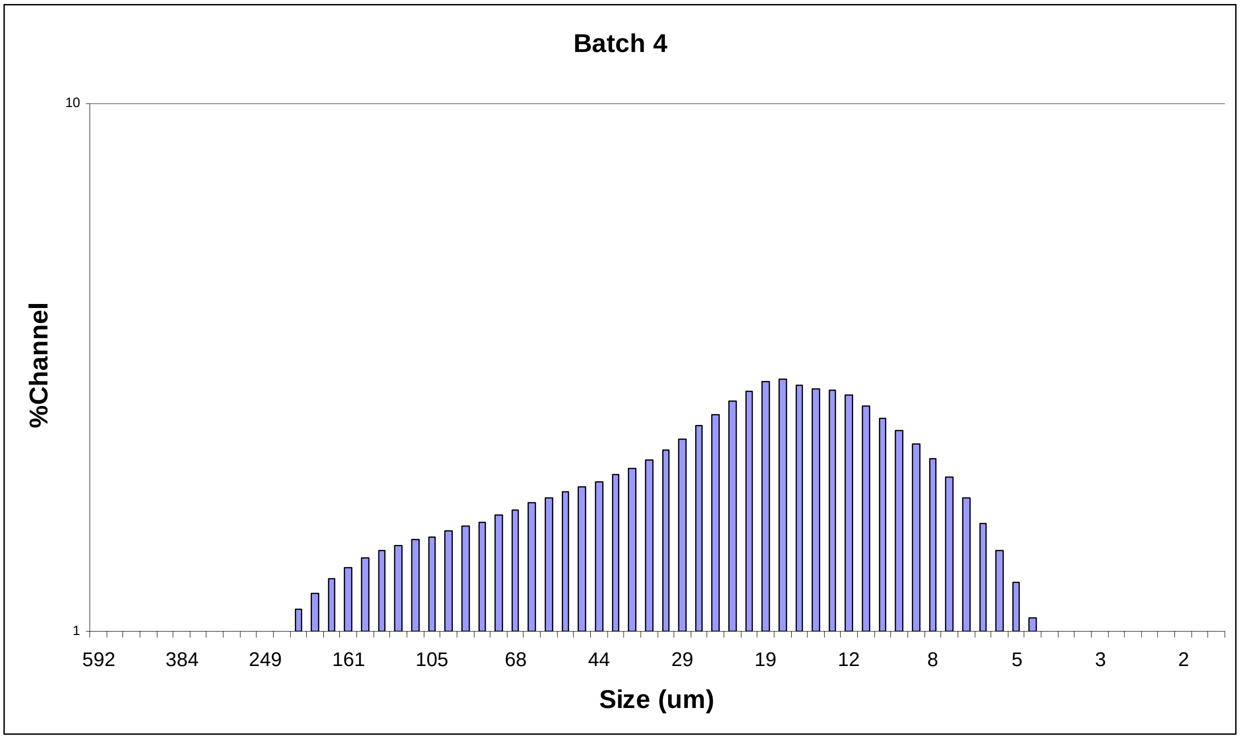
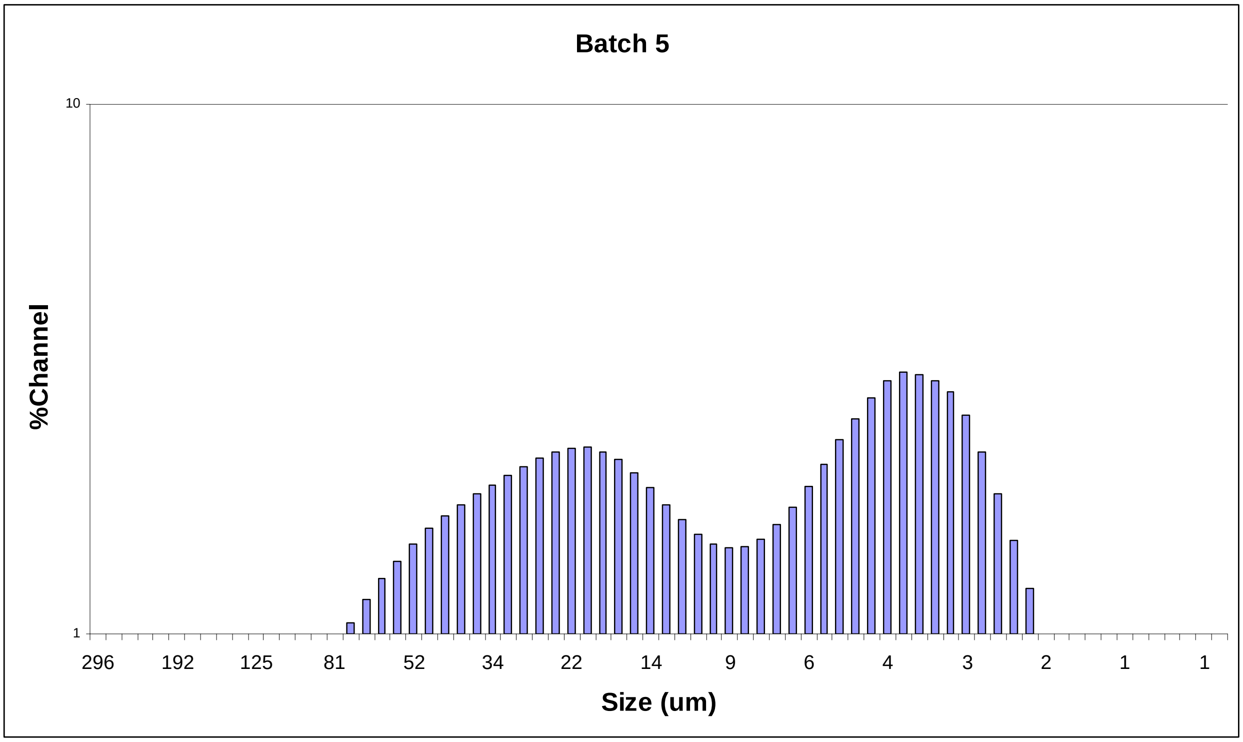
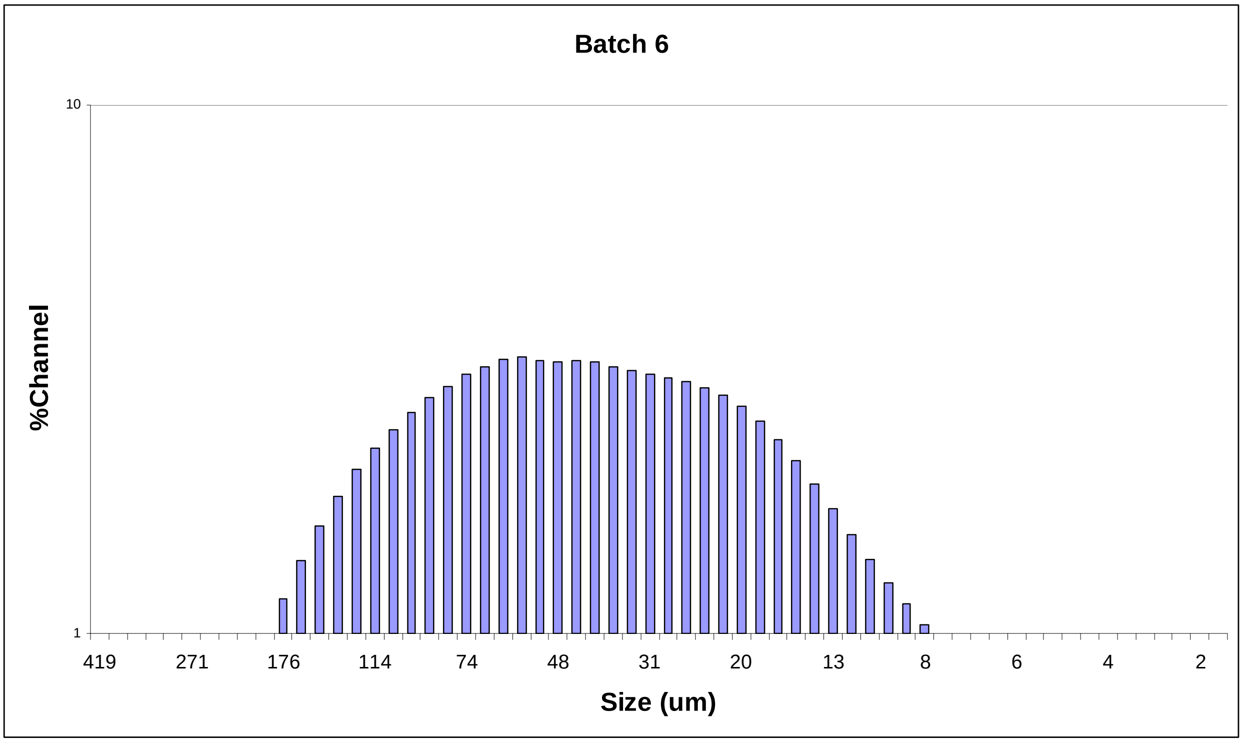


Exhibit A-1: Mean volume distributions for batches 1A-10 (cont.)





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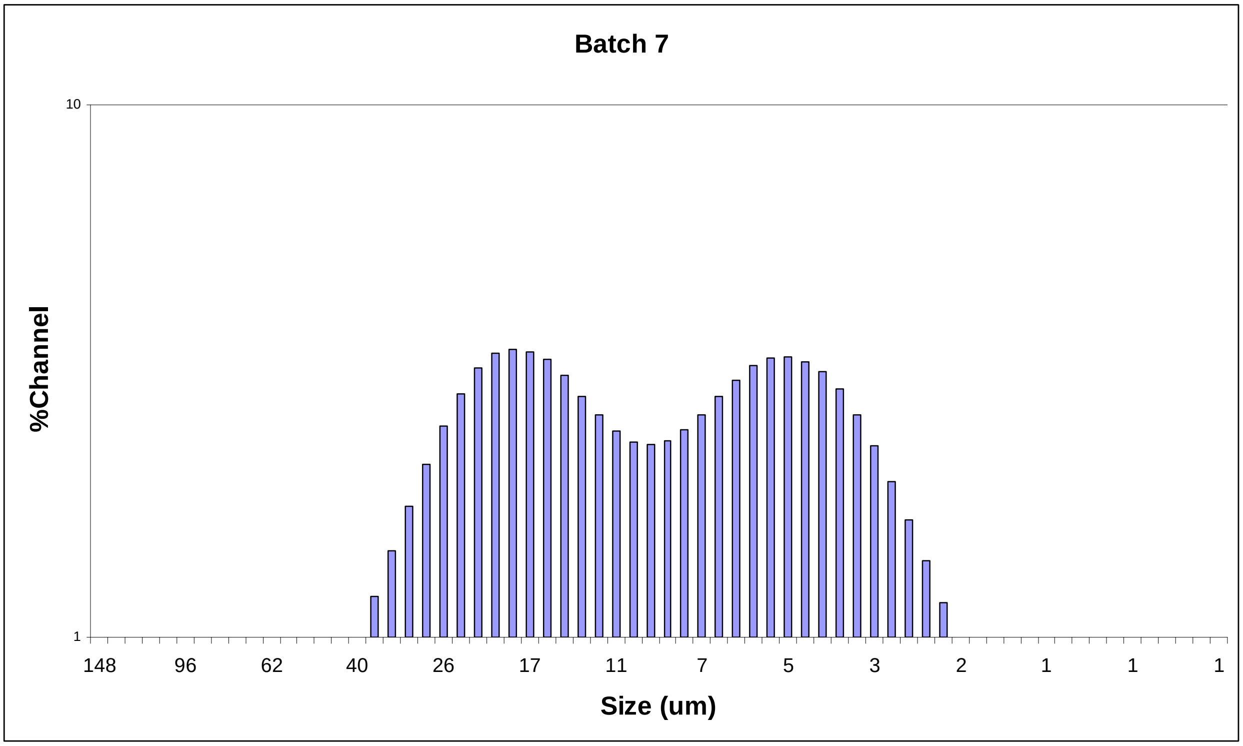

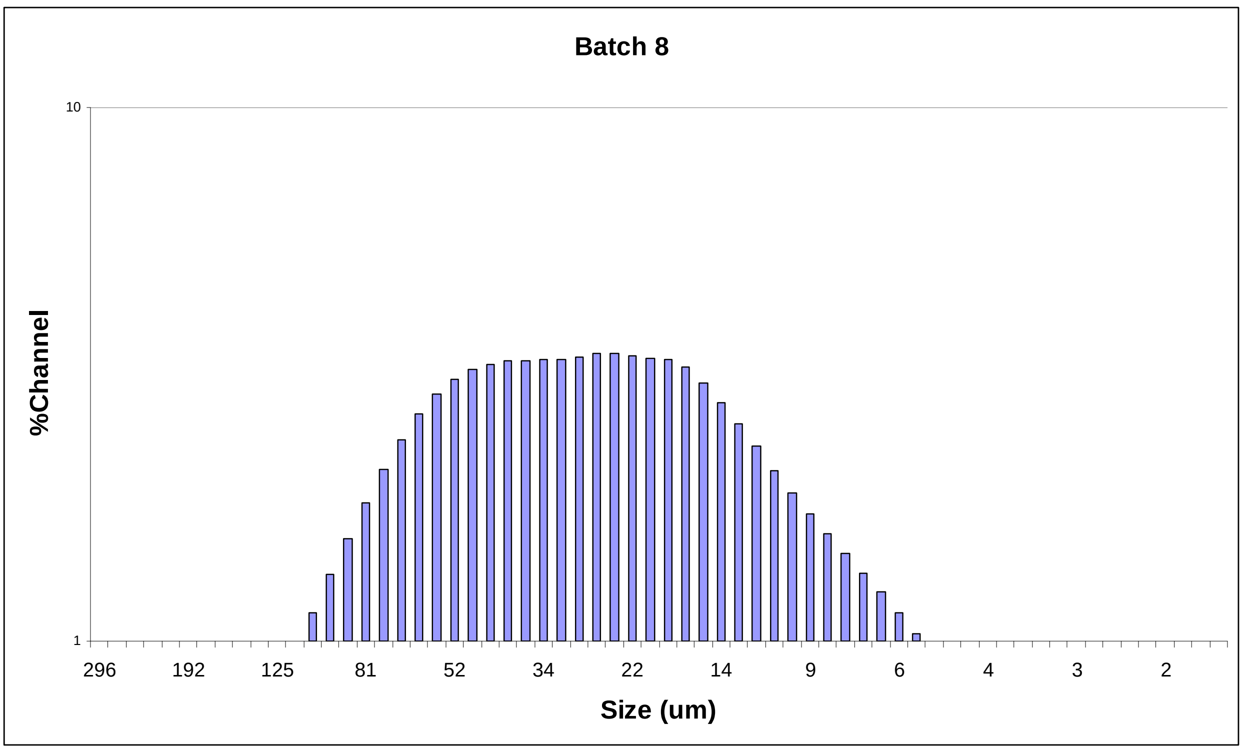

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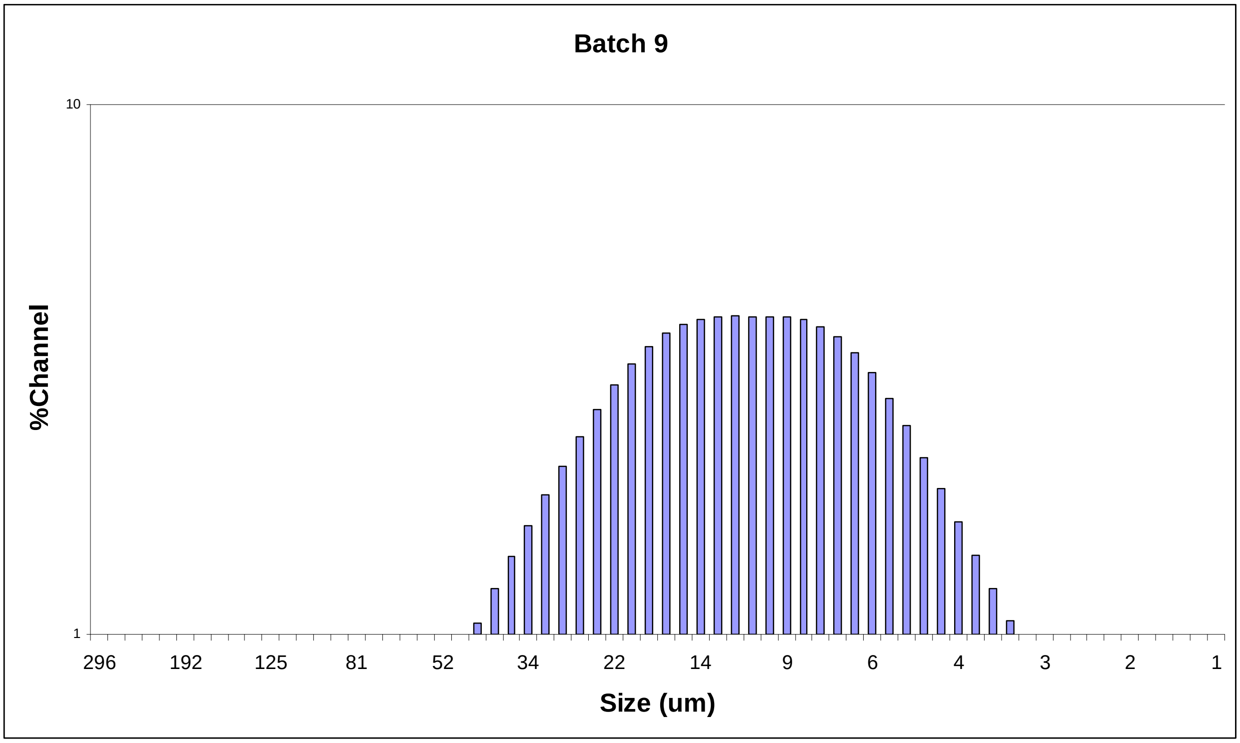


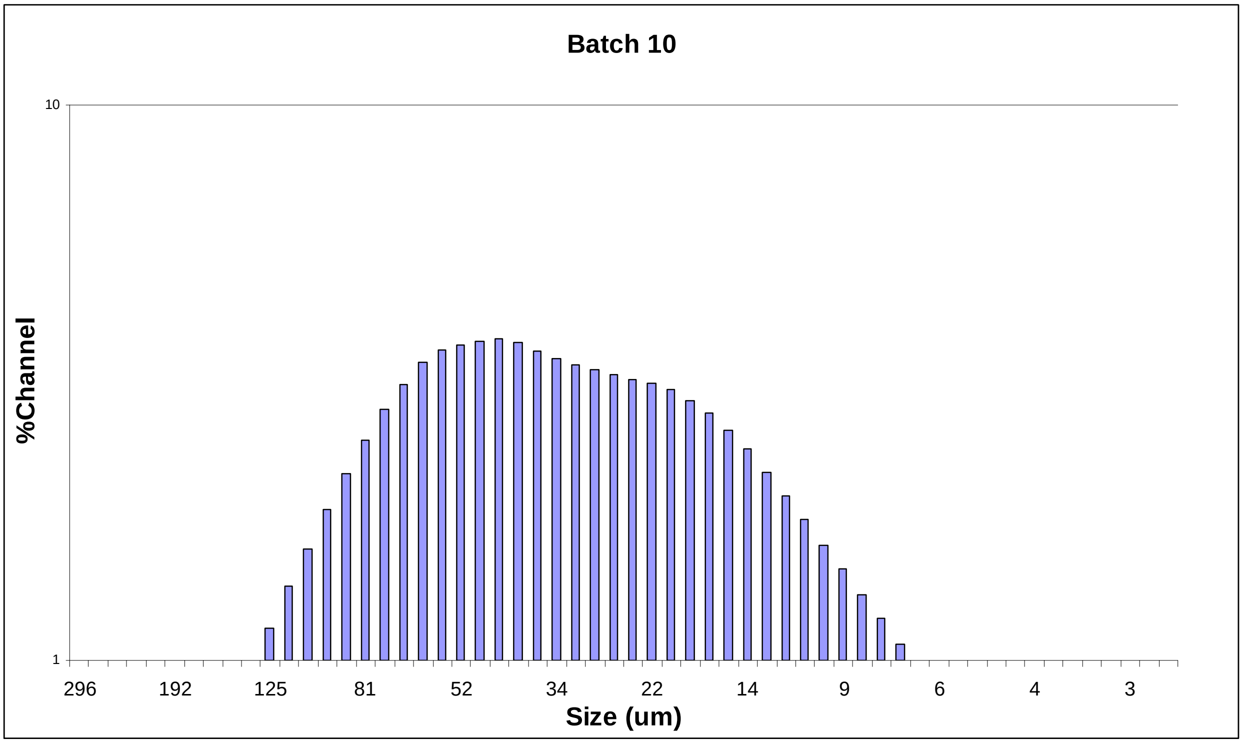
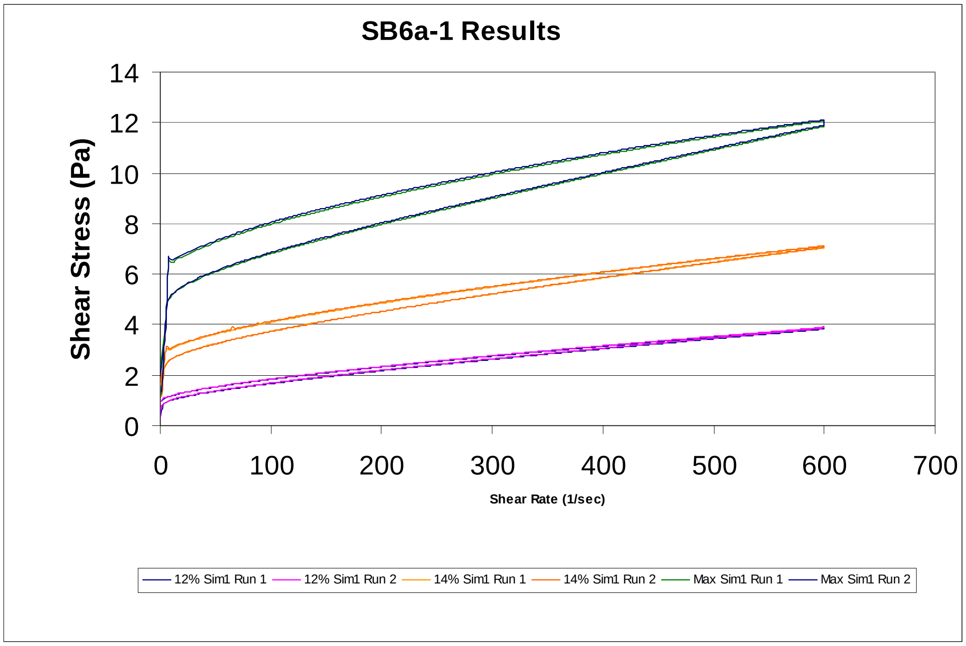


Exhibit A-2: Summary of rheology calculations

Run	Initial IS wt %	Up Yield Pa	Down Yield Pa	2nd IS wt %	Up Yield Pa	Down Yield Pa	Max IS wt %	Up Yield Pa	Down Yield Pa
1A	8.114	1.43	1.19	10.017	3.51	2.97	11.681	7.18	5.71
2	8.499	0.92	0.65	10.492	2.21	1.50	14.194	9.77	3.11
3	8.815	0.75	0.48	10.883	1.61	1.08	14.612	6.04	3.13
4	7.912	0.88	0.70	9.768	2.40	1.87	11.593	8.38	3.92
5	8.109	0.93	0.80	10.012	1.87	1.60	12.778	5.66	3.76
6	8.404	0.76	0.58	10.375	1.72	1.41	13.671	7.33	2.50
7	8.140	0.66	0.55	10.049	1.56	1.27	12.397	5.24	3.11
8	8.701	0.96	0.76	10.742	2.24	1.83	13.343	6.27	4.29
9	8.024	0.50	0.35	9.907	1.06	0.77	13.868	7.06	2.94
10	8.397	1.21	0.90	10.367	2.86	2.11	12.339	6.60	4.19

Exhibit A-2: Rheology data for batches 1A-10



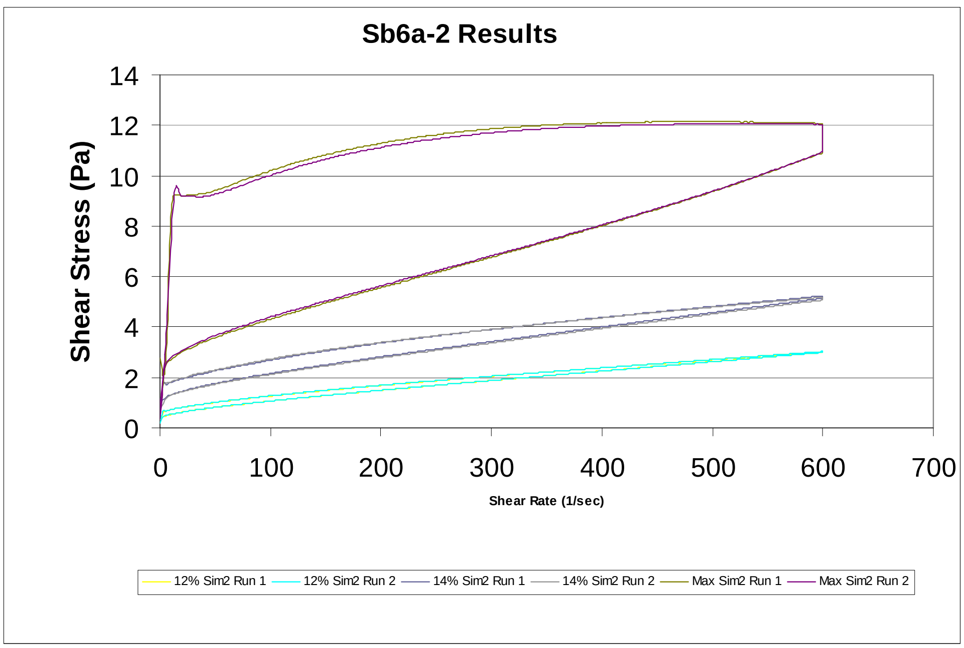
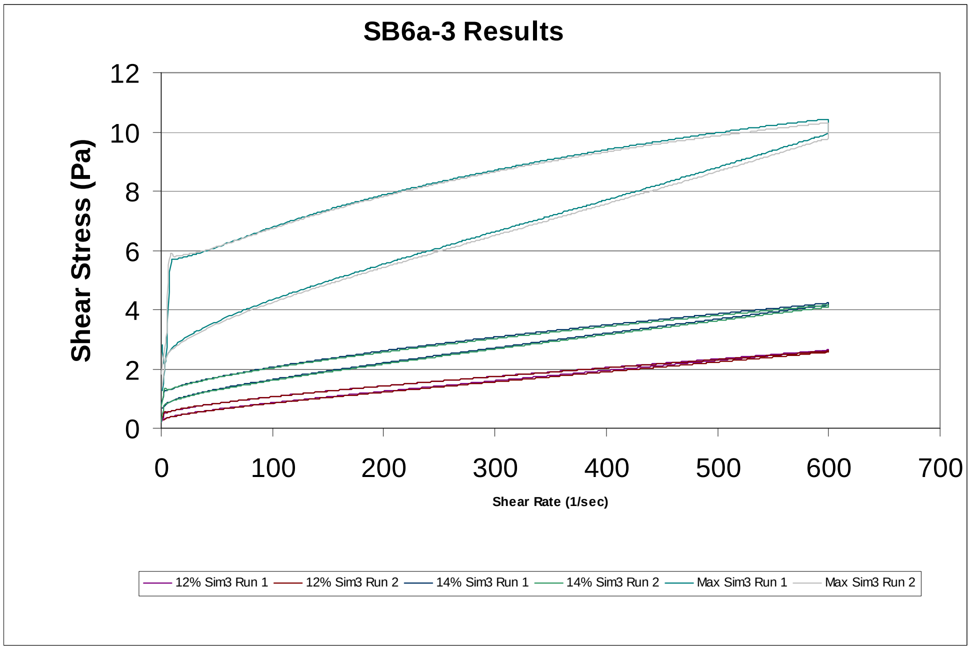
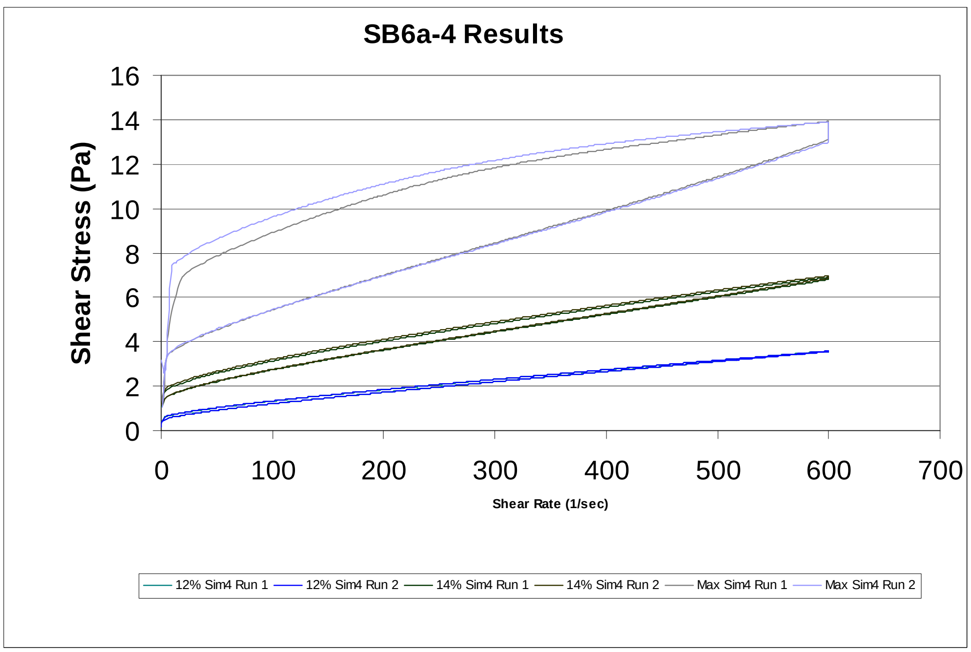


Exhibit A-2: Rheology data for batches 1A-10 (cont.)





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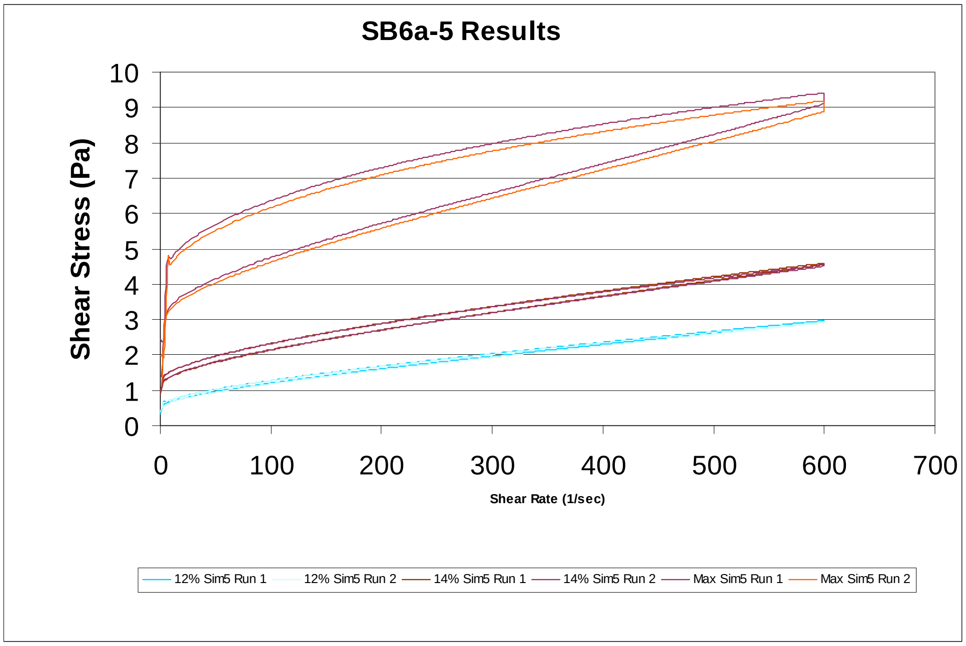


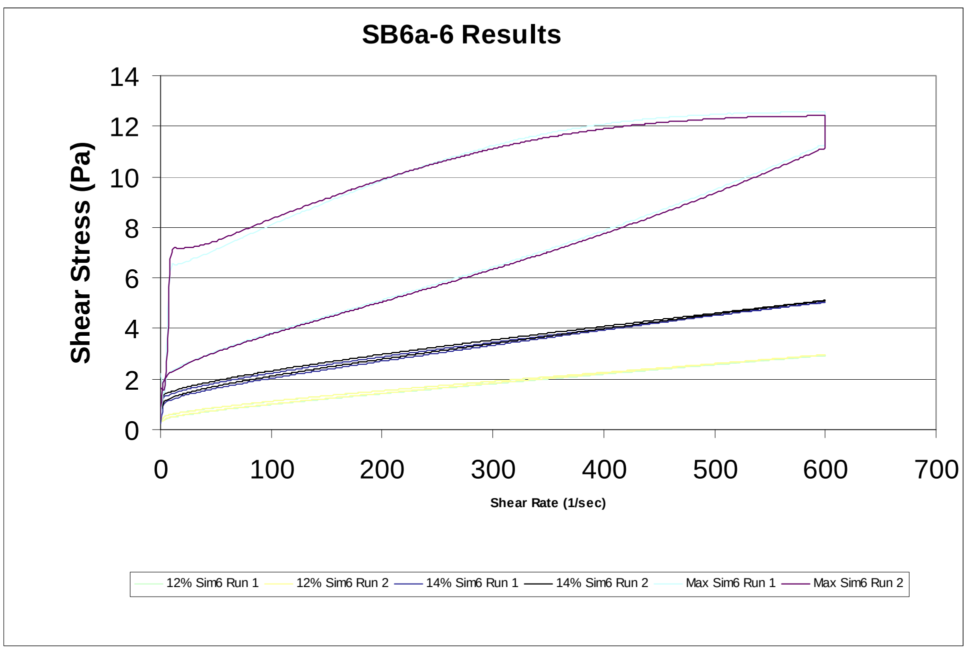
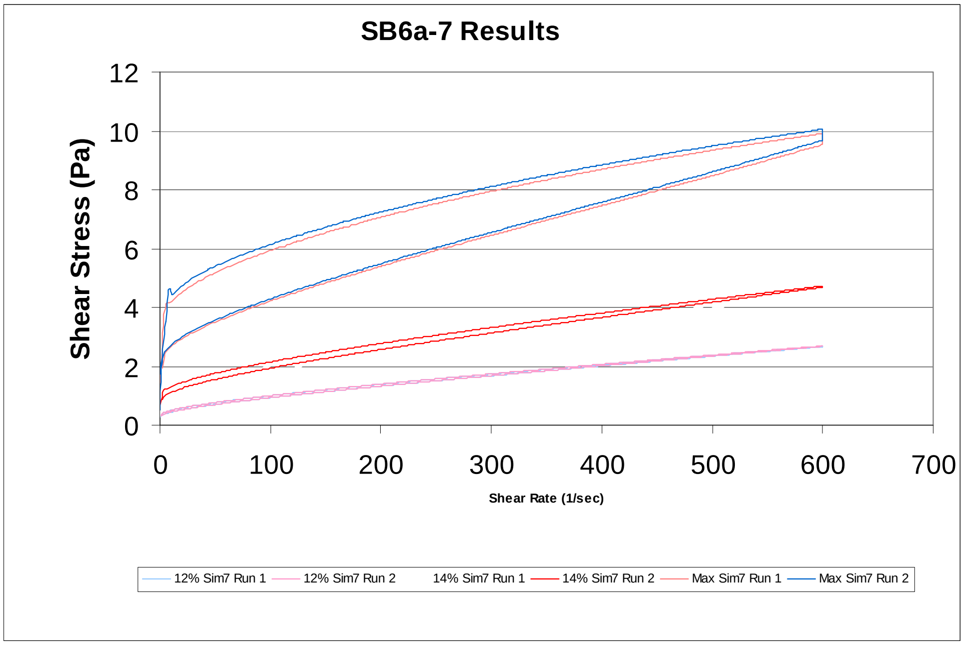
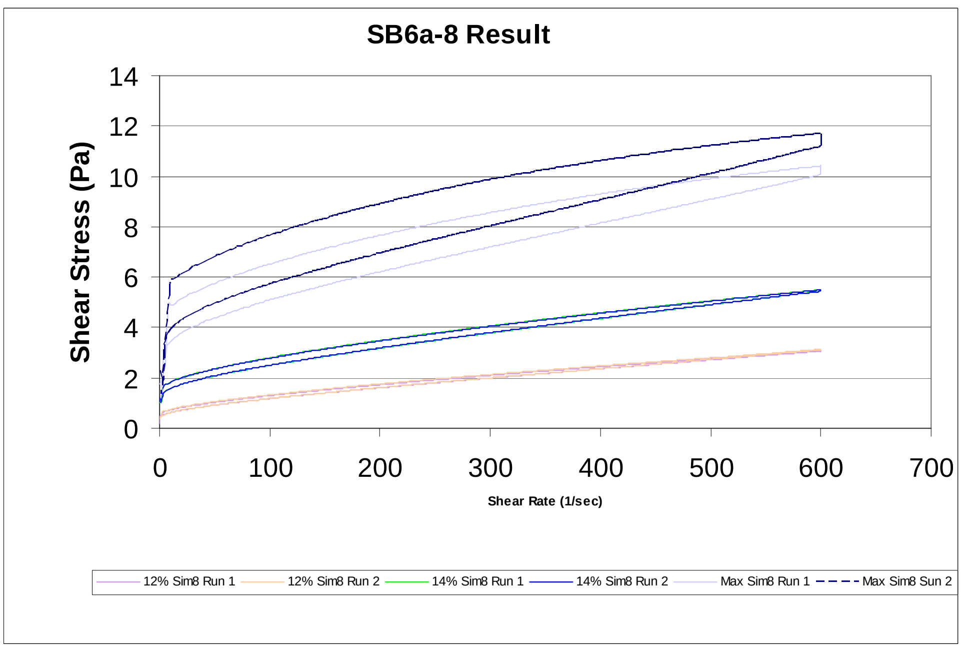


Exhibit A-2: Rheology data for batches 1A-10 (cont.)





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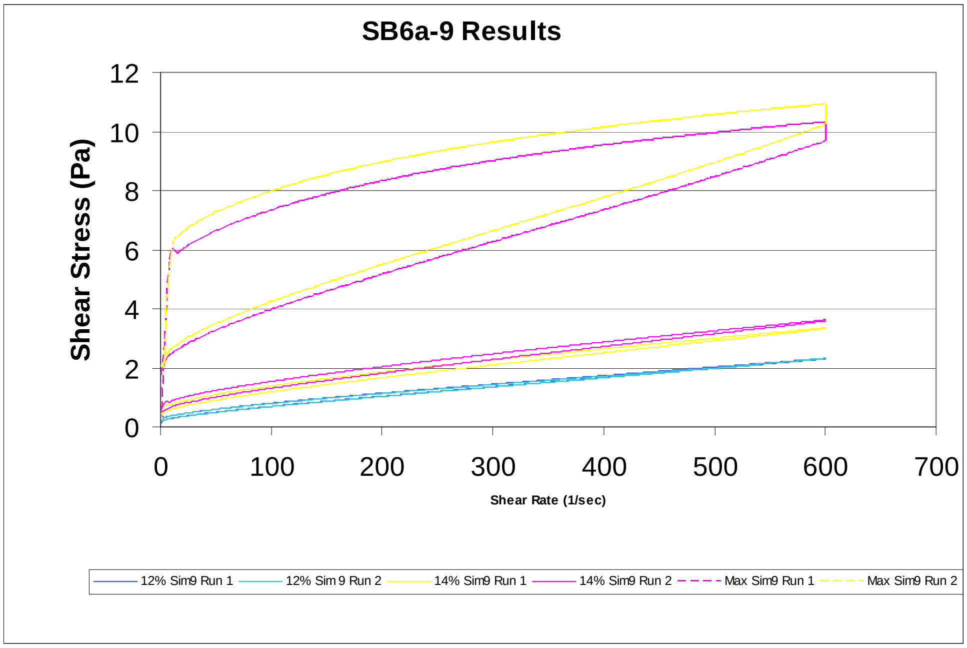

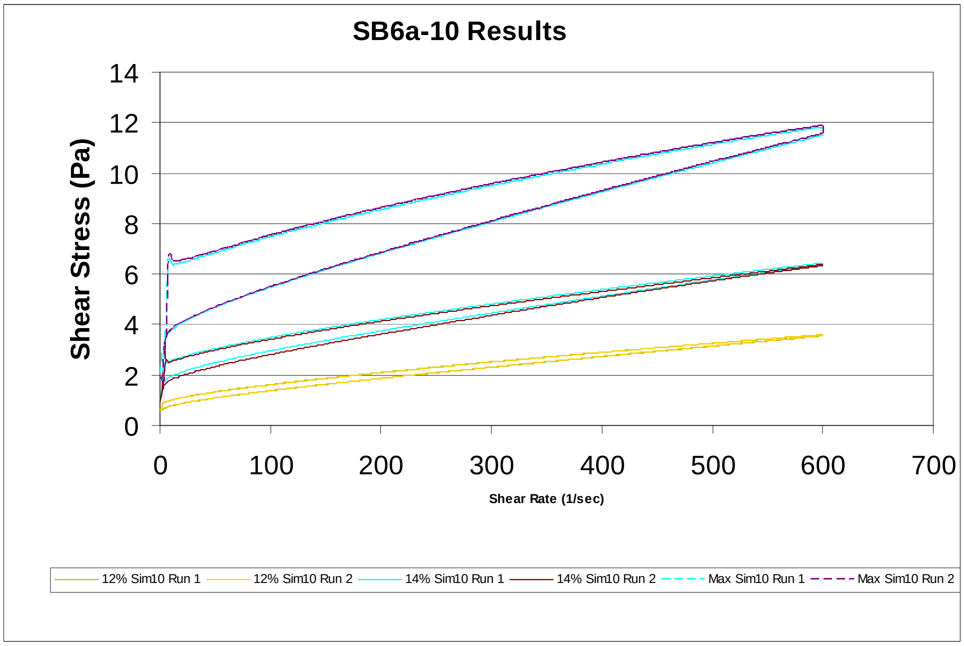

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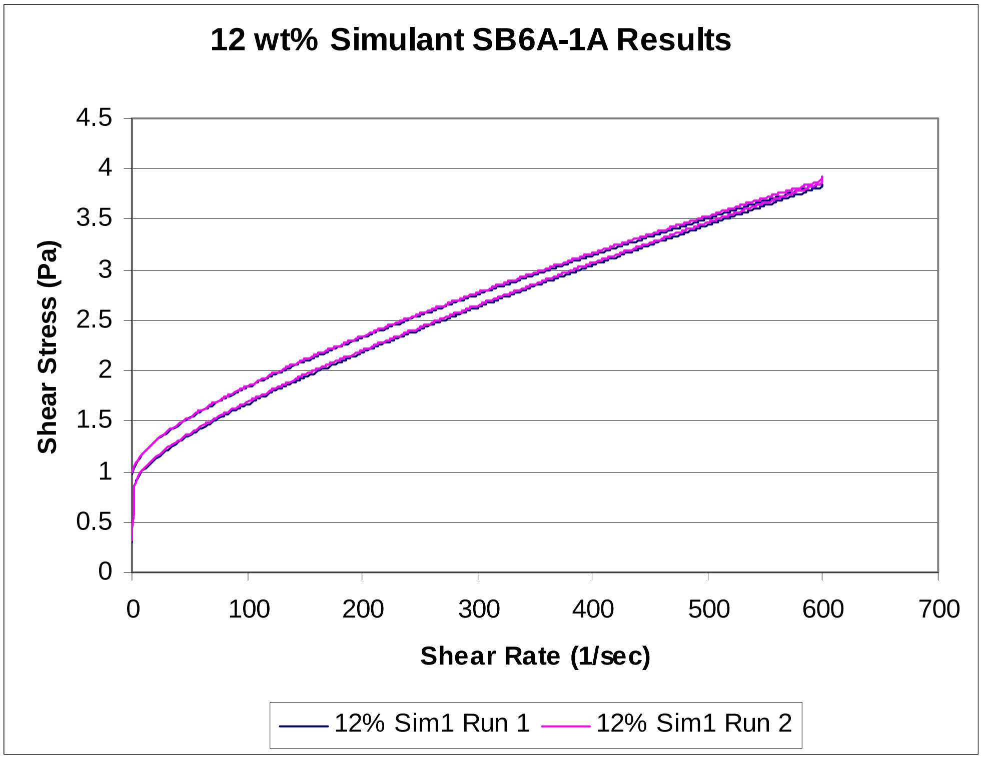

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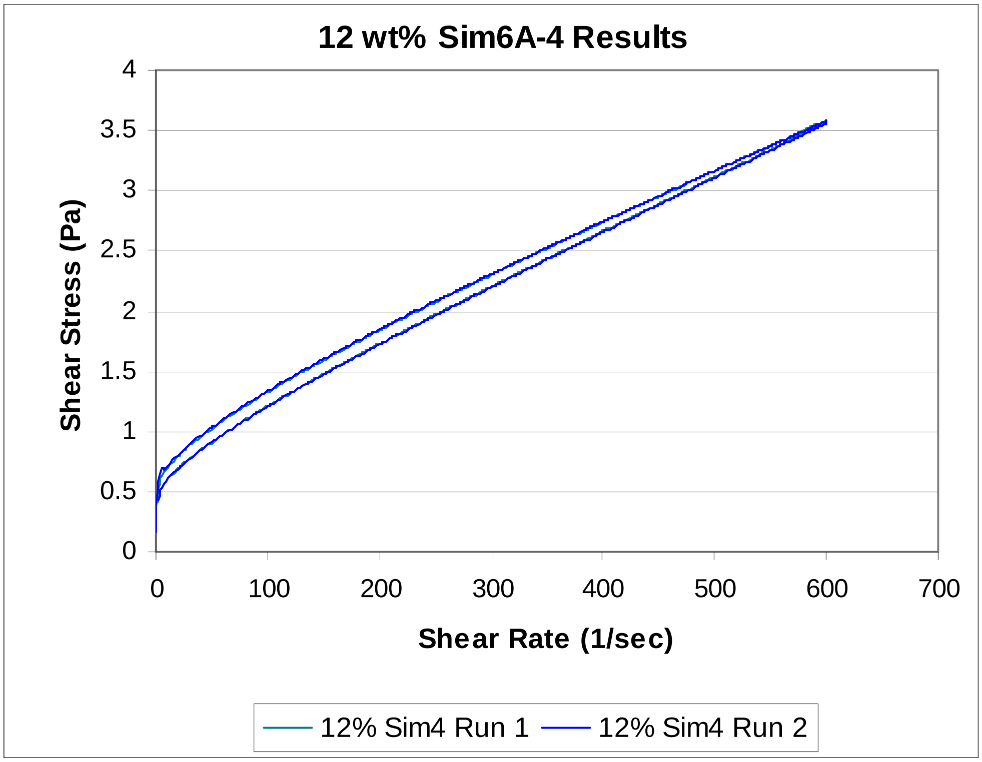

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Exhibit A-2: Rheology data for batches 1A-10 (cont.)

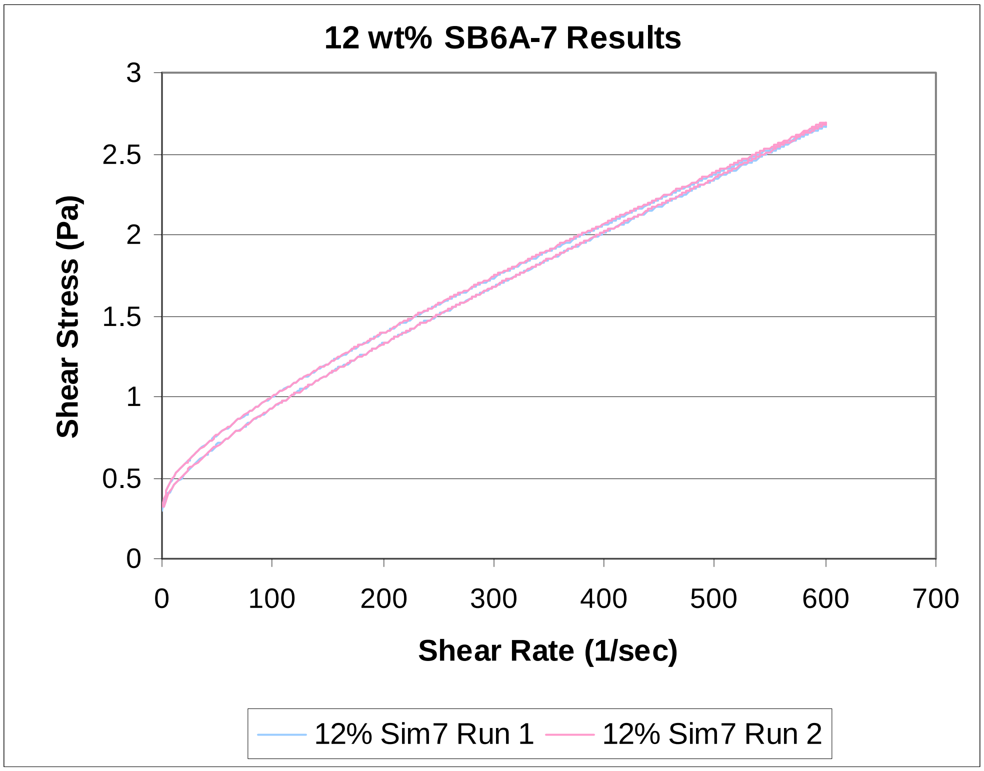
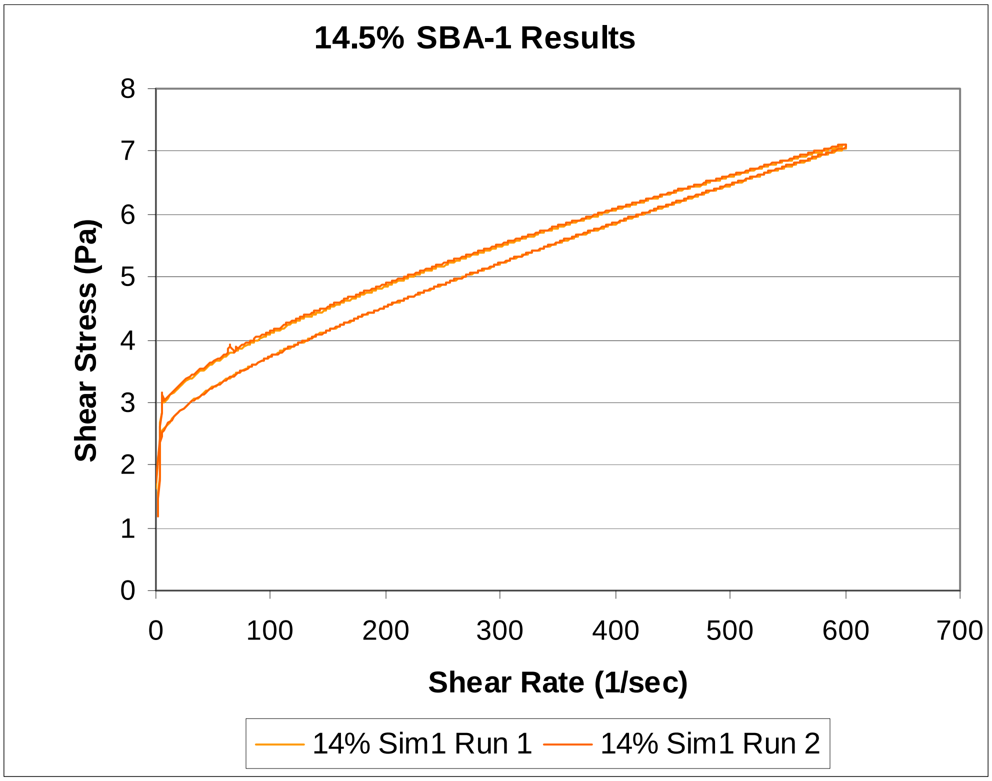
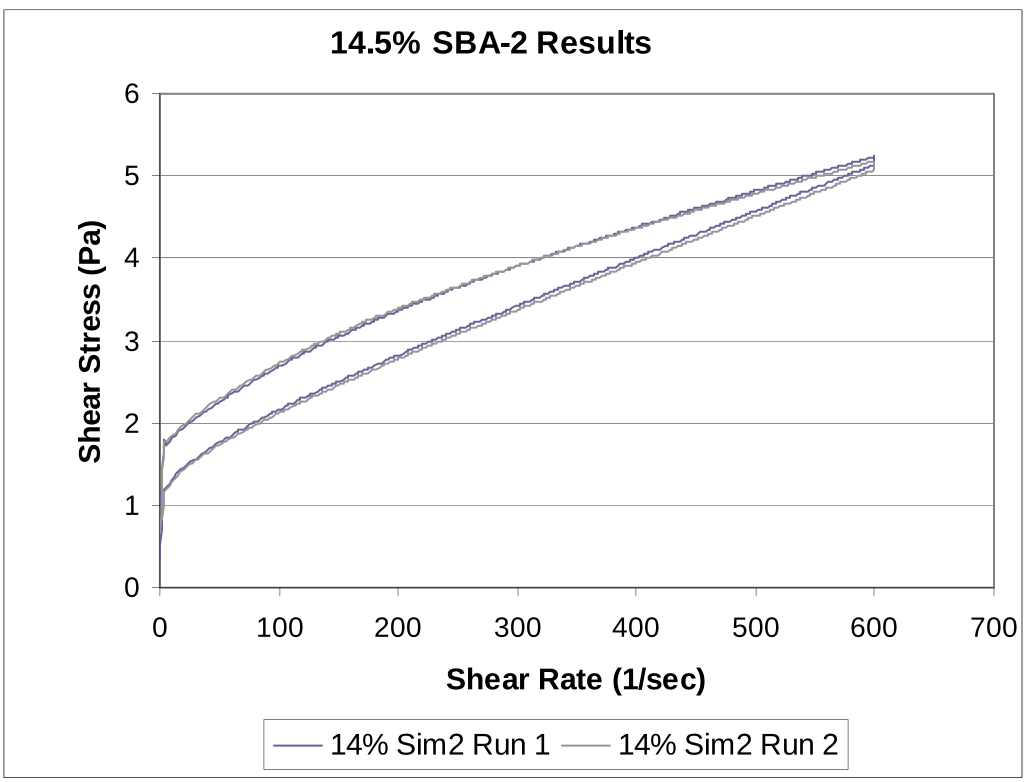


Exhibit A-2: Rheology data for batches 1A-10 (cont.)

Exhibit A-2: Rheology data for batches 1A-10 (cont.)





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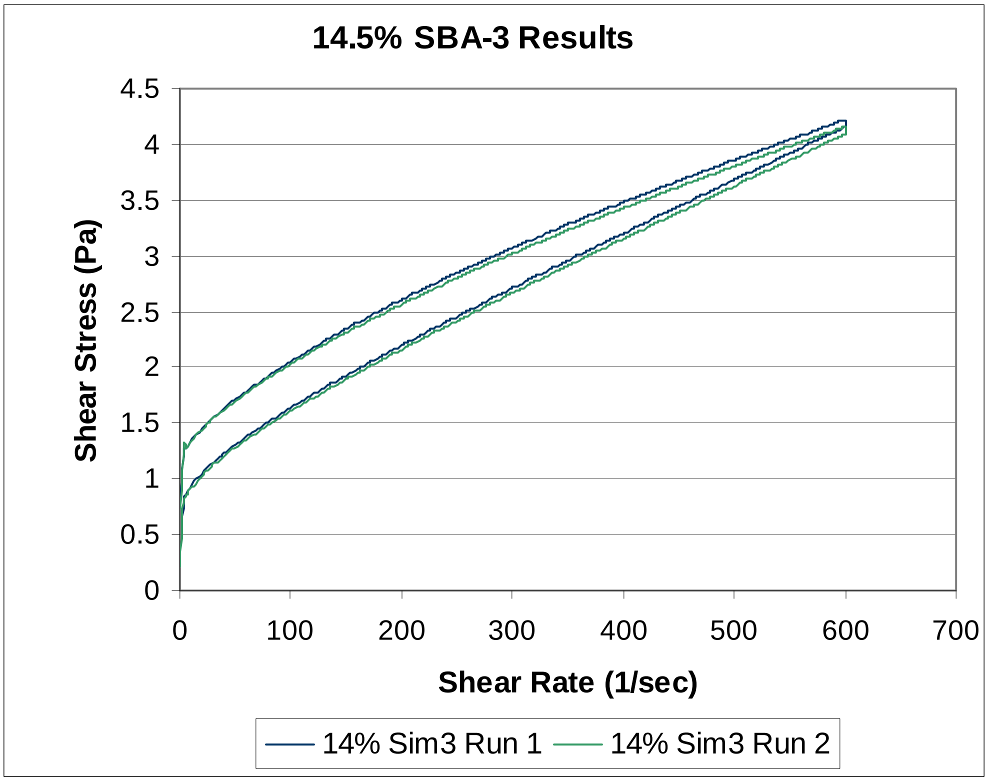

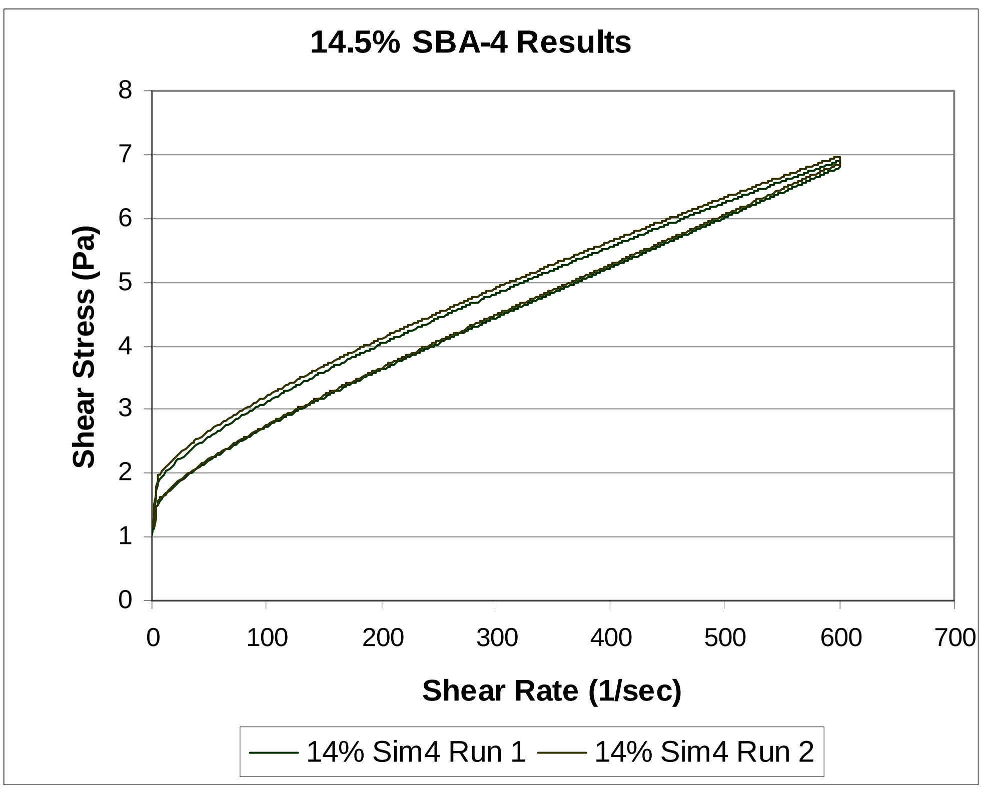

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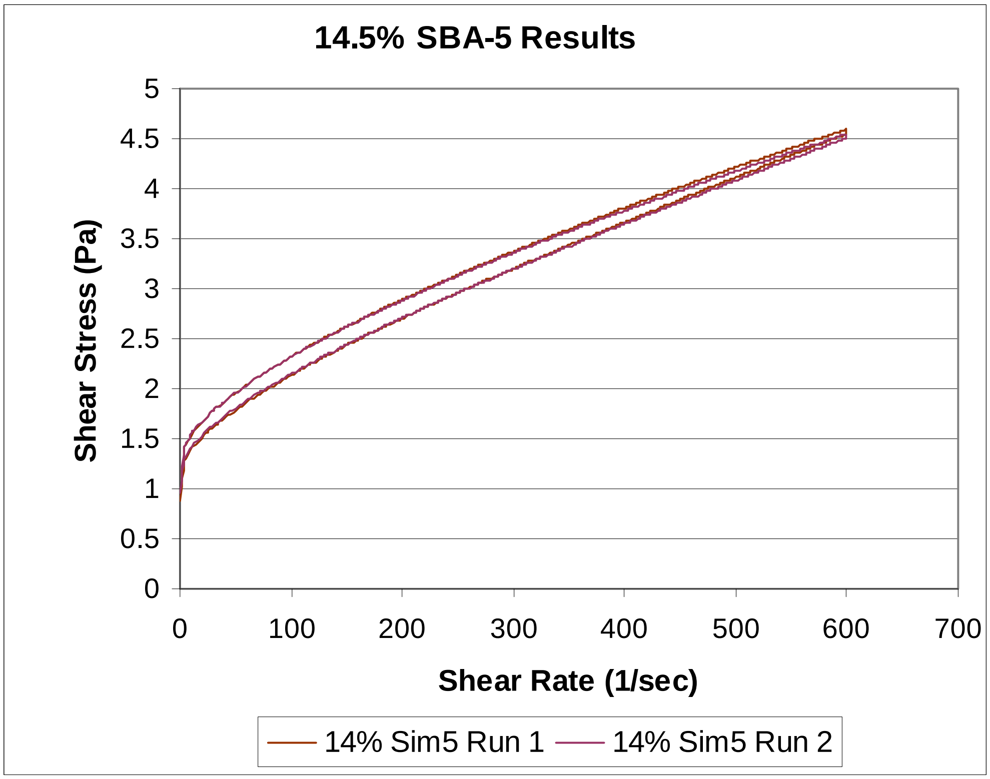

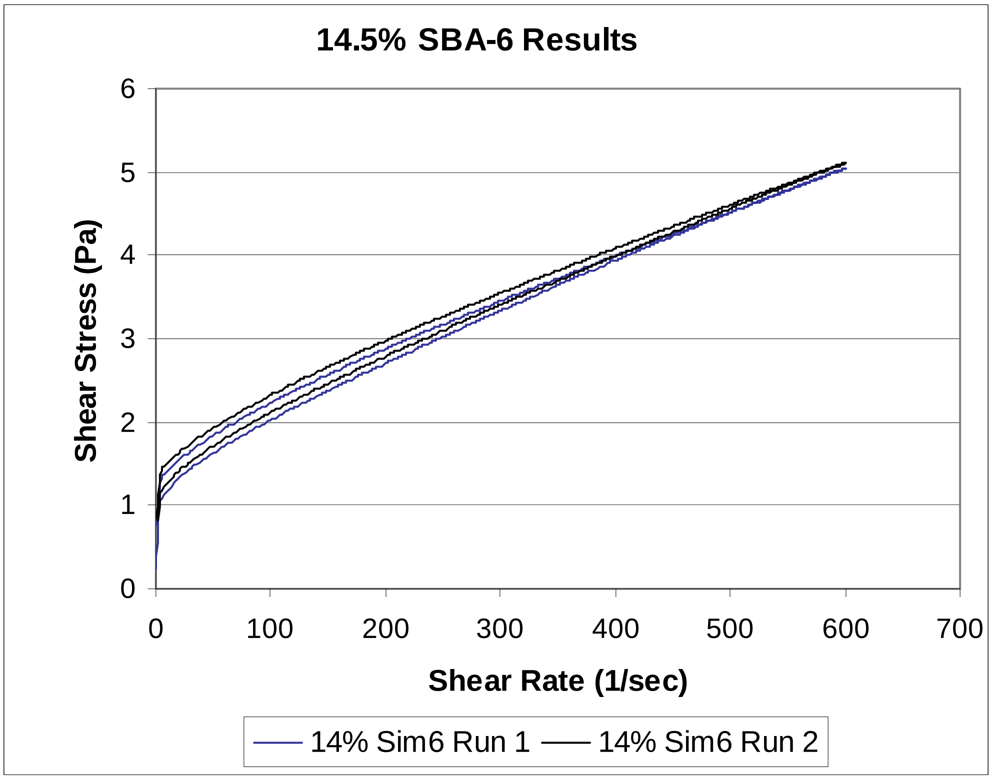

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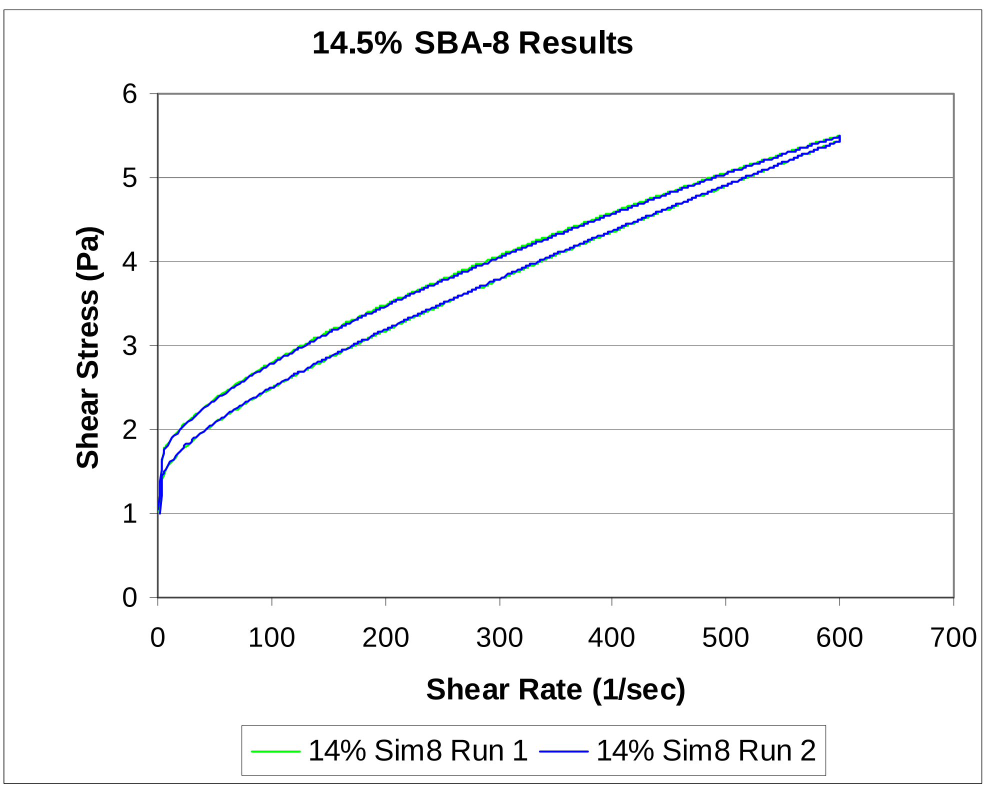

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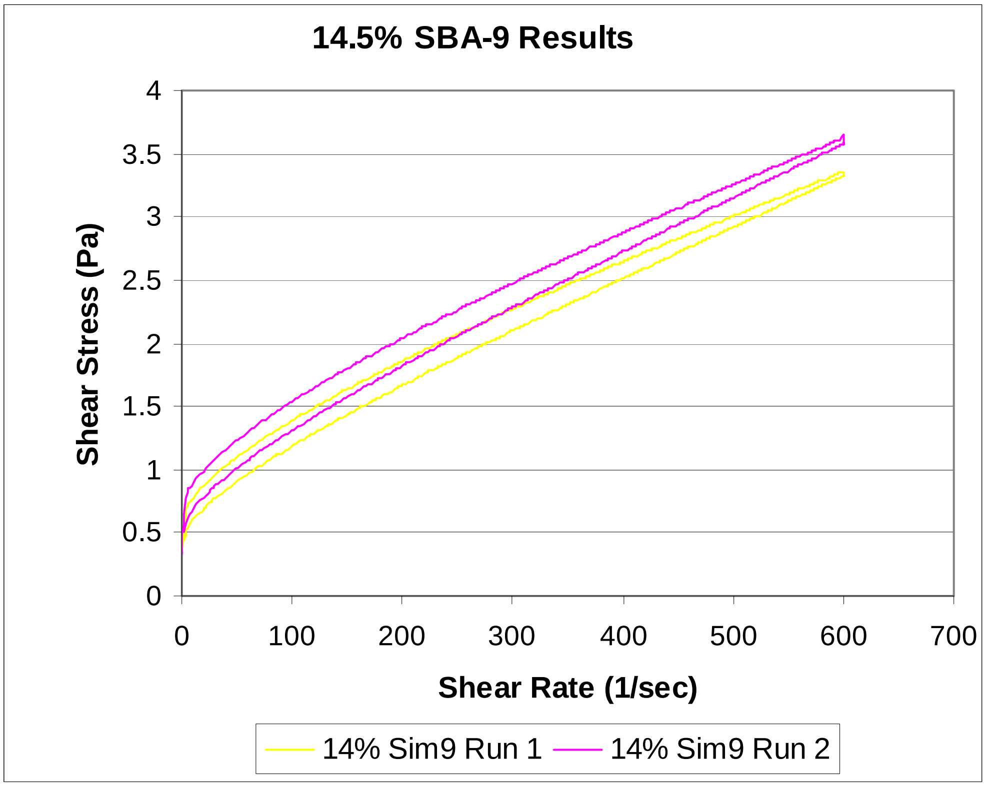

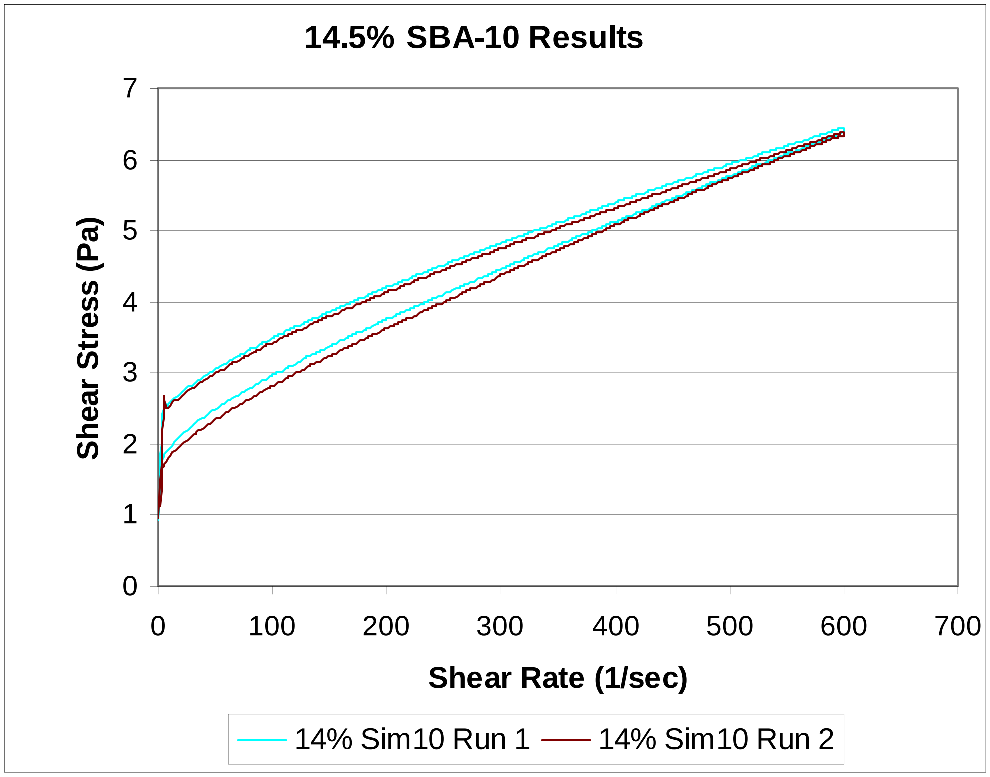

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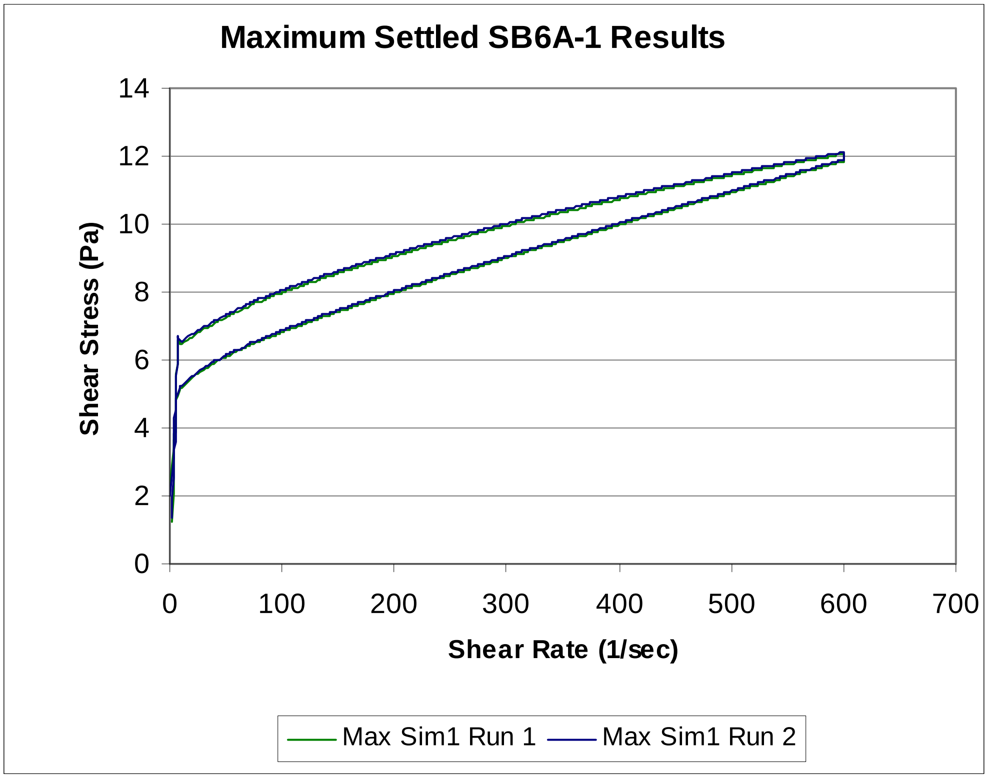

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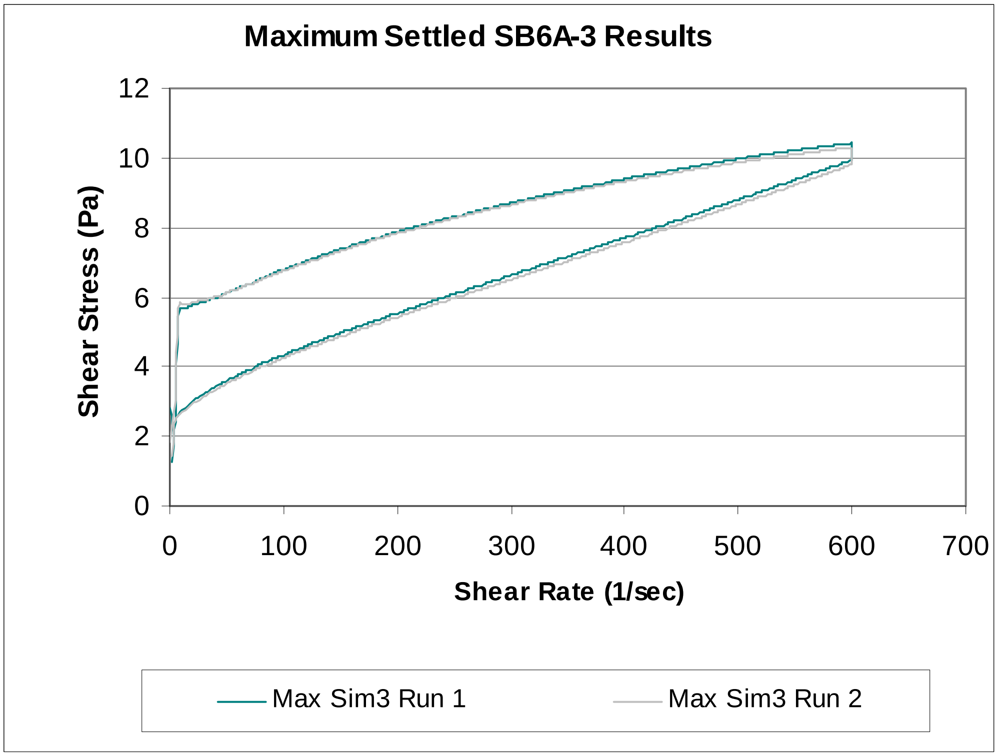

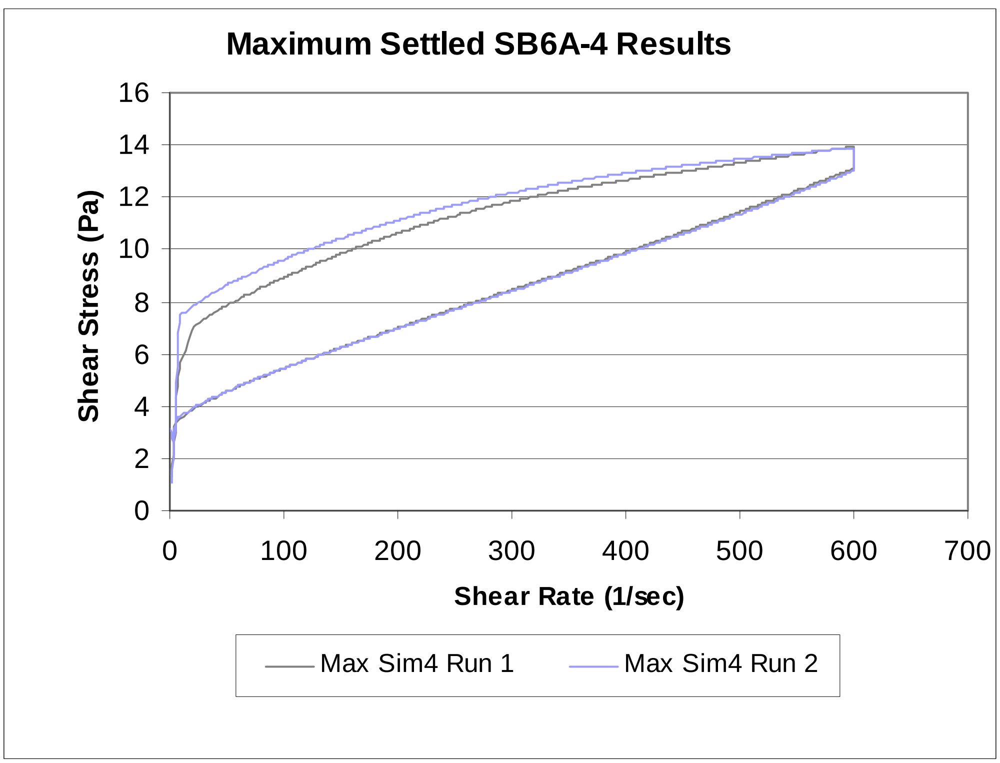

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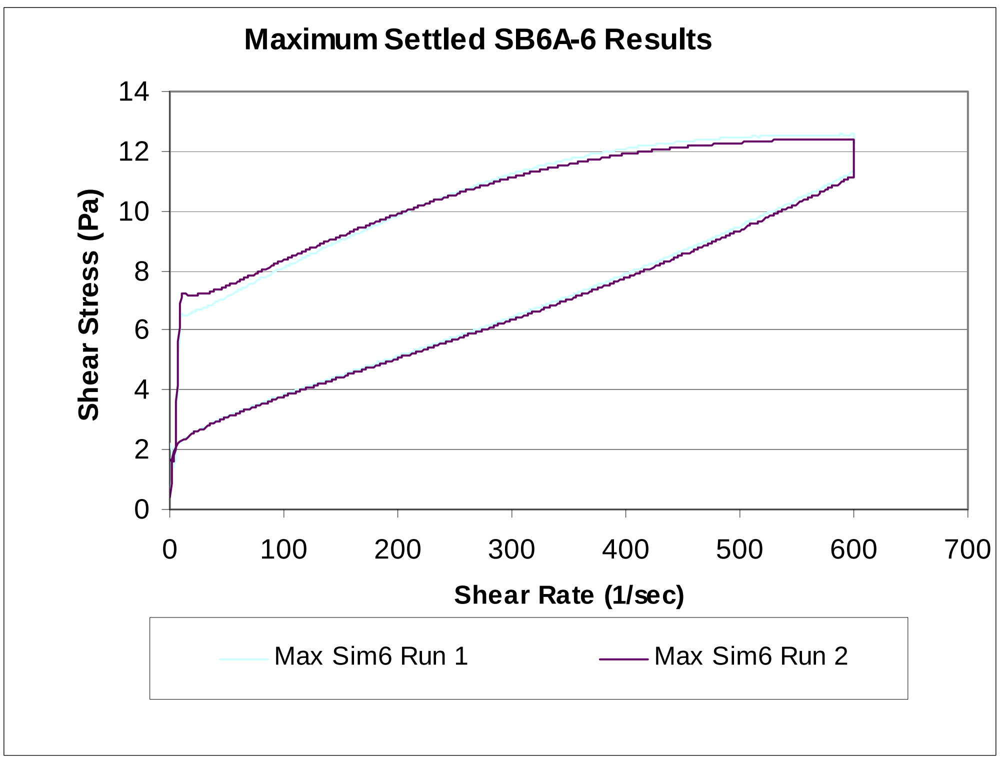


Exhibit A-2: Rheology data for batches 1A-10 (cont.)

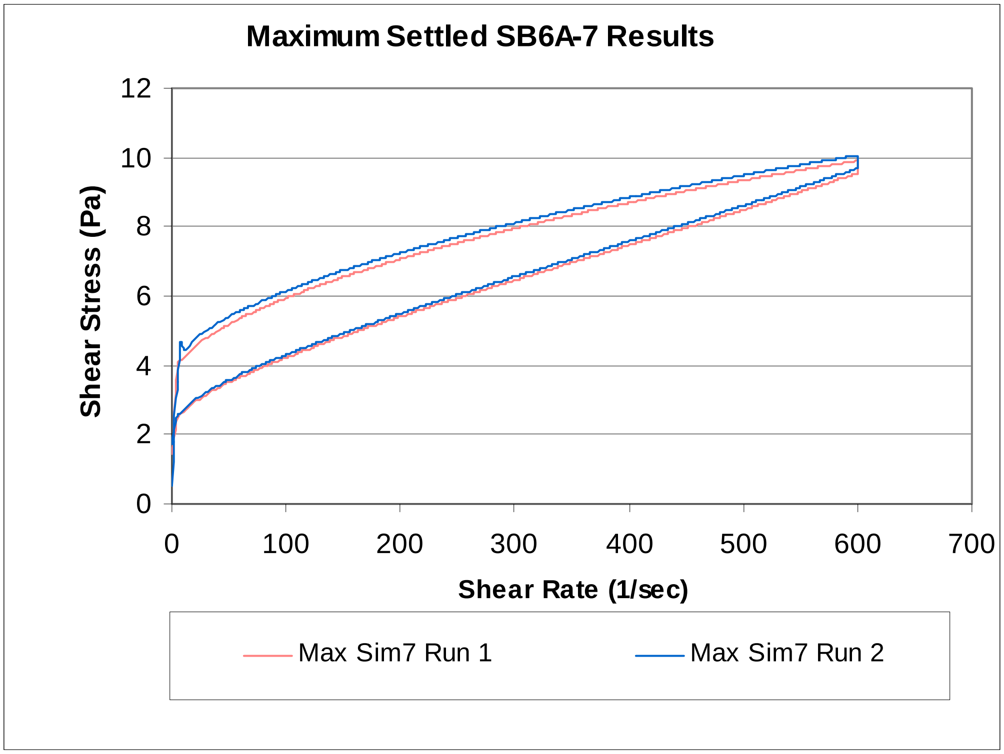
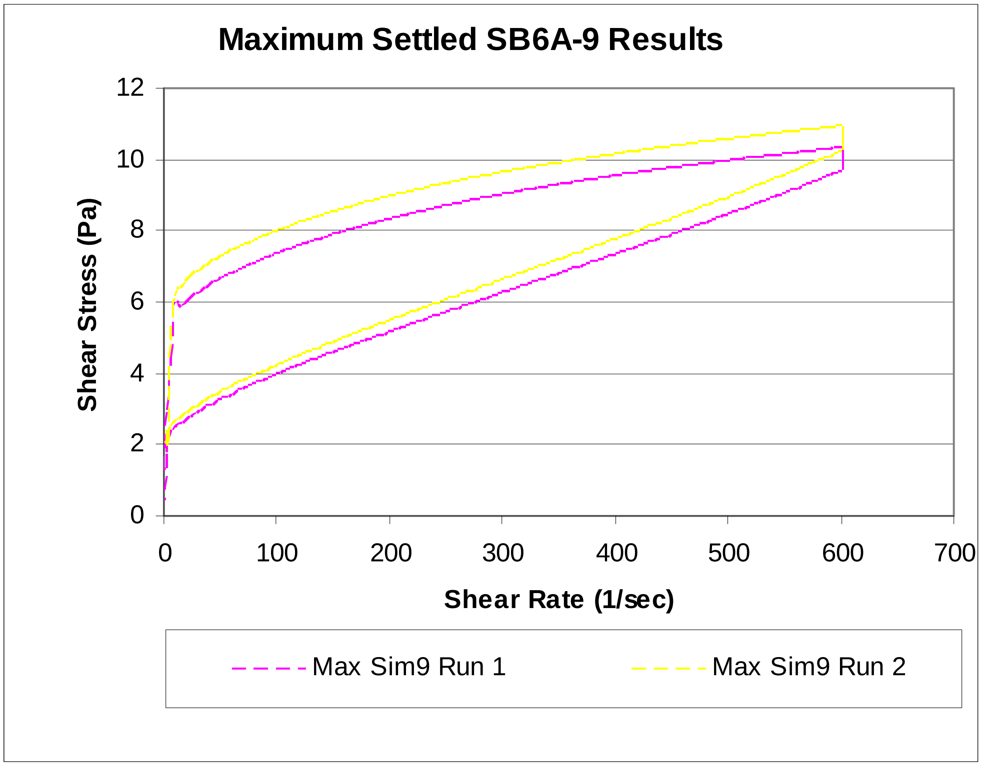
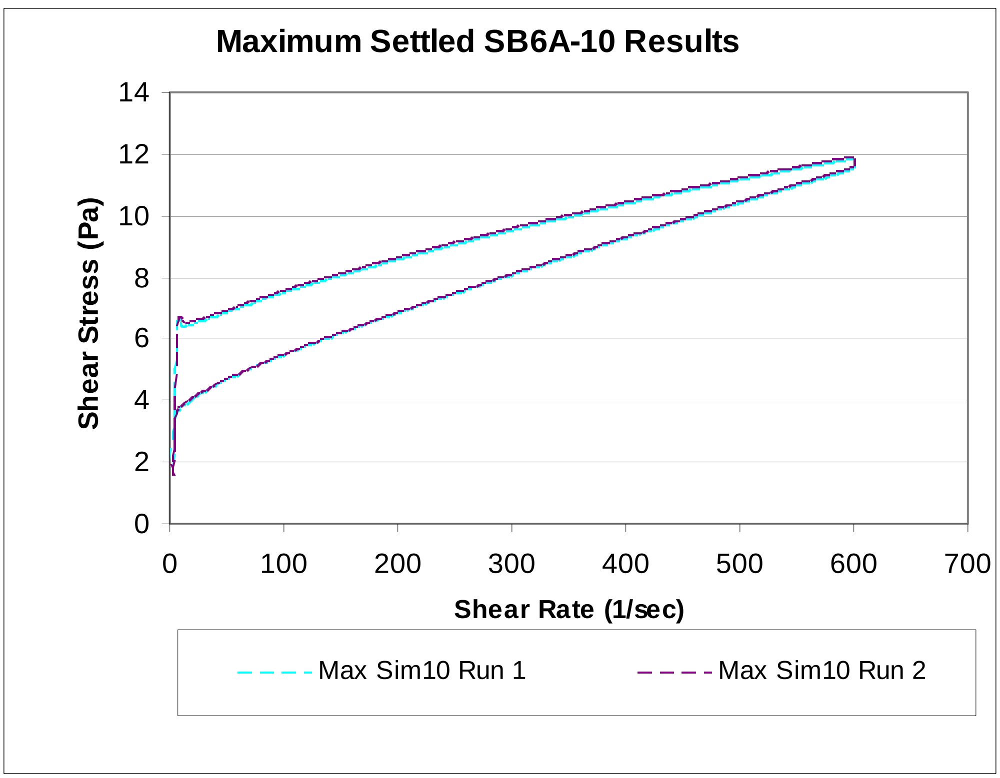


Exhibit A-2: Rheology data for batches 1A-10 (cont.)





Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
C. J. Bannochie, 773-42A
J. M. Gillam, 766-H
B. A. Hamm, 766-H
J. F. Iaukea, 704-30S
R. T. McNew, 704-27S
J. E. Occhipinti, 704-S
D. K. Peeler, 999-W
J. W. Ray, 704-S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
M. E. Stone, 999-W
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
E. W. Holtzscheiter, 704-15S
M. T. Keefer, 766-H
J. D. Newell, 999-W
D. P. Lambert, 999-W
D. C. Koopman, 999-W
A. I. Fernandez, 999-W
B. R. Pickenheim, 999-W