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Revision 0

IMPACT OF URANIUM LEVELS ON SLUDGE BATCH 2 SIMULANT PROCESSING

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May 2004

Immobilization Technology Section
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Prepared for the U.S. Department of Energy Under Contract Number DEAC09-96SR18500

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EXECUTIVE SUMMARY

This study was conducted to address in part whether uranium contributes significantly to processing issues in the Defense Waste Processing Facility. The processing observations for Sludge Batch 2 (SB2) included the ability to transfer process slurries and feed the melter, difficulty maintaining heat transfer in the Slurry Mix Evaporator, and degradation of the operation of the melter. The Savannah River National Laboratory (SRNL) conducted small-scale tests designed to determine the effect of different levels of uranium on sludge processing at the same redox and stoichiometric factor, 0.20 and 130% respectively. Samples used a series of uranium levels, co-precipitated during sludge makeup, in a simulant of SB2. The samples with the different uranium contents were characterized and compared with each other before and after a simulated SRAT cycle process.

The following observations and conclusions were drawn from this study.

- Co-precipitation of U during simulant sludge makeup results in the formation of Clarkeite, $Na((UO_2)O(OH))$, a hydrated uranate containing U(VI), as the final uranium species. This same species has been identified in actual tank waste for SB2.

- There is no increase in calculated acid demand at room temperature as a result of increasing levels of U in SRAT feed. Whether or not there is an impact on acid demand at elevated temperature or in the presence of mixed acids has not been addressed.

- Essentially no soluble U was found in the SRAT products with pH values above pH 6. This is consistent with observations from SRNL Shielded Cells SRAT cycles with SB2/3 blended waste[17] and SB3 waste[18] which did see soluble U in the SRAT products but which had final pH's below 6. Since DWPF operated SB2 processing at approximately pH 5.5, they should have seen more soluble U and potentially thinner SRAT products.

- Different U species can be produced in the SRAT product suggesting the potential for some U redox activity. The primary species, $U_2O_7^{2-}$ contained fully oxidized U(VI), while one product contained the mixed U oxidation state species $U_3O_9^{2-}$. The impact of redox target on the SRAT product U species could not be addressed since only a single redox target was studied.

- XRD data suggests there was some dissolution and re-precipitation of U as a result of SRAT processing since the SRAT product U-containing species were fine and not fully crystalline.

- SRAT vessel contents entrain gas and the volume increases during processing when the temperature is raised from 93 to 100 °C, and the degree of expansion is greatest at the highest levels of U (Batches 11.25 and 15).

- All six sludges and seven SRAT products were *thixotropic* slurries, i.e. the apparent viscosity decreased with time under shear on a time scale of ten minutes. This produced down ramp flow curves that were always below the up ramp flow curves.

- The six sludges and seven SRAT products were generally *pseudo-plastic* slurries, i.e. the apparent viscosity decreased with increasing shear rate. There were some transient phenomena early in some of the up ramp flow curves during which this was not true.

- The six sludges and seven SRAT products were relatively thin and free-flowing slurries that when shaken vigorously did not retain any significant quantity of air bubbles.

- Rheological properties of the six new simulants were effectively independent of the time since preparation over a time scale of one to six weeks.

- The six new simulants had rheological properties that were bounded by those of the two Batch 7.5 preparations. This indicates that the impact of co-precipitated U on rheology was no more significant than other variations in properties that occur during simulant preparation.

- SRAT product samples showed more anomalous rheological behavior than the starting sludges. This was seen in the occurrence of more transient phenomena in the up ramp flow curves. There was also a greater spread in the rheological results for the seven SRAT products than for the six starting sludges. This indicated that SRAT processing had a variable impact on rheology.

- Both the SRAT product yield stress and consistency were found to increase with an increase in uranium concentration in a statistically significant manner.

- Transient phenomena (humps) in the up flow curves never re-occurred when a sample in the rheometer was run through a second up flow curve.

- The impact of SRAT processing on rheology was most apparent in the results for the Batch 11.25 and 15 slurries. These slurries thickened significantly during SRAT processing. SRAT products have generally been thinner than the starting sludges in previous work.

There does not appear to be a straightforward relationship between the level of uranium in the feed, at least to the degree we were able to isolate this contribution from other factors such as particle size, and the processing behavior of the sludge. There are still uncertainties related to uranium and the following recommendations may help address these issues.

- Evaluation of the impact of lower pH during the SRAT cycle on the uranium solubility in the SRAT product may help determine if a significant dissolution of uranium has an impact on the rheological properties of the material. This may help us gain a better understanding of the relationship between rheological behavior and plant operational issues.

- Based upon the uranium species produced in the SRAT product ($U_2O_7^{2-}$ and $U_3O_9^{2-}$), it may be useful for melter operations to understand how the redox target (ratio of nitric acid to formic acid) impacts the uranium species formed during SRAT processing. A series of SRAT tests varying the acid ratios may address this issue.

- Evaluate the impact of particle size variations on the starting sludge rheology as well as the resulting SRAT product.

- Begin to characterize the tank waste for particle size distribution to develop an understanding of the impact of this parameter on processing behavior and assess the variability of this parameter in various samples received for qualification and study. Previous methods involving extremely high dilutions into unmatched matrices, i.e. water, for

Microtrac analysis may alter the particle size of the sludge solids. Installation of a Lasentek instrument in the SRNL Shielded Cells would address this shortcoming.

- Characterize more actual tank waste solids and SRAT product solids produced from actual tank waste by XRD to develop a better understanding of the species present and formed as a result of processing. This information can then be related back to processing issues as they arise in the plant to help explain what may be causing any given issue.

- The scale of sludge makeup should be larger than the 1L scale used in this study. Samples taken for analyses prior to completion of each slurry represent too large a fraction of the total material and results in unnecessary variability.

- The scale of SRAT cycle simulations should be larger than 300 g. At this level noble metal additions are miniscule and acid addition rates are very low leading to considerable variability and potential error.

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LIST OF ACRONYMS

Å	Angstrom (10^{-10} meters)
ACTL	Aiken County Technical Laboratory
ASP	Analytical Study Plan
cfm	cubic feet per minute
CETL	Clemson Environmental Technology Laboratory
CPC	Chemical Processing Cell
DWPF	Defense Waste Processing Facility
eq/L	Equivalents per liter
GC	Gas Chromatograph
IC	Ion Chromatography
ICP-AES	Inductively Couple Plasma – Atomic Emission Spectroscopy
L	Liter
M	Molar
mn	Mean diameter of the number distribution
MnO_2	Manganese dioxide
mv	Mean diameter of the volume distribution
PNNL	Pacific Northwest National Laboratory
RSD	Relative Standard Deviation
SB2	Sludge Batch 2
sccm	Standard cubic centimeters
scfm	Standard cubic feet per minute
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
Std. Dev.	Standard Deviation
TIC	Total Inorganic Carbon
TTQAP	Task Technical and Quality Assurance Plan
wt %	Weight percent
XRD	X-ray Diffraction

1.0 INTRODUCTION AND BACKGROUND

The Defense Waste Processing Facility (DWPF) began processing Sludge Batch 2 (SB2) in December of 2001. Since the introduction of the first SRAT batch of SB2, processing issues have been observed in the Sludge Receipt and Adjustment Tank (SRAT), Slurry Mix Evaporator (SME), Melter Feed Tank (MFT) and the melter. These issues coincided with the start of Batch 209, the first full batch from SB2[a5]. The issues involved the ability to transfer process slurries and feed the melter, difficulty maintaining heat transfer in the SME, and degradation of the operation of the melter. One of the primary differences between Sludge Batch 2 and the previous Sludge Batches is the increased content of uranium.

The Savannah River National Laboratory (SRNL) was requested by DWPF via Technical Task Request HLW/DWPF/TTR-02-0035 to determine if the processing issues are related to the elevated levels of uranium in SB2[1]. The work reported here is intended to address only a portion of TTR-0035, specifically the impact of uranium on Sludge Batch 2. This work is governed by a Task Technical and Quality Assurance Plan (TTQAP)[2] and an Analytical Study Plan (ASP)[3].

SRNL conducted small-scale tests designed to determine the effect of different levels of uranium on sludge processing at the same redox and stoichiometric factor, 0.20 and 130% respectively. Samples used a series of uranium levels in a simulant of SB2. The samples with different uranium contents were compared with each other before and after undergoing a simulated SRAT cycle process.

Documented in this report are:

- Preparation and evaluation of SB2 simulants containing a series of depleted uranium concentrations.
- Demonstration of the DWPF SRAT process using SB2 based simulants with varying levels of uranium.
- Rheological properties of uranium containing SB2 simulants before and after SRAT processing.
- Comparison of the rheology with other SB2 simulants.
- Resolution of several issues raised in the previous work with uranium[5].

[a] Note: Batch 208 was actually the first batch of SB2.

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2.0 DEPLETED URANIUM SIMULANTS

2.1 Approach

2.1.1 Simulant Preparation

A series of six sludge simulants with five levels of depleted uranium were prepared for this study. Samples were targeted with no uranium content, 3.75, 7.5, 11.25, and 15 wt % of uranium (total dried solids basis). The 7.5 wt % target sludge corresponds to the approximate level of uranium determined to be in the actual Sludge Batch 2 feed[4]. The 15 wt % level represented a high concentration to determine if increasing the content of uranium impacts simulant properties during Chemical Processing Cell (CPC) processing. The initial work conducted in this area indicated the 0-15 wt % interval may have bracketed the range of uranium content that adversely impacts the physical properties of the slurry[5]. In light of this, two additional uranium levels were included in this study to better understand this phenomenon. To evaluate the degree of variability in sludge makeup, duplicate center points targeted at 7.5 wt % uranium were prepared. Additionally, one sludge, at nominally 3.75 wt % uranium, was processed in replicate SRAT cycles.

The sludge batch preparations are designated Batch 0, for the batch without uranium; Batch 3.75, for the batch containing nominally 3.75 wt % uranium; Batch 7.5i, the first nominally 7.5 wt % uranium batch; Batch 7.5ii, the second nominally 7.5 wt % uranium batch; Batch 11.25, for the batch containing nominally 11.25 wt % uranium; and Batch 15, for the batch containing nominally 15 wt % uranium.

Uranium was added during Phase 1 of the preparation protocol[b,6] and precipitated along with iron (Fe) and nickel (Ni) in the presence of manganese dioxide (MnO_2). Appendix A contains a sample sludge makeup procedure, and the recipes for targeted compositions these sludge preparations are given in Appendix B. As the uranium content increased, there was a proportional reduction in the metal ion and oxide additions of the other reagents with the exception of sodium (Na). Reagents added for their anion contribution were held constant throughout the recipes.

During precipitation the slurry temperature was maintained between 35 – 40°C with a jacketed vessel connected to a recirculating water bath. Sludge was transferred from the jacketed preparation vessel to a bottle and allowed to settle. Phase 2 sampling was not conducted. Phase 3 of the preparation began when the settled sludge volume dropped to approximately 1 L, the supernate was removed and the remaining slurry agitated with 3.6 L of pH 10.5 adjusted water for 30 minutes and allowed to settle again. This process was repeated for four consecutive washes until the soluble solids value was below 0.15-0.20 wt % and/or the soluble Na concentration was below 0.025M. Table 2-1 provides the inductively coupled plasma – atomic emission spectroscopy (ICP-AES) data for some key elements.

The Batch 7.5i Phase 3 slurry was more dilute than the Batch 7.5ii Phase 3 slurry. An average of the Fe, Mn, Ni, and U ratios between Batch 7.5i and Batch 7.5ii yields 0.95, while a ratio of the total solids between these two batches yields 0.92, a reasonably close agreement. Differences observed in the rheology of these two batches will be discussed in Section 2.1.2 of this report.

[b] Phase 1 involves precipitation of Mn, Fe, and Ni metal salts as hydroxides/oxides. Phase 2 involves sampling and analysis for wt % total solids and Fe, Mn, Na, and Ni concentrations. Phase 3 involves multiple washing of the slurry. Phase 4 involves the addition of all remaining trim reagents. Phase 5 is the final analysis of the slurry.

Table 2-1. Phase 3 Slurry Elemental Characterization Data in mg/kg Slurry (Std. Dev., %RSD)

Batch No.	Fe	Mn	Ni	U
0	52,400 (1160, 2.2)	5420 (70, 1.3)	3080 (56, 1.8)	<1000
3.75	49,400 (250, 0.5)	5300 (15, 0.3)	2990 (68, 2.3)	8690 (190, 2.2)
7.5i	45,700 (150, 0.3)	4930 (35, 0.7)	2770 (10, 0.4)	15,900 (58, 0.4)
7.5ii	47,700 (210, 0.4)	5010 (12, 0.2)	3080 (280, 9.2)	16,600 (58, 0.3)
11.25	45,300 (150, 0.3)	4860 (32, 0.7)	2760 (120, 4.4)	25400 (950, 3.8)
15	38,800 (100, 0.3)	3980 (12, 0.3)	2310 (21, 0.9)	31,500 (830, 2.6)

Table 2-2 provides the soluble Na and U levels measured in the supernate liquid of the fourth wash, while Table 2-3 summarizes the wt % total and soluble solids.

Table 2-2. Phase 3 Supernate Elemental Characterization Data in mg/L Supernate (Std. Dev., %RSD)

Batch No.	Na	U
0	566 (6, 1.1)	<10
3.75	337 (8, 2.3)	<10
7.5i	325 (10, 2.9)	<10
7.5ii	447 (5, 1.1)	<10
11.25	404 (20, 4.9)	<10
15	498 (8, 1.5)	<10

Table 2-3. Phase 3 Wt % Total and Soluble Solids (Std. Dev., %RSD)

Batch No.	Total Solids	Soluble Solids
0	10.2 (0.15, 1.5)	0.11 (0.01, 10.2)
3.75	10.8 (0.26, 2.4)	0.11 (0.01, 5.1)
7.5i	10.9 (0.10. 0.9)	0.11 (0.01, 9.1)
7.5ii	11.8 (0.21, 1.8)	0.13 (0.01, 4.6)
11.25	12.5 (0.12, 0.9)	0.10 (0.01, 5.6)
15	12.0 (0.25, 2.1)	0.12 (0.02, 13.1)

Following characterization of the sludges prepared during Phase 3, the remaining trim reagents were added separately, with 15 minutes agitation between additions, to each slurry batch (refer to Appendix A). It was necessary to adjust the recipe trim additions to account for the solids removed during Phase 3 sampling. The following adjustment factors were calculated for each recipe trim component shown in Table 2-4.

Table 2-4. Adjustment Factors for Trim Reagents Shown in Appendix A Recipes

Batch No.	Adjustment Factor
0	0.9471
3.75	0.9484
7.5i	0.9481
7.5ii	0.9474
11.25	0.9494
15	0.9544

2.1.2 Rheology

Rheological characterizations of sludges and SRAT products were accomplished using the Haake RV20/M5 rheometer located in the 773-A, B-111 radiohood. Rheological measurements were not made on, nor a sample pulled, at the minimum pH point of the SRAT cycle due to the smaller scale of these SRAT cycles than those in previous work[5]. Measurements were made with a viscosity standard to ensure that the rheometer was performing within expected limits. No issues with rheometer performance were noted during the test period. Flow curve data given in this report have not been corrected for slip, non-Newtonian behavior, etc.

Slurry samples containing depleted uranium were characterized with the MV1 concentric cylinder sensor. A shear rate range of 0-500/second was used for the routine measurements. The shear rate was ramped from 0-500/s over five minutes, held at 500/s for one-half minute, and then ramped down from 500-0/sec over five minutes. (A few tests designed to look at rheological anomalies in some of the samples were performed using a smaller shear rate range and shorter times.) Rheological measurements were made at 25°C. A jacket around the sample beaker was connected to a constant temperature, circulating, water bath to maintain temperature control.

Sufficient sample volume was provided to make two independent measurements without reusing any sample, except in the case of the SRAT product from the second run with the Batch 3.75 simulant. In that one case, the replicate measurement used a small amount of material recovered from the initial measurement mixed with fresh material. None of the DU slurry samples were observed to form a clear supernate layer after fifteen minutes at rest. Therefore, partial settling of slurry solids during the rheological measurements was not considered to be an issue.

Rheological data were fitted to the *Bingham plastic* fluid rheological equation.

$$\textit{Bingham plastic fluid:} \quad \tau = \tau_{o,B} + \eta_B \cdot D \qquad [1]$$

Where τ is the shear stress, D is the shear rate, $\tau_{o,B}$ is the Bingham plastic *yield stress*, and η_B is the plastic viscosity, or *consistency*. Rheometer data for the shear stress are typically expressed in Pascals, Pa. One Pa corresponds to 10 dynes/cm^2. The Bingham plastic equation tends to give conservative yield stress values, i.e. values greater than the true yield stress of the sample. Regressions were made using

the data analysis tools in Microsoft Excel. Up ramp and down ramp flow curve data were not coincident. Therefore, the up and down ramp data were fitted separately. Significantly nonlinear regions of the flow curves were excluded before performing the regressions.

2.2 Sludge Preparation Results

Following trim reagent additions, each completed sludge was sampled, and chemical and physical characterizations were performed. Results of the characterizations are given in the sections below.

2.2.1 Chemical Characterization

Samples of the final sludge compositions were submitted for ICP-AES analysis to look at total as well as soluble elemental composition. The total analyses are shown in Table 2-5 while Table 2-7 contains the two soluble components, Na and U, which were measured. The final wt % U values varied from the target values by an average of 9% with a standard deviation of 2% and all final U concentrations were lower than the target values while still spanning a range of U concentrations from zero to nearly 14%. Throughout this report, the batches will be referenced based upon their "target" rather than "actual" uranium content for simplicity, but Table 2-5 can be referred to for the actual values. The soluble uranium in the feeds was negligible, but due to refinement of the detection limits since the initial data given in Table 2-2, the level was measurable, on the order of 1-3 ppm. Previous work[5] had an actual U range from zero to 11.4 wt %, also below the target values, but soluble U levels in the starting feeds were not measured.

The Al values were found to be higher than anticipated when the feeds were analyzed. This resulted from the use of $Al(OH)_3 \bullet nH_2O$, 32-35% H_2O, to satisfy the $Al(OH)_3$ recipe request. Apparently this reagent is not 65-68% $Al(OH)_3$ as was assumed in the calculations, but 65-68% Al_2O_3, resulting in an excess of Al in the final sludges.

A comparison of Batch 7.5i and Batch 7.5ii data in Table 2-5 indicates that the former batch is enriched in many Phase 4 reagents (Al, Ca, Cu, K, and Mg) and reduced in Phase 1 species (Fe, Mn, Ni, and U). The Phase 4 trim chemicals were added to produce consistent final total solids values. It is possible that more of the Batch 7.5i was removed prior to trimming than was realized. There were difficulties in weighing the large sludge batches in the hood, hence they had to be bagged for removal from the hood prior to measurement – this operation inserted a degree of uncertainty in the measured masses removed through sampling prior to trim reagent addition.

Table 2-5. Elements in the SRAT Cycle Feeds in Wt % of Total Solids (Std. Dev., %RSD)

Element	Batch 0	Batch 3.75	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Al	10.9 (0.2, 1.5)	10.3 (0.2, 1.6)	9.83 (0.07, 0.7)	9.48 (0.20, 2.2)	8.63 (0.05, 0.6)	8.12 (0.08, 1.0)
Ca	2.24 (0.03, 1.3)	1.98 (0.02, 1.1)	2.10 (0.03, 1.5)	2.07 (0.02, 1.2)	1.91 (0.03, 1.8)	1.72 (0.03, 1.6)
Cu	0.118 (0.014, 12)	0.122 (0.004, 3.6)	0.109 (0.005, 4.8)	0.0796 (0.0014, 1.7)	0.0981 (0.0045, 4.5)	0.0912 (0.0026, 2.8)
Fe	21.0 (0.02, 0.1)	19.2 (0.6, 2.9)	18.3 (0.4, 1.9)	19.3 (0.1, 0.4)	17.7 (0.3, 1.5)	16.6 (0.1, 0.4)
K	0.0417 (0.0020, 4.8)	0.0463 (0.0005, 1.0)	0.0755 (0.0022, 2.9)	0.0667 (0.0011, 1.7)	0.0616 (0.0013, 2.2)	0.0943 (0.0028, 3.0)
Mg	0.109 (0.005, 4.6)	0.103 (0.003, 3.1)	0.0937 (0.002, 2.5)	0.0869 (0.0002, 0.2)	0.0856 (0.0020, 2.3)	0.0790 (0.0017, 2.1)
Mn	2.29 (0.01, 0.2)	2.08 (0.03, 1.5)	2.00 (0.05, 2.3)	2.10 (0.01, 0.3)	1.91 (0.04, 1.9)	1.78 (0.01, 0.
Na	5.97 (0.09, 1.5)	6.37 (0.26, 4.0)	6.66 (0.15, 2.3)	6.83 (0.14, 2.0)	6.83 (0.19, 2.7)	7.20 (0.05, 0.7)
Ni	1.21 (0.002, 0.2)	1.08 (0.05, 4.2)	1.05 (0.02, 2.1)	1.10 (0.01, 0.8)	0.999 (0.016, 1.6)	0.926 (0.003, 0.3)
S	0.211 (0.004, 2.0)	0.194 (0.005, 2.4)	0.197 (0.003, 1.7)	0.213 (0.004, 1.8)	0.168 (0.001, 0.7)	0.174 (0.004, 2.1)
U	<0.074	3.46 (0.04, 1.0)	6.52 (0.12, 1.8)	7.02 (0.09, 1.2)	10.2 (0.05, 0.5)	13.7 (0.04, 0.3)

†1100°C

From the data in Table 2-5 the Fe:Mn ratio for each of the sludge batches can be calculated. These ratios are found in Table 2-6. There was good consistency between theses ratios for the various batch preparations. The targeted Fe:Mn was 9.8. The Fe:Mn in the previous study varied from 7.4 – 8.2[5].

Table 2-6. Ratio of Iron to Manganese in SRAT Cycle Feeds

Batch No.	Fe:Mn
0	9.2
3.75	9.3
7.5i	9.1
7.5ii	9.2
11.25	9.3
15	9.3

Table 2-7. Soluble Sodium and Uranium in SRAT Cycle Feeds in Wt% of Total Solids (Std. Dev, %RSD)

Element	Batch 0	Batch 3.75	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Na	6.74 (0.07, 1.1)	6.57 (0.08, 1.2)	6.86 (0.06, 0.9)	6.76 (0.10, 1.4)	6.70 (0.08, 1.1)	6.91 (0.04, 0.6)
U	<3.54E-04	4.17E-04 (0.03E-04, 0.6)	8.31E-04 (4.95E-04, 60)	4.34E-04 (0.20E-04, 4.7)	7.52E-04 (0.27E-04, 36)	5.32E-04 (0.63E-04, 12)

Note, there was significantly more measured soluble sodium for Batch 0 than total sodium, indicating that one or both of these numbers may have more error than the other Batch data sets.

Samples of each slurry were also submitted for ion chromatograph (IC) analysis of formate, nitrite, nitrate and sulfate. In general the precision of these measurements was poor with relative standard deviations approaching 10% in many instances. For the SRAT acid calculations, an average nitrite and nitrate concentration was selected and used for all of the batches. Formate was not included in the recipes and no formate was measured in the final sludges.

Table 2-8. Supernate Anion Data in mg/kg Slurry (Std. Dev., %RSD)

Batch No.	Formate	Nitrite	Nitrate	Sulfate
0	< 8	8990 (230, 2.5)	4330 (130, 3.0)	1500 (160, 5.2)
3.75	< 8	9010 (0, 0)	3890 (50, 1.3)	1230 (6, 0.5)
7.5i	< 8	7450 (360, 4.8)	3210 (170, 5.4)	1260 (110, 9.0)
7.5ii	< 8	8260 (670, 8.2)	3730 (310, 8.2)	1290 (11, 0.9)
11.25	< 79	8340 (780, 9.4)	3670 (360, 9.8)	1240 (110, 8.7)
15	< 79	8210 (110, 1.4)	3810 (60. 1.5)	1110 (110, 10)
Average	NA	**8380**	**3770**	

Initial samples submitted for total inorganic carbon (TIC) had very poor precision due to sub-sampling issues with heterogeneous particles; hence the mass of carbon was calculated from the added $CaCO_3$ and Na_2CO_3 for each sludge slurry. Table 2-9 shows the inputs for each sludge batch, the mass of the final slurry, and the calculated carbon concentration used in the acid calculation for each batch's SRAT cycle.

Table 2-9. Acid Calculation Inputs for TIC

Batch No.	Mass of $CaCO_3$ (g)	Mass of Na_2CO_3 (g)	Mass of Slurry (g)	Mass of Carbon (mg/kg slurry)
0	12.218	4.514	1067.98	1852
3.75	11.506	4.526	1088.60	1740
7.5i	10.722	4.521	1100.88	1640
7.5ii	10.763	4.517	1101.02	1638
11.25	10.057	4.526	1104.64	1557
15	9.379	4.550	1193.12	1375

Solids were isolated from each slurry, dried at 110°C, and submitted for x-ray diffraction (XRD) analysis. The spectra from these analyses are shown in Figure 2-1 through Figure 2-6. The uranium was added to the recipe as uranyl nitrate, $UO_2(NO_3)_2 \bullet 6H_2O$. Following precipitation the identified sludge species was a hydrated uranate (Clarkeite), $Na(UO_2)O(OH)$ in each of the sludge preparations. The

broadness of the Clarkeite peaks is consistent with the less than completely crystalline nature of the species. The absence of the hydroxylapatite, $Ca_5(PO_4)_3(OH)$ or $3Ca_3(PO_4)_2 \bullet Ca(OH)_2$, a species added during the final Phase 4 trimming of each slurry, in the Batch 7.5 through Batch 15 spectra is thought to be due to a combination of its decreasing concentration as the U concentration increased, and its being obscured by other phases.

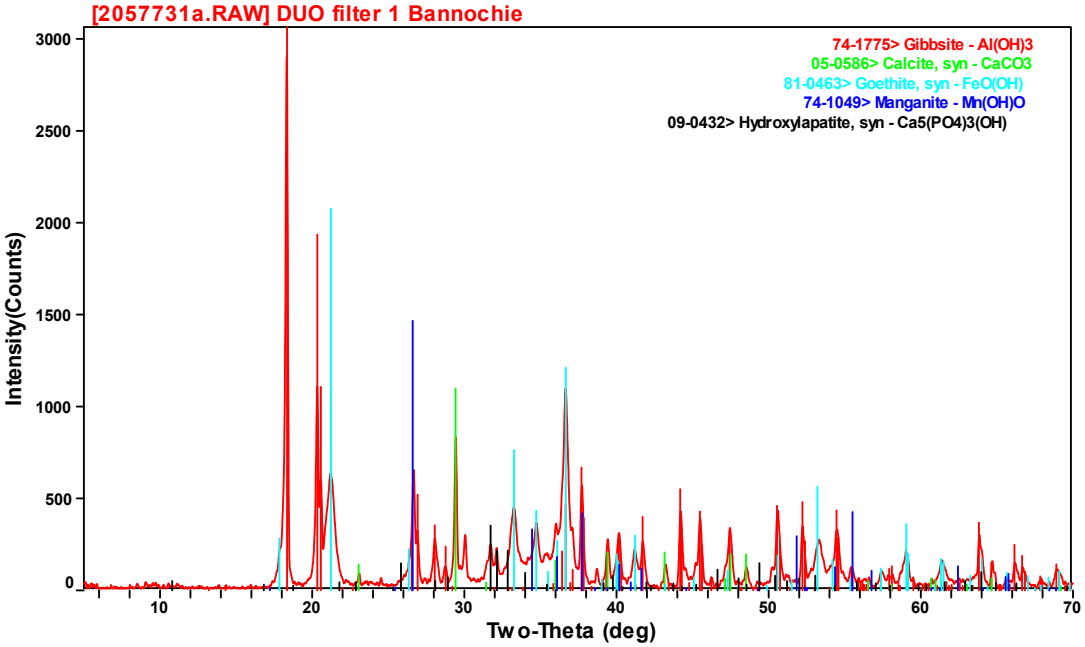

Figure 2-1. XRD Spectra of the Batch 0 SB2 Simulant

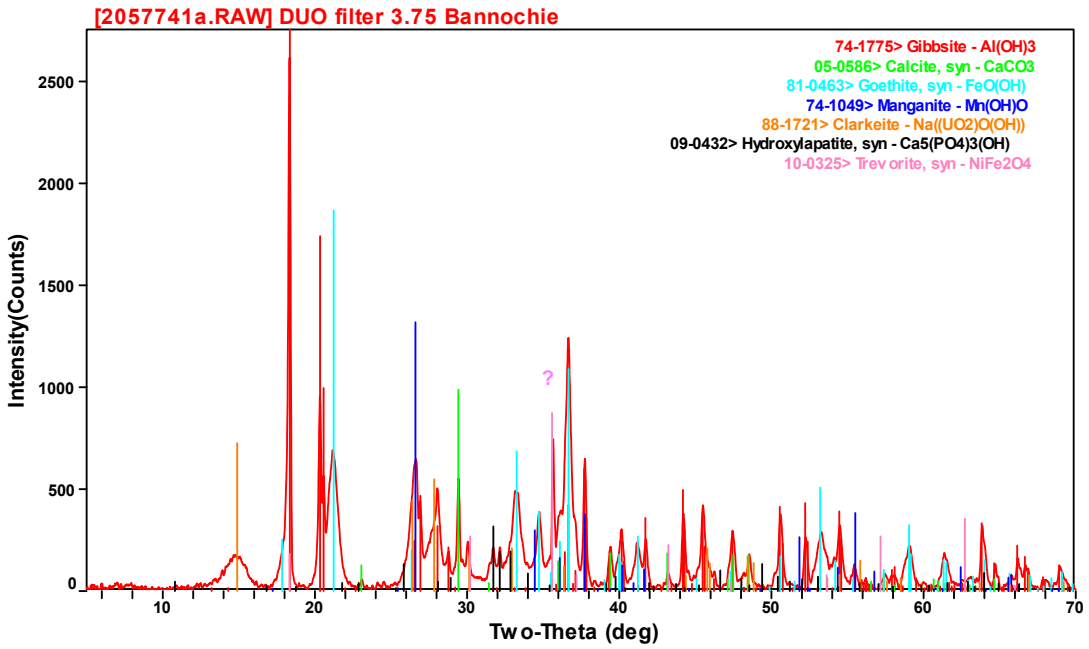

Figure 2-2. XRD Spectra of the Batch 3.75 Uranium SB2 Simulant

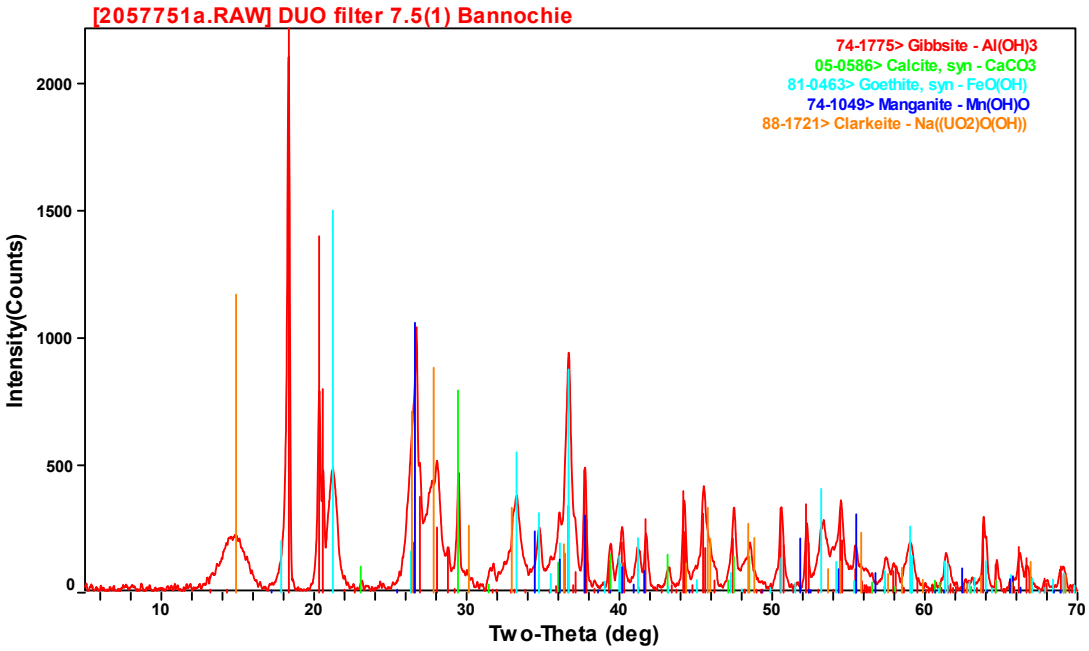

Figure 2-3. XRD Spectra of the Batch 7.5i Uranium SB2 Simulant

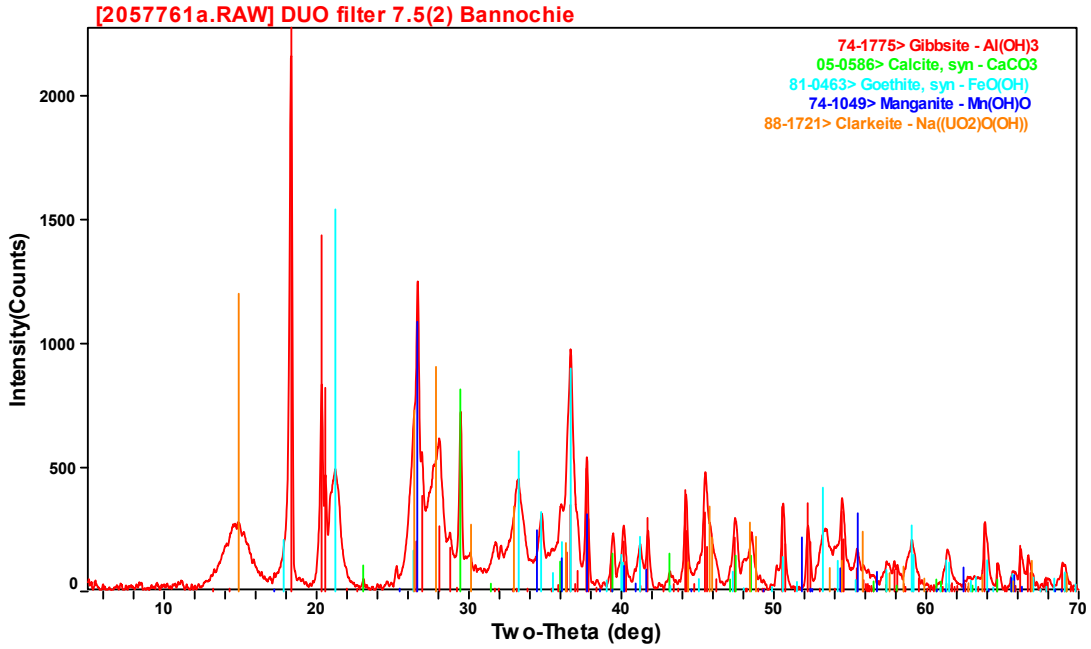

Figure 2-4. XRD Spectra of the Batch 7.5ii Uranium SB2 Simulant

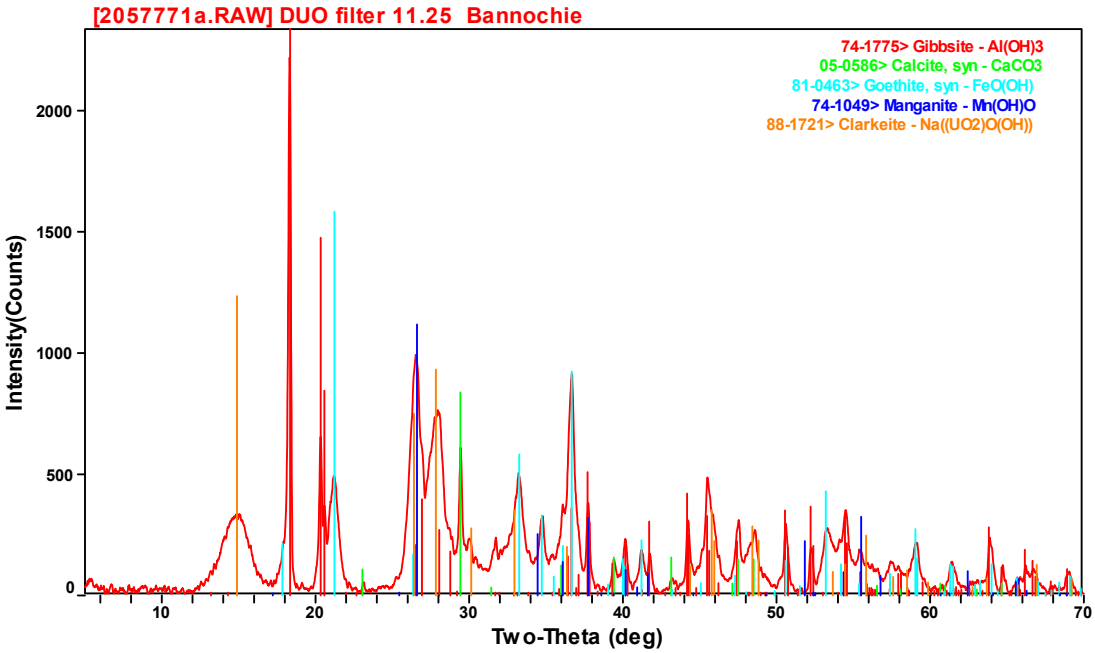

Figure 2-5. XRD Spectra of the Batch 11.25 Uranium SB2 Simulant

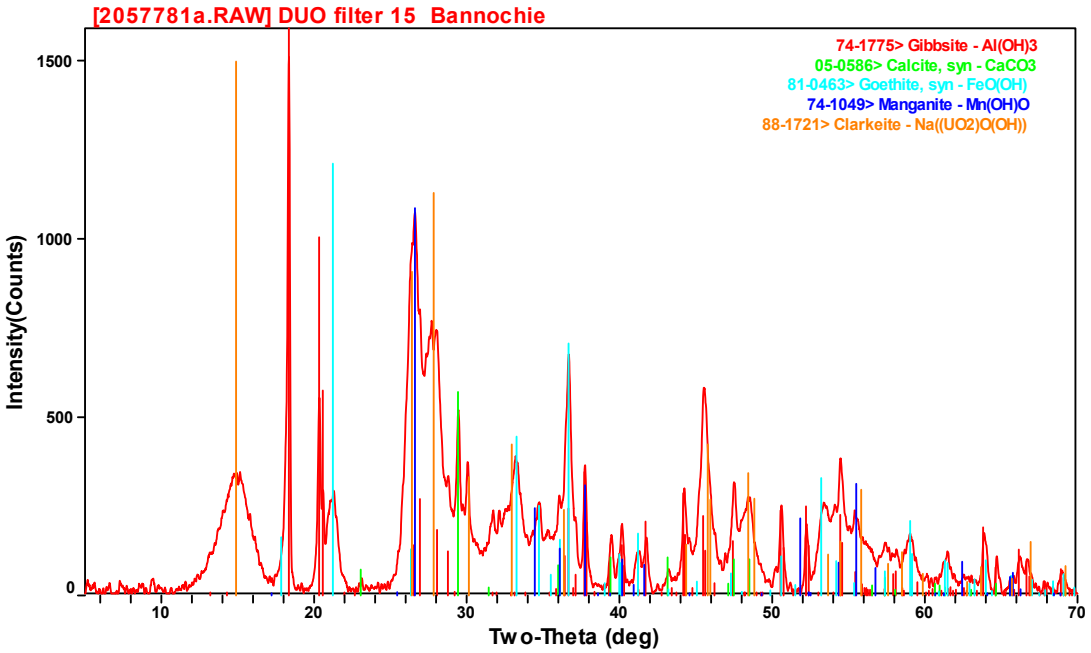

Figure 2-6. XRD Spectra of the Batch 15 Uranium SB2 Simulant

In preparation for SRAT acid calculations, each sludge batch was titrated to approximately pH 4 with 1.034M nitric acid and the base equivalents at pH 7 calculated. The titrations were performed with the SRNL Shielded Cells protocol using a 20 – 30 g sample with 1 mL additions of acid, mixing for three minutes, followed by a pH reading. No attempt was made to address the rate of acid addition issues raised in the previous study[5], since these are being addressed in other ongoing studies. Table 2-10 summarizes the pH measurements and the titration data measurements for the best two of three titrations. Even when all three replicates for each batch are considered and the overall average taken for all of the batches, the average base equivalents calculates to 0.324 eq/L (Std. Dev. 0.010, %RSD 3.0). Based upon these measurements, there did not appear to be an acid demand resulting from an increase in the uranium content. For the acid calculations the base equivalents were held constant at 0.325 eq/L for all the batches. By holding the base equivalents constant in the calculation, changes in the acid demand during the SRAT processing of each sludge would be easier to detect.

Table 2-10. Uranium Sludges pH and Base Equivalents to pH 7

Batch No.	pH	Average Base Equivalents, Eq/L (Std. Dev., %RSD)
0	11.92	0.327 (0.004, 1.3)
3.75	11.93	0.325 (0.001, 0.3)
7.5i	11.83	0.328 (0.002, 0.7)
7.5ii	11.79	*
11.25	11.77	0.320 (NA, NA)
15	11.93	0.324 (0.004, 1.2)
Average	**NA**	**0.325 (0.003, 0.9)**

* pH probe calibration issues invalidated data

2.2.2 Physical Characterization

Table 2-11 summarizes the wt % solids determinations made on each simulant batch. Elemental compositions were obtained for samples calcined at 1100°C. The overall average total solids were 21.5 wt % (Std. Dev. 0.5%, %RSD 2.4), insoluble solids were 17.8 wt % (Std. Dev. 0.4%, %RSD 2.2), soluble solids were 3.71 wt % (Std. Dev. 0.14%, %RSD 3.7), and calcined solids were 16.4 wt % (Std. Dev. 0.3%, %RSD 1.9), indicating reasonably good consistency of preparation batch to batch. The spread in the two replicate 7.5 wt % U batches gives some indication of the degree of repeatability when conducting sludge preparations of this kind.

Table 2-11. SRAT Cycle Feeds Wt % Solids (Std. Dev., %RSD)

Batch No.	Total Solids	Insoluble Solids	Soluble Solids	Calcined†
0	22.2 (0.03, 0.15)	18.2 (0.04, 0.21)	3.96 (0.01, 0.21)	16.4 (0.00, 0.01)
3.75	21.5 (0.04, 0.21)	17.8 (0.06, 0.35)	3.72 (0.02, 0.49)	16.1 (0.03, 0.21)
7.5i	21.1 (0.03, 0.16)	17.4 (0.06, 0.36)	3.69 (0.05, 1.4)	16.0 (0.02, 0.12)
7.5ii	21.8 (0.01, 0.05)	18.1 (0.04, 0.22)	3.71 (0.03, 0.87)	16.7 (0.04, 0.22)
11.25	21.7 (0.06, 0.29)	18.0 (0.05, 0.28)	3.69 (0.03, 0.78)	16.8 (0.02, 0.12)
15	20.6 (0.14, 0.70)	17.1 (0.11, 0.63)	3.51 (0.04, 1.1)	16.2 (0.08, 0.50)

† 1100°C

Samples of each slurry were submitted for particle size analysis. The diluent requirement was higher than the amount of slurry which could be dedicated for this purpose, so the diluent was derived from Clemson Environmental Technology Laboratory (CETL) SB2 untrimmed simulant supernate. It was felt that this material would be more representative of the actual supernate than would deionized water. The data collected is summarized in Table 2-12 and the full Microtrac volume and number distribution diagrams are provided in Appendix C. The mean diameter of the volume distribution (mv) varies from 14 – 29 μm, while the mean diameter of the number distribution (mn) varies from 1.9 – 3.9 μm. The last column of Table 2-12 indicates that 95% of the particles measured have a mean diameter less than the value provided. Unfortunately, there is no particle size data on recent tank samples due to activity limits on samples that can be run outside of the SRNL Shielded Cells. Future addition of a particle size capability to the Shielded Cells would provide a mechanism for comparing future sludge samples, and the development of correlations between particle size characteristics and processing behaviors.

Table 2-12. SRAT Cycle Feeds Particle Size Analyses (values in mμ)

Batch No.	mv	mn	95th Percentile
0	29	2.3	≤ 5.6
3.75	24	2.8	≤ 6.6
7.5i	16	3.9	≤ 7.4
7.5ii	14	3.6	≤ 6.4
11.25	17	3.4	≤ 6.6
15	26	1.9	≤ 5.0

The supernate and slurry densities for each batch were measured and are summarized in Table 2-13. For the purposes of the acid calculation an average supernate and slurry density were used since the measured densities varied by only ±0.01 g/mL, or less, from the average. The slurry density would be expected to increase with the U concentration, but the observations indicate the wt % total solids probably had an influence.

Table 2-13. Measured Slurry and Supernate Densities (g/mL)

Batch No.	Slurry Density	Supernate Density
0	1.19_2	1.04_3
3.75	1.19_1	1.04_2
7.5i	1.19_0	1.03_9
7.5ii	1.18_5	1.04_3
11.25	1.18_5	1.04_0
15	1.17_2	1.03_2
Average	**1.18_5**	**1.04**

2.2.3 Rheological Properties of SRAT Feeds

Rheological measurements were planned for all six sludge simulants and for all six SRAT products. There was an interest in assessing the rheological stability of the six starting sludges, since the ages of the sludges ranged from a few days to several weeks. This was driven by the need to spread the SRAT cycles over a period of about five weeks. Each sludge slurry had two preliminary rheological characterizations, one on January 22 and one of January 26 of 2004.

There were two preliminary findings. First, there was an indication that four to five of the six sludges might still be thickening over the course of the two measurements. Second, the Batch 7.5ii sludge was found to be significantly more viscous than the other five sludges, including the 7.5i sludge. This could not be attributed to any significant difference in the wt % total solids content. Therefore, a fresh sample was taken from the 7.5ii sludge. This was rechecked on February 3, 2004. The preliminary finding was confirmed at this time. The reason for the difference between the two Batch 7.5 sludge rheograms has not been identified.

Based on the preliminary findings, the rheological plan was updated to recheck the sludge rheology on the day before each SRAT cycle. The SRAT product measurements were made on the day following completion of the SRAT cycle. This ensured a valid comparison between the sludges and their corresponding SRAT products that was free of potential aging issues. After reviewing all of the data, it appeared that any effect of aging on the sludge rheology was minor. Once this was clearly demonstrated, the pre-run sludge testing was discontinued. When the Batch 3.75 sludge was run through a second SRAT cycle, the sludge rheology was not re-measured the day before the run (this also

increased the mass of material available for the SRAT test). An additional pair of SRAT product measurements was made, however, when the Batch 3.75 sludge test was repeated.

This revised rheological plan led to the following data set of sludge rheological measurements. Two preliminary and two pre-run measurements were made on each sludge slurry. Readers interested in the individual flow curve results should consult Appendix E. The Batch 7.5ii sludge slurry also had the two follow-up characterizations described above. There were a total of 26 flow curve measurements made on the six sludge slurries. The six pairs of pre-run measurements were made on the days shown in Table 2-14.

Table 2-14. Dates of Pre-Run Sludge Rheology Measurements

Batch No.	Date Measured
0	2/17/2004
3.75	2/23/2004
7.5i	2/9/2004
7.5ii	3/3/2004
11.25	2/26/2004
15	3/1/2004

The six starting sludges, when well mixed, can all be classified as thin homogeneous slurries (with the possible exception of Batch 7.5ii which was thick and homogeneous). This was somewhat unexpected, since the DU study sludges were prepared with higher wt % total solids (21-22%) than the USC and CETL SB2 simulants (16 wt % and 19.4 wt % total solids, respectively), and these previous simulants were fairly viscous. The six new sludges also exhibited varying degrees of thixotropy, or the tendency to thin with time under shear. This was more pronounced than in other recent sludge simulants. It may partially have been a consequence of the low apparent viscosities. The six samples when vigorously shaken showed a negligible tendency to entrain air. Figure 2-7 compares the rheology of CETL sludge used in the 2003 U testing[5] (Batch 0 case) with the Batch 0 sludge prepared for this study. The 7/29/03 CETL sludge measurement was also made on the RV20/M5 instrument that was used for the current study. It was chosen over measurements on the cold rheometers at the ACTL to eliminate any questions related to rheometer characteristics.

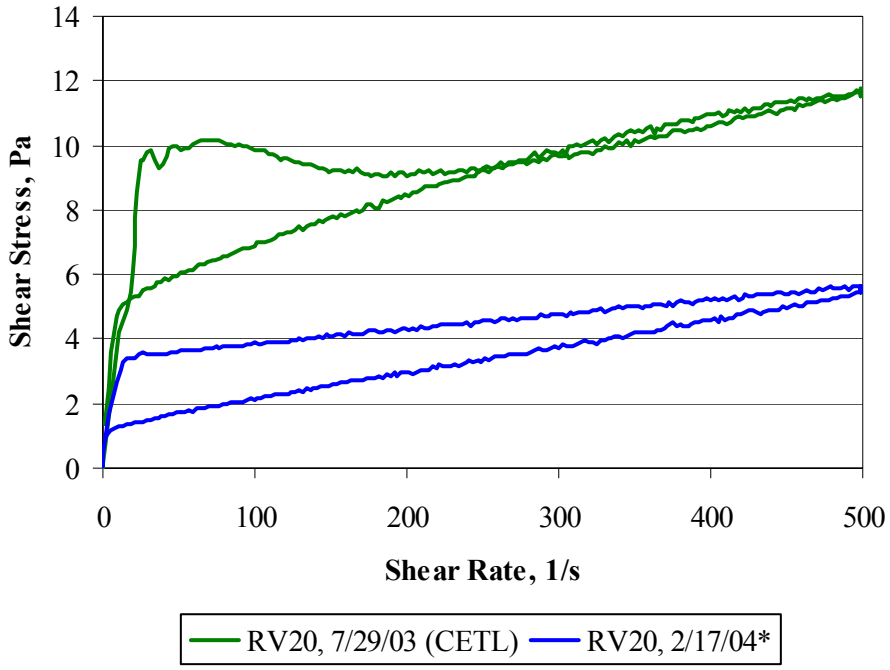

Figure 2-7. Comparison of the Rheology of CETL and SRNL SB2 Simulants without Uranium

The CETL sludge[5] was 17.2 wt % total solids while the SRNL sludge (marked with an *) was 22.2 wt % total solids. The SRNL sludge was only 20-50% as viscous as the CETL sludge over most of the shear rate range tested. The SRNL Batch 0 sludge was considered an improvement over the CETL sludge, because the flow curve did not have the distinctive hump in the up ramp portion.

Typical up and down ramp flow curves for the six starting sludges are shown in the two composite graphs, Figure 2-8 and Figure 2-9. In every instance the down flow curve was below the up flow curve. The Batch 7.5ii slurry stands out on both figures as being thicker than the other five slurries.

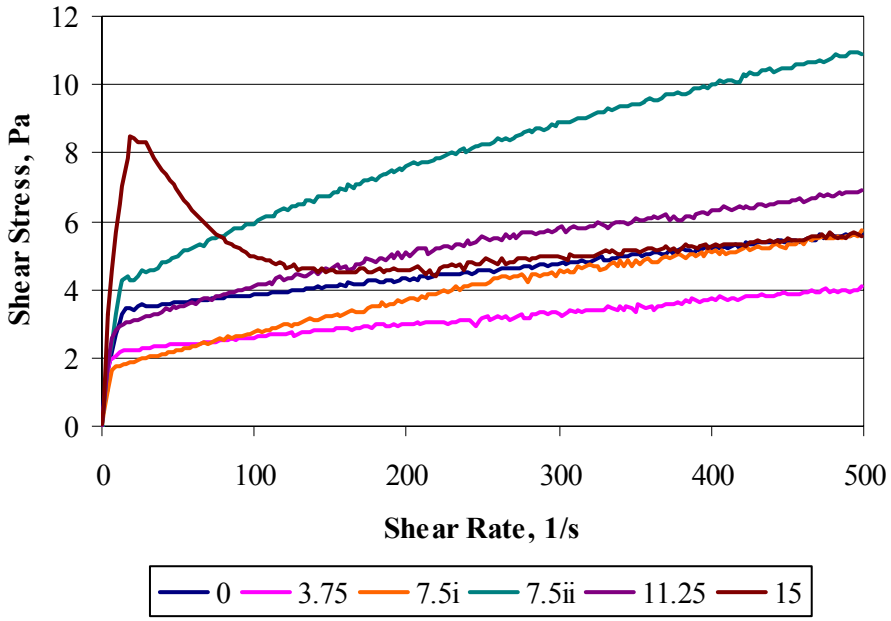

Figure 2-8. Typical Up Ramp Flow Curves for the Starting Sludges

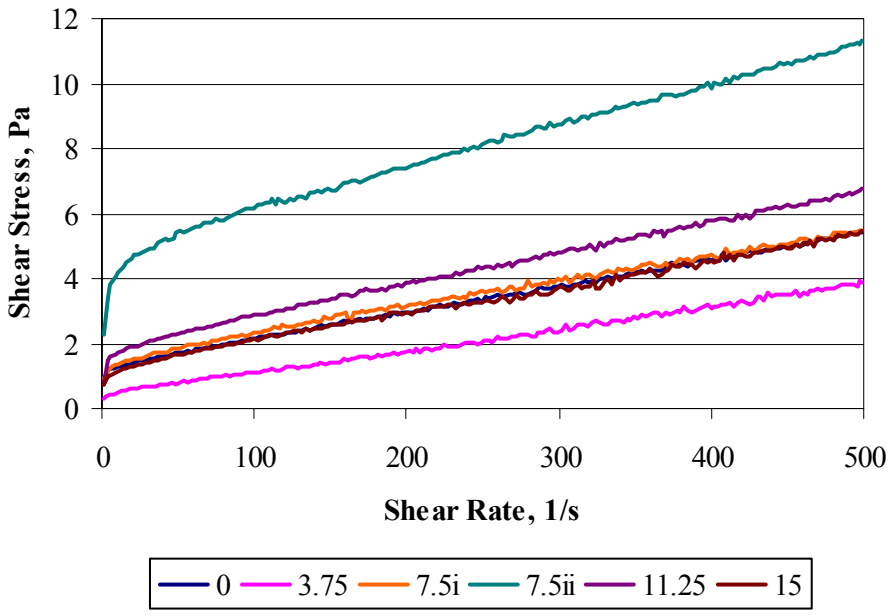

Figure 2-9. Typical Down Ramp Flow Curves for the Starting Sludges

The Batch 0 and 15 down ramp flow curves are nearly superimposed. The Batch 15 sludge was considered rheologically problematic. This slurry exhibited a large hump in the up ramp flow curve (in all replicates), similar to that seen in the CETL SB2 simulant. The hump occurred between 0/s and 200/s. The size of this hump varied from measurement to measurement, but seemed larger in the later pre-run measurements than in the earlier preliminary measurements. The humps limited Bingham plastic model fits to the region from 200/s to 500/s for this sludge, i.e. the region far from zero shear rate. Since the Bingham plastic yield stress is the extrapolation of the linear rheology data to zero shear rate, the

hump increased the range of shear rates that had to be extrapolated through to reach zero shear rate. More discussion on the hump in the sludge rheograms is given near the end of the section. The other up ramp flow curves and all down ramp flow curves were fitted to the shear rate data between 30/s to 500/s.

There was a second issue with this set of sludge simulants. Fitting data to the Bingham plastic model was only satisfactory in providing a relative ranking of the sludges due to the thixotropic nature of the samples (Bingham plastic time-independent model being fit to time-dependent data). A relative ranking appears permissible, since the samples were handled and analyzed in a consistent manner. The DWPF operating region for sludges was taken to be a yield stress between 25 and 100 dynes/cm^2 and a consistency of 4-12 cP[4]. Table 2-15 below summarizes average regression results for the six starting sludges.

Table 2-15. Sludge Bingham Plastic Model Parameters

Batch No.	Yield Stress Up ramp Dynes/cm^2	Yield Stress Down ramp Dynes/cm^2	Consistency Up ramp cP	Consistency Down ramp cP	Wt % Total Solids
0	33	17	5.9	8.7	22.2
3.75	22	7.0	4.7	7.3	21.5
7.5i	20	1.4	8.0	8.5	21.1
7.5ii	53	45	14	15	21.8
11.25	33	22	8.3	9.7	21.7
15	37	13	3.9	8.2	20.6
DWPF Operating Region	25-100	25-100	4-12	4-12	13-19

Two trends are evident in the rheological data. The yield stress fell and the consistency increased between the up ramp and the down ramp in all six cases. There were no exceptions to either trend. The yield stress fell by roughly 8 – 24 dynes/cm^2, and the consistency increased by roughly 1 – 4 cP. No trend due to the depleted uranium content was detected. The slurry rheological data tended to lie near the lower end of the range (least viscous boundary) of the operating region for DWPF. See comments in Section 3.2.5 concerning why trend exists.

Figure 2-10 shows the individual yield stresses calculated from the up ramp portions of the flow curves for five sludges (excluding the Batch 15 case which had the hump in the up ramp curve). The notation (-a) indicates the initial pre-run measurement and (-b) indicates the replicate pre-run measurement. Dates for the pre-run measurements are given in Table 2-14 above. Full flow curves are given in Appendix D, and regression analyses are given in Appendix E.

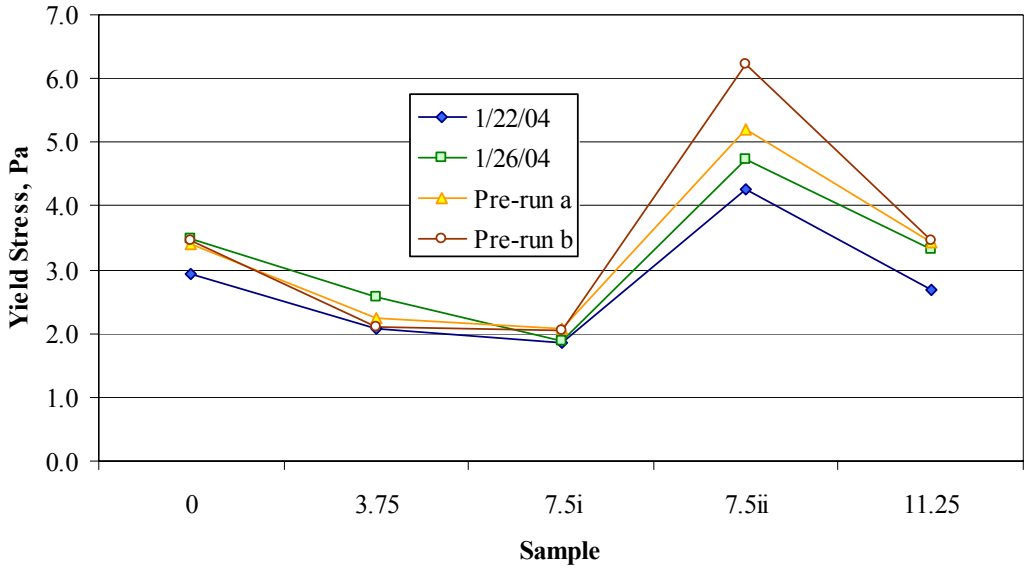

Figure 2-10. Variation of Sludge Yield Stress – Up Ramp Basis

The two re-sample results for the Batch 7.5ii sludge are not shown. Those yield stresses were 5.19 and 5.27 Pa and fell within the range of Batch 7.5ii results given on the graph. The yield stresses for the other three U levels fall in between those of the two Batch 7.5 preparations. This leads to the conclusion that small variations in sludge simulant preparation are as significant as any effect due to the presence of the uranium.

The significance of the hump in the Batch 15 sludge simulant was investigated at the time of the pre-run measurements. Following the primary flow curve measurement, the sample was kept in the concentric cylinder sensor and subjected to a second flow curve measurement, i.e. re-ramped through the shear rate region containing the hump. This measurement was only made from 0/s to 200/s with two minute ramps up and down and a six second hold. The re-ramp test was done on both replicates of the pre-run sludge simulant sample. Results are shown in Figure 2-11.

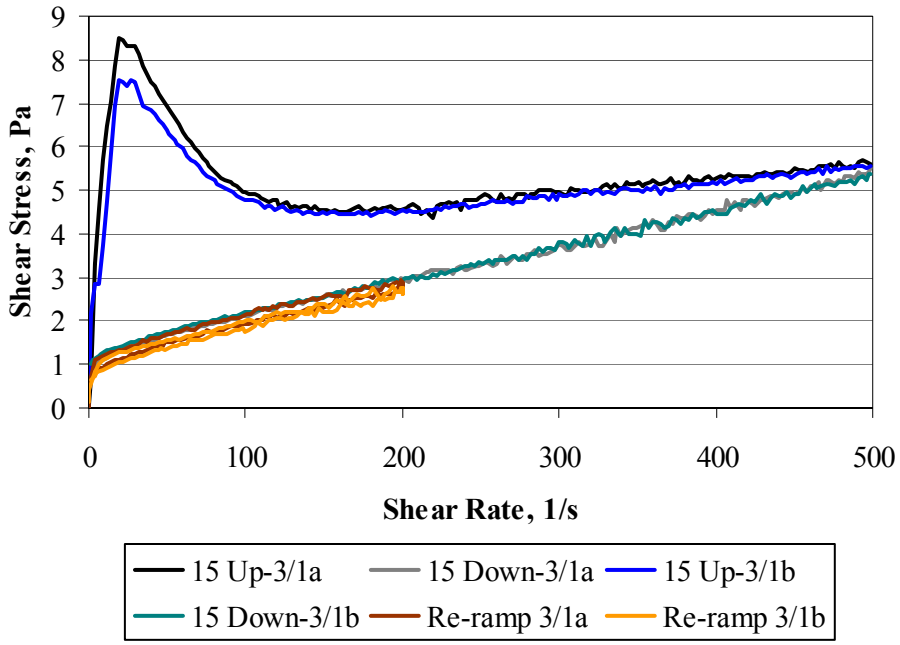

Figure 2-11. Transient Nature of Up Ramp Flow Curve Hump for Batch 15 Sludge

Noteworthy observations on Figure 2-11 include the excellent reproducibility obtained on the two primary replicates (-a and -b), the significant thinning between the up ramp and the down ramp portions of the primary measurements (0/s-500/s-0/s), the complete lack of a hump in the re-ramp curves, and the negligible subsequent thinning indicated in the re-ramp curves. This data indicate that the hump is a transient phenomenon. This observation, and a similar observation on a SRAT product with a hump, led to the decision to neglect the hump portion of the flow curve in calculating the Bingham plastic yield stress and consistency.

3.0 SRAT CYCLE

3.1 Approach

3.1.1 Equipment Set-Up

The vessel used with each of the six prepared sludge batches was a glass cylinder approximately 6.75 inches in height and 3.5 – 3.825 inches in diameter. The vessel has a capacity of approximately one liter. The top of the vessel consisted of a glass lid fitted with a set of ports. These ports were for the installations of supporting equipment, e.g. the primary off-gas line from the SRAT condenser, the air purge inlet, the formic and nitric acid addition lines, and for antifoam addition. The vessel setup was similar to that used in the SRNL Shielded Cells SB3 Qualification (refer to Figure 3-1) except no GC (and hence no manometer) or repeater pipette for antifoam additions was used. Agitation was provided with an overhead mounted drive with variable speed control.

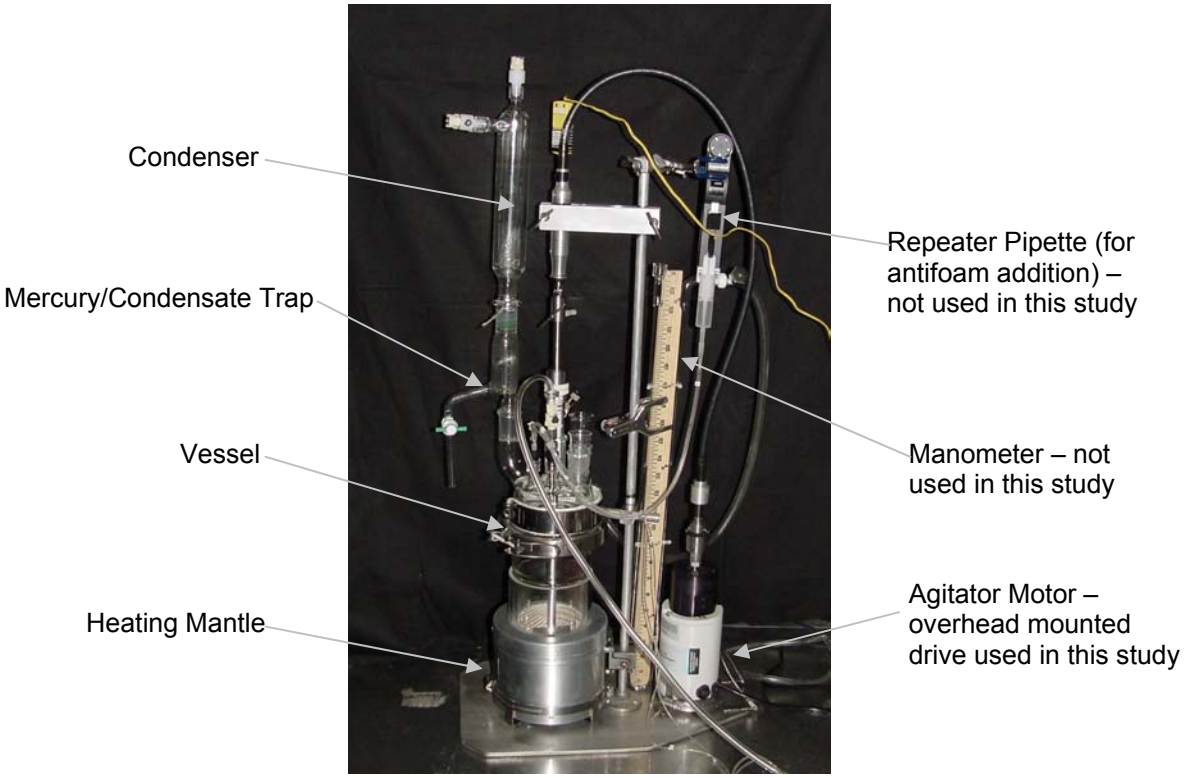

Figure 3-1. Photograph of the 1-L SRAT vessel similar to that used in this study.

Acid additions for the 7.5i wt % U sludge run were done with a MasterFlex cartridge pump as used in the Shielded Cells. Separate lines were used for nitric acid and formic acid but with the same cartridge head. A variable speed controller was used to adjust the flow rate to achieve the equivalent of two gallons/min in DWPF. For all remaining SRAT cycles, a piston style acid addition pump (TOA Limited, Japan) was used for nitric acid and formic acid addition as used at ACTL. This allowed for digital selection of the scaled addition rate and total volumes of nitric and formic acids in each run.

A SRAT condenser/decanter was calibrated and used in each of the experiments. The condenser was cooled using chilled water at between 8 – 20°C. The temperature was initially set at 10°C and lowered during the first run in an attempt to increase the boil-up condensate collection rate, but it may have had the opposite impact in that it resulted in more condensate condensing prior to reaching the decanter. In later runs the condenser was held at 15 or 20°C in order to achieve the desired DWPF-scaled boil-up rate.

The heat source to the SRAT was an electric heating mantle that covered the lower two inches (180 mL) of the vessel. The mantle was controlled by a multipurpose DigiTrol II controller connected to the SRAT thermocouple. This controller was used for both temperature set-point control, e.g. during acid addition at 93°C, and for boil-up rate control, i.e., achieving the bench-scale equivalent to a DWPF-scale 5000 lbs/hr boil-up rate.

The agitator had variable speeds and the impeller consisted of three blades perpendicular to the shaft. The agitator was driven by a variable speed mixer (Lightnin Lab Master, Model L1U10F). The speed was adjusted until a small vortex was visible on the surface of the slurry which corresponded to 260 rpm. The same rate of agitation was used in all the experiments.

Air was supplied for purging the SRAT vessel from the Building 773-A house line. The flow rate was adjusted and controlled with a MKS flow controller. A DWPF scaled SRAT purge flow was used during the test. The DWPF purge rate is 230 cfm[c]. Off-gas measurements with a GC were not made for these experimental SRAT cycles.

3.1.2 Acid Calculations for the SRAT Cycles

Analytical data from Section 2.0, along with data presented in this section, were entered into the Immobilization Technology Section's (ITS) acid addition calculation spreadsheet[7]. The total acid requirements were determined for each experiment. These were then divided into nitric acid and formic acid using projected anion reaction outcomes and an iron in glass redox target of 0.20 $Fe^{2+}/\Sigma Fe$.

Samples of the nitric and formic acids used in these experiments were checked with a DMA-4500 density meter at Aiken County Technical Laboratory (ACTL). The nitric acid was 10.28M (49.6 wt %) and the specific gravity at this molarity and 20°C is 1.307. The analysis for formic acid was 23.59 M (90.1 wt %) with a specific gravity at this molarity and 20°C of 1.205.

The recommended target for acid in these SRAT cycles was 130% of the calculated stoichiometric requirement. This recommendation was based upon the results of simulant work conducted during the processing issues study (Refer to Figure 3-2)[8]. While DWPF has used between 125 – 180% of the calculated stoichiometric requirement, we wanted to avoid the low SRAT product pH's found in the previous U work[5] and the corresponding solubilization of sludge metal oxides that accompanies the low pH. Figure 3-2 indicates that at 130% of the calculated acid stoichiometric requirement the product pH will be around 5.3. The redox equation developed and recommended for SB3 processing instead of the F-3N equation was used. The new redox equation was described in WSRC-TR-2003-00126 (C. M. Jantzen et al.)[9].

[c] DWPF purge rates are referenced to 70°F and 1 atmosphere.

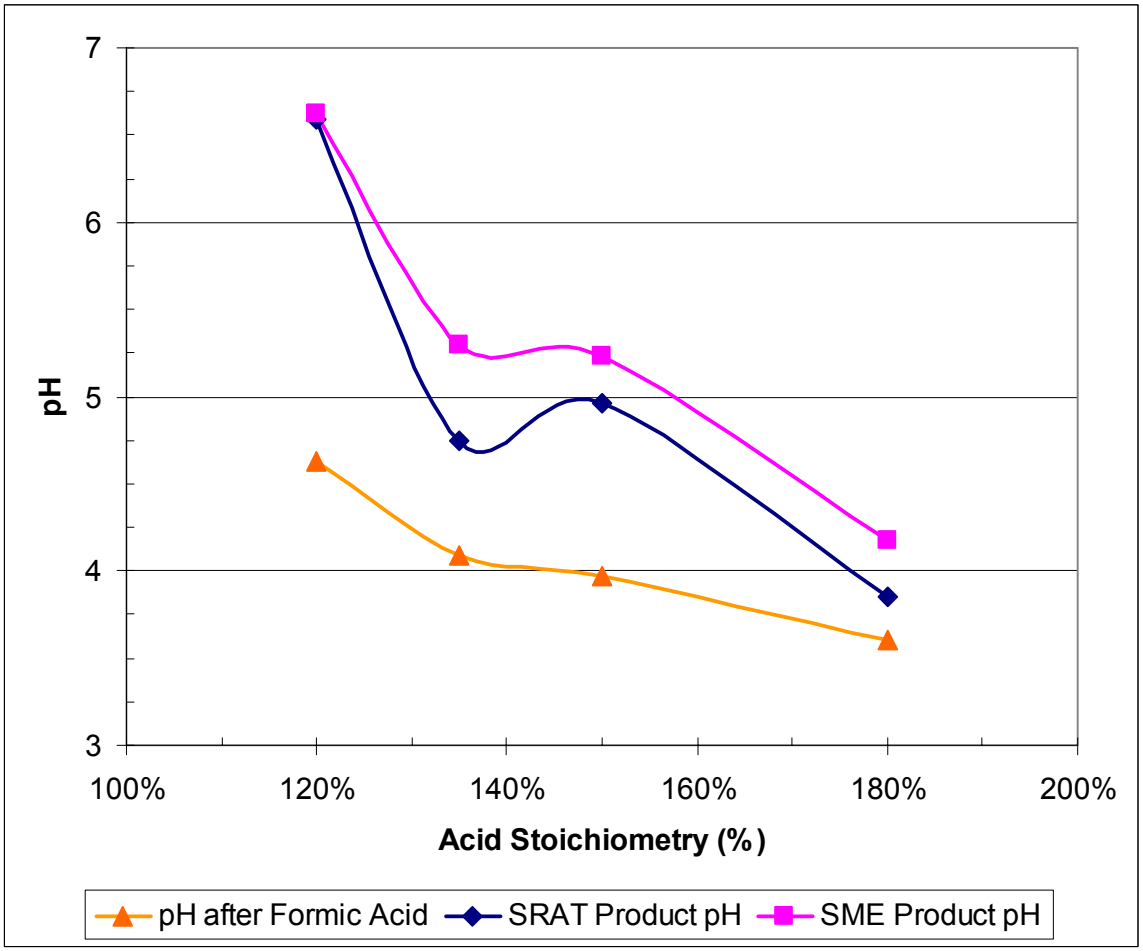

Figure 3-2. Impact of Acid Stoichiometry on pH observed during the SB2 Processing Issues Study

Table 3-1 summarizes the inputs to and output from the SRAT cycle acid calculations performed for these experiments.

Table 3-1. Summary of Inputs and Outputs for Uranium Sludge SRAT Cycle Acid Calculations

	0	3.75	7.5i	7.5ii	11.25	15
Nitrite (mg/kg)†	8390	8390	8390	8390	8390	8390
Nitrate (mg/kg)†	3690	3690	3690	3690	3690	3690
Oxalate (mg/kg)	0	0	0	0	0	0
TIC (mg/kg)	1852	1740	1640	1638	1557	1375
Base Equivalents (M)†	0.325	0.325	0.325	0.325	0.325	0.325
Mn (wt % in dried solids)	2.29	2.08	2.00	2.10	1.91	1.78
Hg (wt % in dried solids)†	0.195	0.195	0.195	0.195	0.195	0.195
Total Solids (wt %)	22.2	21.5	21.1	21.8	21.7	20.6
Sludge Density (kg/L)	1.185	1.185	1.185	1.185	1.185	1.185
Assumed Formate Destruction	26%	26%	26%	26%	26%	26%
Assumed Nitrite Destruction	100%	100%	100%	100%	100%	100%
Assumed Nitrite to Nitrate Conversion	12%	12%	12%	12%	12%	12%
Receipt Mass (g)	300	300	300	300	300	300
Acid Stoichiometry	130%	130%	130%	130%	130%	130%
Redox Target (Fe2+/ΣFe)	0.20	0.20	0.20	0.20	0.20	0.20
Moles of Acid/Liter of Slurry	1.19	1.14	1.11	1.12	1.09	1.03

†value held constant for all sludge calculations

3.1.3 Description of SRAT Cycles

Each SRAT cycle was completed per a run plan[10,11,12,13,14,15]. The same run plan was used for both Batch 3.75 SRAT cycles. A summary of processing parameters and acid addition amounts is presented in Table 3-2. A summary of the SRAT cycle is given below:

The DWPF antifoam addition strategy was used:

- Add 200 ppm antifoam to vessel prior to acid addition (at around 50°C).
- Add 100 ppm antifoam after nitric acid addition (prior to formic acid addition).
- Add 500 ppm antifoam after formic acid addition (prior to boiling).
- Add 100 ppm additional antifoam every 8 hours, as necessary, until the vessel temperature is below 50°C[d].

The slurry was heated to 93°C.
Nitric acid was added.
Formic acid was added.
The slurry was heated to boiling.
Water was removed – the water removed was equivalent to the volume of acid and flush water additions.
The slurry was refluxed for 12 hours.

At the completion of the SRAT cycle, the slurry was sampled and characterized. During the Batch 0 SRAT cycle, the nitric acid target of 5.02 mL was missed. The actual amount of nitric acid addition was 6.56 mL. To compensate, the amount of formic acid added was reduced to 10.90 mL from the original target of 11.57 mL. The resulting redox target was then calculated as 0.149, rather than the desired 0.200.

[d] No additional antifoam was employed in any of these SRAT cycles since there were no signs of foaming during reflux.

Table 3-2. DWPF and SRNL Scale SRAT Processing Parameters and Target Acid Addition Amounts

Parameter	DWPF Scale	Batch 0†	Batch 3.75	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
SRAT Contents	6,000 gal	300 g	300 g	300 g	300 g	300 g	300 g
Gas Purge Rate	230 scfm	78.5 sccm	78.5 sccm	78.5 sccm	78.5 sccm	78.5 sccm	78.5 sccm
Acid Addition Rate	2 gal/min	0.09 mL/min	0.09 mL/min	0.09 mL/min	0.09 mL/min	0.09 mL/min	0.09 mL/min
Boil Up Rate	5,000 lbs/hr	28 g/hr	28 g/hr	28 g/hr	28 g/hr	28 g/hr	28 g/hr
Acid Stoichiometry	130%	130%	130%	130%	130%	130%	130%
Nitric Acid	94 - 110 gal	5.02 mL	4.86 mL	4.70 mL	4.74 mL	4.60 mL	4.30 mL
Formic Acid	221 - 254 gal	11.57 mL	11.12 mL	10.82 mL	10.92 mL	10.61 mL	10.07 mL

† Actual acid additions differed from target, see text for details.

3.2 Results

The SRAT cycles were completed per the run plans with the exception of Batch 0 already noted in Section 3.1. Two portions of feed from Batch 3.75 were processed due to uncertainties in the recorded starting and product volumes, which could not be readily explained. No additional antifoam was necessary after the initiation of boiling, since there was no foaming observed in the systems. At the end of the cycle, nitrite was destroyed from all the feeds. Some of the feeds showed more of a tendency to swell upon being brought to boiling than others perhaps due to air entrainment.

3.2.1 Product Characterization

The following tables summarize the solids, density, pH, anion, and elemental composition of the SRAT cycle products produced from the uranium containing SB2 slurries. There are no clear trends in this data with respect to uranium content. Comparison of the two nominal 7.5 wt % sludges gives some estimate of the variability in synthesizing consistent sludges, while the nominal 3.75 wt % sludge data represents two SRAT cycles with the same starting material.

Uncertainty surrounding the final volume of SRAT product for Batch 3.75-1 which could not be explained necessitated the second processing of this batch. The second Batch 3.75 SRAT cycle had the lower final SRAT product pH that was expected based on the first SRAT cycle.

The low supernate densities measured for Batches 0, 3.75-1 and 15 are suspect. It is more likely that the 1.06 – 1.07 g/mL values measured for the other sludge batches are correct for SB2 simulants. The average value of 1.063 g/mL was used for supernate conversion of elemental data to mg/kg slurry as shown in Table 3-8.

Table 3-3. Weight Percent Solids, Density, and Final pH of the SRAT Cycle Products (Std. Dev. and %RSD)

Property	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Total Solids[a]	26.1 (0.05, 0.2)	25.5 (0.03, 0.1)	26.9 (0.3, 1.1)	24.9 (0.04, 0.2)	27.2 (0.07, 0.3)	26.1 (0.2, 0.6)	24.9 (0.004, 0.02)
Dissolved Solids[b]	10.4 (0.07, 0.7)	9.94 (0.11, 1.1)	10.8 (0.2, 1.1)	9.47 (0.18, 2.0)	10.6 (0.02, 0.2)	9.81 (0.16, 1.6)	9.46 (0.11, 1.1)
Soluble Solids[c]	8.60 (0.06, 0.7)	8.22 (0.10. 1.2)	8.86 (0.2, 1.8)	7.86 (0.17, 2.1)	8.61 (0.03, 0.3)	8.04 (0.14, 1.7)	7.85 (0.10, 1.2)
Insoluble Solids[d]	17.5 (0.03, 0.2)	17.3 (0.07, 0.4)	18.0 (0.2, 1.1)	17.0 (0.15, 0.9)	18.6 (0.1, 0.5)	18.0 (0.2, 0.9)	17.0 (0.1, 0.6)
Calcined Solids[a,e]	17.4 (0.06, 0.3)	17.7 (0.008, 0.05)	18.1 (0.3, 1.5)	17.5 (0.01, 0.1)	19.1 (0.05, 0.3)	18.5 (0.06, 0.3)	17.9 (0.03, 0.2)
Slurry Density	1.22 (NA, NA)	1.17 (0.01, 1.2)	1.20 (0.01, 1.1)	1.19 (0.01, 0.8)	1.23 (0.01, 1.1)	1.20 (0.007, 0.6)	1.20 (0.01, 1.2)
Supernate Density	1.02 (0.006, 0.6)	1.02 (0.006, 0.6)	1.07 (0.004, 0.4)	1.06 (0.01, 1.0)	1.07 (0.002, 0.1)	1.06 (0.006, 0.6)	1.01 (0.01, 1.1)
pH	4.81	6.62	5.79	6.54	6.37	6.40	6.16

[a] Wt % of slurry, measured value
[b] Wt % of supernate, measured value
[c] Wt % of slurry, calculated from wt % total and insoluble solids
[d] Wt % of slurry, calculated from wt % total and dissolved solids
[e] 1100°C

3.2.2 Nitrite and Formate Destruction

Anion measurements were made on each of the SRAT products at the end of dewater and on the final SRAT product. Table 3-4 summarizes this data at the completion of the dewater phase of the SRAT cycle. As can be seen by a comparison with the data in Table 2-8, average starting nitrite concentration of 8380 mg/kg of slurry, most of the nitrite was destroyed prior to the start of reflux. The nitrite value measured here can be subject to considerable variability depending upon the amount of time expended to

Table 3-4. Measured Ion Chromatography Anions in the Post Dewater SRAT Material (mg/kg slurry)

Anion	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Formate	32,300	26,600	29,100	32,400	29,000	27,200	31,100
Nitrate	28,000	17,800	18,600	22,800	19,000	18,600	19,500
Nitrite	<84	2170	<63	870	706	279	769
Sulfate	1380	1470	1060	1460	1490	1430	1390

reach the point of reflux as a result of acid addition time variations and more significantly, the time to achieve the desired boil-up rate. These factors may be reflected in the significant variation observed between the two Batch 3.75 SRAT cycle values (2170 vs. <63 mg/kg slurry).

Table 3-5 summarizes the anion data collected on the final SRAT product. All measurements were made in triplicate and averaged. At the completion of each of the SRAT cycles, the nitrite ion concentration was below detection.

Table 3-5. Measured Ion Chromatography Anions in the SRAT Products (mg/kg slurry)

Anion	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Formate	30,200 (1100, 3.7)	27,400 (1640, 6.0)	30,900 (2210, 7.2)	33,600 (4070, 12)	30,000 (1940, 6.5)	28,300 (3400, 12)	28,400 (2870, 10)
Nitrate	28,800 (764, 2.6)	21,700 (1360, 6.3)	22,500 (1410, 6.3)	26,000 (3350, 13)	23,300 (1310, 5.6)	21,500 (2310, 11)	22,100 (2100, 9.5)
Nitrite	<89	<89	<46	<92	<91	<94	<90
Sulfate	1920 (95, 5.0)	1550 (17, 1.1)	1180 (79, 6.7)	1070 (47, 4.4)	1370 (75, 5.5)	1540 (40, 2.6)	1420 (74, 5.2)

Several assumptions for anion destruction/conversion were made for the acid calculation (see Table 3-1). These assumptions involve nitrite to nitrate conversion, nitrite destruction, and formate destruction. Although the assumptions are based on overall processing (SRAT and SME cycles), SRAT cycle destruction/conversion is presented for information in Table 3-6. It should be noted that the Batch 0 SRAT cycle had more nitric acid added than necessary, so the formic acid level was reduced to keep the total moles of acid constant. The Batch 7.5i results are likely influenced by the high %RSD for the nitrate and formate data used in the calculation (refer to Table 3-5).

Table 3-6. Calculated SRAT Cycles Nitrite Destruction, Nitrite to Nitrate Conversion, and Percent Formate Destruction

	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Nitrite Destruction	100%	100%	100%	100%	100%	100%	100%
Nitrite to Nitrate Conversion	81%	60%	67%	122%	84%	70%	81%
Formate Destruction	9%	32%	23%	15%	24%	26%	22%

3.2.3 Elemental Composition of SRAT Products

Table 3-7 and Table 3-8 provide the slurry and supernate elemental compositions, respectively, determined from each processed SRAT batch. When this data is related to the final SRAT product pH's (see Table 3-3) the concentration of soluble Cu, Mn, Ni, and Zn show characteristic dependence on the final pH (see Figure 3-3 derived from data in Table 3-9).

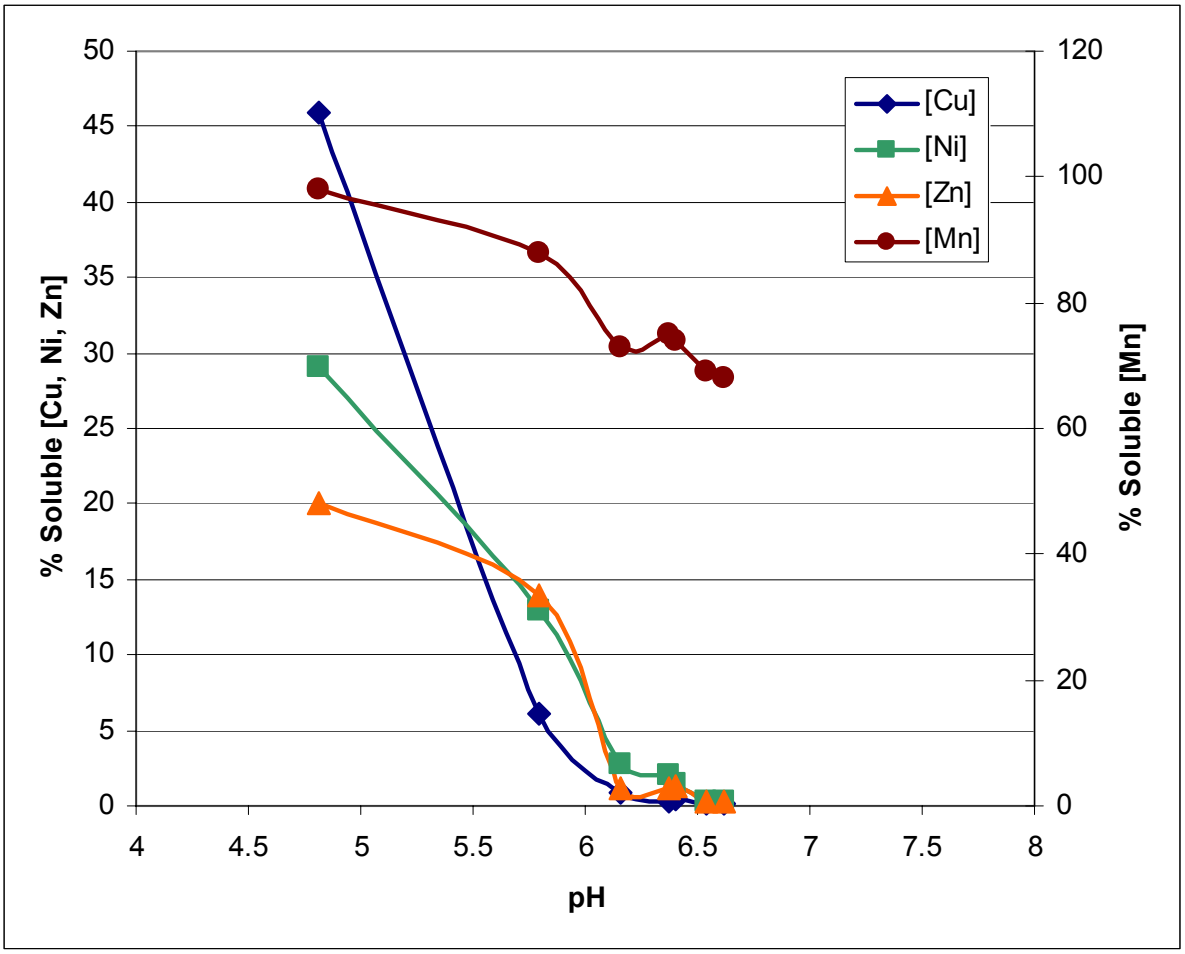

Figure 3-3. Percent Soluble Metal Ion Concentration vs. SRAT Product pH

Unlike these metal ions, the U was largely insoluble above pH 6, only in the Batch 3.75 second SRAT cycle product when the pH was 5.79, was any appreciable soluble U measured.

Table 3-7. Slurry Elements Measured in the SRAT Products in mg/kg slurry (Std. Dev., %RSD)

Element	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Al	26,000 (270, 1.0)	24,800 (180, 0.7)	25,500 (360, 1.4)	22,600 (200, 0.9)	23,200 (110, 0.5)	21,300 (390, 1.8)	18,900 (100, 0.5)
Ca	4940 (27, 0.5)	4300 (54, 1.3)	4970 (48, 1.0)	4230 (18, 0.4)	4590 (58, 1.3)	4180 (70, 1.7)	3640 (31, 0.8)
Cu	230 (1.7, 0.8)	245 (1.8, 0.7)	233 (3.1, 1.3)	210 (1.0, 0.5)	238 (12, 5.1)	252 (4.3, 1.7)	251 (4.5, 1.8)
Fe	50,100 (360, 0.7)	48,500 (620, 1.3)	49,000 (730, 1.5)	43,800 (100, 0.2)	48,600 (44, 0.9)	44,800 (520, 12)	39,200 (100, 0.3)
K	142 (2.0, 1.4)	147 (2.0, 1.4)	160 (2.8, 1.7)	193 (6.6, 3.4)	192 (2.2, 1.2)	200 (6.4, 3.2)	277 (7.8, 2.8)
Mg	239 (2.7, 1.1)	230 (2.7, 1.2)	237 (8.3, 3.5)	207 (2.0, 1.0)	203 (4.0, 2.0)	203 (2.1, 1.1)	179 (1.8, 1.0)
Mn	5290 (40, 0.8)	5050 (45, 0.9)	5240 (54, 1.0)	4640 (27, 0.6)	5130 (29, 0.6)	4800 (85, 1.8)	4190 (21, 0.5)
Na	15,400 (240, 1.6)	15,300 (220, 1.4)	16,700 (190, 1.1)	15,600 (56, 0.4)	16,700 (61, 0.4)	16,600 (230, 1.4)	17,200 (90, 0.5)
Ni	2460 (56, 2.3)	2670 (51, 1.9)	2770 (280, 1.0)	2510 (10, 0.4)	2760 (29, 1.1)	2600 (39, 1.5)	2220 (10, 0.5)
S	585 (3.5, 0.6)	562 (11, 1.9)	534 (2.8, 0.5)	538 (12, 2.3)	514 (2.2, 0.4)	506 (12, 2.4)	446 (1.0, 0.2)
Si	1720 (16, 0.9)	1640 (9, 0.5)	1730 (26, 1.5)	1720 (46, 2.7)	1640 (16, 1.0)	1530 (19, 1.2)	1330 (9.8, 0.7)
U	<174	7920 (0, 0)	8510 (28, 0.3)	15,200 (130, 0.9)	17,000 (100, 0.6)	25,300 (570, 2.2)	32,100 (410, 1.3)
Zn	585 (3.6, 0.6)	544 (4.7, 0.9)	563 (3.8, 0.7)	517 (4.6, 0.9)	528 (2.9, 0.6)	496 (6.0, 1.2)	435 (3.7, 0.9)
Zr	886 (22, 2.5)	772 (18, 2.3)	837 (15, 1.8)	782 (14, 1.8)	821 (13, 1.6)	747 (37, 5.0)	678 (37, 5.5)

Table 3-8. Supernate Elements Measured in the SRAT Products in mg/kg slurry (Std. Dev., %RSD)

Element	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Al	7.24 (0.005, 0.8)	0.0863 (0.0022, 2.6)	1.15 (0, 0)	0.0471 (0, 0)	0.0599 (0.0038, 6.3)	0.0847 (0.0038, 4.5)	0.0730 (0.0039, 5.3)
Ca	5180 (130, 2.4)	4390 (6, 0.1)	4330 (76, 1.8)	4330 (28, 0.6)	4270 (0, 0)	4120 (33, 0.8)	3390 (55, 1.6)
Cu	105 (0.6, 0.5)	0.212 (0.0033, 1.6)	14.2 (0, 0)	0.292 (0, 0)	0.839 (0, 0)	1.17 (0, 0)	2.16 (0, 0)
Fe	<0.00776	<0.00807	<0.00768	<0.00785	<0.00762	<0.00773	<0.00780
K	514 (1.6, 0.3)	376 (0.6, 0.1)	456 (3.3, 0.7)	464 (2.8, 0.6)	488 (22, 4.4)	362 (0, 0)	441 (2.2, 0.5)
Mg	229 (0.5, 0.2)	189 (0.6, 0.3)	213 (1.1, 0.5)	178 (1.1, 0.6)	185 (2.7, 1.5)	170 (0.5, 0.3)	157 (1.1, 0.7)
Mn	5200 (110, 2.1)	3430 (16, 0.5)	4620 (110, 2.5)	3190 (11, 0.3)	3870 (5, 0.1)	3550 (11, 0.3)	3050 (22, 0.7)
Ni	718 (1.6, 0.2)	8.67 (0.055, 0.6)	356 (0.5, 0.2)	7.20 (0.0056, 0.1)	58.5 (0.05, 0.1)	40.2 (0.27, 0.7)	60.8 (0.39, 0.6)
S	414 (5.7, 1.3)	348 (3.3, 0.9)	423 (9.2, 2.2)	360 (1.7, 0.5)	401 (2.7, 0.7)	339 (4.4, 1.3)	373 (0.6, 0.1)
Si	94.3 (0.57, 0.6)	15.5 (0.72, 4.6)	33.4 (0.11, 0.3)	24.7 (0.06, 0.2)	24.1 (0.05, 0.2)	41.5 (0.98, 2.4)	20.9 (0.39, 1.8)
U	NA	<0.778	662 (3.8, 0.6)	<0.785	7.02 (0.038, 0.5)	5.46 (0.027, 0.5)	12.3 (0, 0)
Zn	117 (0, 0)	1.65 (0.011, 0.7)	76.0 (0.38, 0.5)	1.59 (0, 0)	5.77 (0.022, 0.4)	6.46 (0.016, 0.3)	4.78 (0.033, 0.7)
Zr	<0.00776	<0.00778	<0.00768	<0.00785	<0.00762	<0.00773	<0.00780

Table 3-9. Percent Soluble of Select Elements in SRAT Products

Element	Batch 0	Batch 3.75-1	Batch 3.75-2	Batch 7.5i	Batch 7.5ii	Batch 11.25	Batch 15
Al	0.03%	0*%	0%	0%	0%	0%	0%
Ca	105%	102%	87%	102%	93%	98%	93%
Cu	46%	0.09%	6.1%	0.14%	0.35%	0.46%	0.86%
Fe	0%	0%	0%	0%	0%	0%	0%
Mg	96%	82%	90%	86%	91%	84%	88%
Mn	98%	68%	88%	69%	75%	74%	73%
Ni	29%	0.32%	13%	0.29%	2.1%	1.5%	2.7%
S	71%	62%	79%	67%	78%	67%	84%
Si	5.5%	0.94%	1.9%	1.4%	1.5%	2.7%	1.6%
U	NA	0.01%	7.8%	0.01%	0.04%	0.02%	0.04%
Zn	20%	0.30%	14%	0.31%	1.1%	1.3%	1.1%
Zr	0%	0%	0%	0%	0%	0%	0%

* 0% means less than 0.00% of the total is soluble.

The values in Table 3-8 which are larger than 100% reflect the uncertainties in the individual measurements used to calculate these percentages.

3.2.4 X-ray Diffraction and Particle Size Analyses of Solids and Entrainment Observations

Solids were again isolated from each of the SRAT product slurries, dried at 110°C, and submitted for XRD analysis. The spectra obtained from these analyses are shown in Figure 3-4 through Figure 3-10. There are spectra for both SRAT cycles conducted with the nominally 3.75 wt % uranium containing slurry. The two spectra for the Batch 7.5 materials are separate SRAT cycle products on independently prepared SRAT feed slurries. None of the unidentified species in these spectra were uranium containing, they appeared more likely to be alumino-silicate compounds. As discussed in Section 2.1.1, the identified uranium species in the feed slurries was a hydrated uranate (Clarkeite), $Na(UO_2)O(OH)$. The SRAT products gave no indication of Clarkeite, but generally the uranium containing species was still U(VI), specifically Na or K salts of $U_2O_7^{2-}$. The product uranium containing species were very fine, on the order of 100Å. The compounds were also not completely crystalline resulting in the broad peaks seen in the spectra.

One observation made during the SRAT cycles with several of these feeds does suggest a connection with the plant observed air-entrainment concern. The vessel volumes swelled by as much as 33% between the end of acid addition and the heat-up to boiling. The heat-up to boiling took 10 – 15 minutes and therefore corresponded well with the DWPF procedural heat-up rate of 0.5°C/minute. The Batch 11.25 SRAT cycle had the largest volume change factor. Table 3-10 below, gives a rough estimate of the swelling factors observed for each batch of sludge material.

Table 3-10. Observed SRAT Cycle Feed Volume Change Factors Upon Going From 93°C to 100°C

Batch No.	Volume Change Factor
0	6.2%
3.75-1	4.2%
3.75-2	no change observed
7.5i	4.6%
7.5ii	6.3%
11.25	33%
15	21%

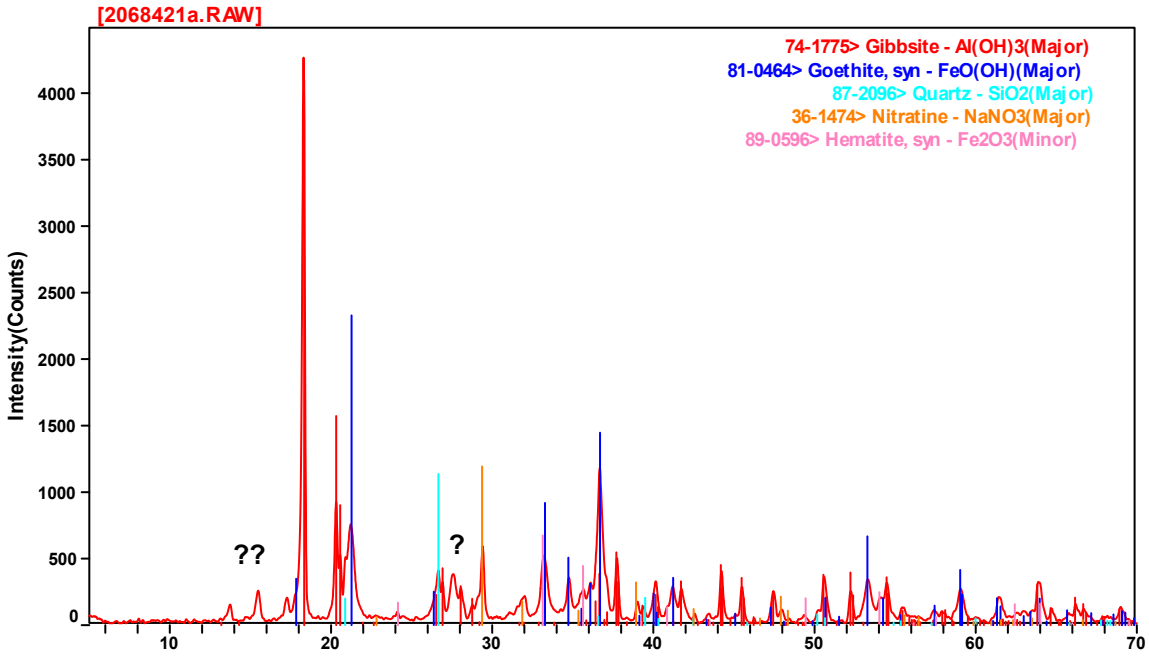

Figure 3-4. XRD Spectra of the Batch 0 SB2 SRAT Product

Unlike the starting materials, the uranium containing species in one SRAT product contained other than the U(VI) oxidation state. Specifically, the first Batch 3.75 product contained a mixed valence $U_3O_9^{2-}$ species, possibly a single U(IV) and two U(VI).

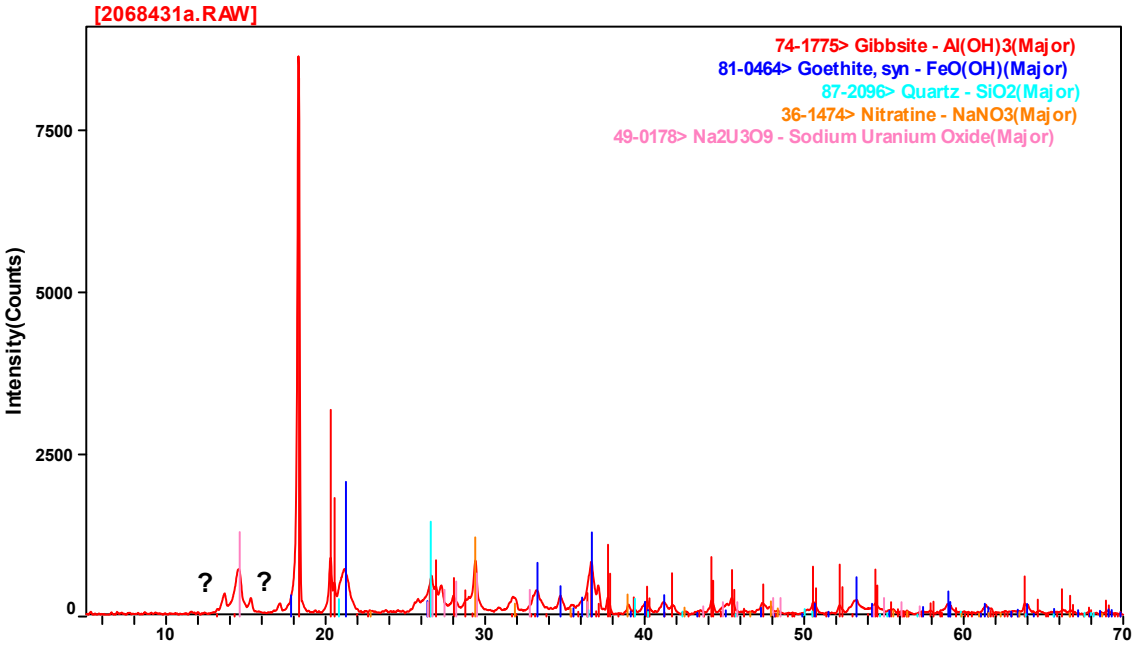

Figure 3-5. XRD Spectra of the Batch 3.75 Uranium SB2 SRAT Product, Run 1

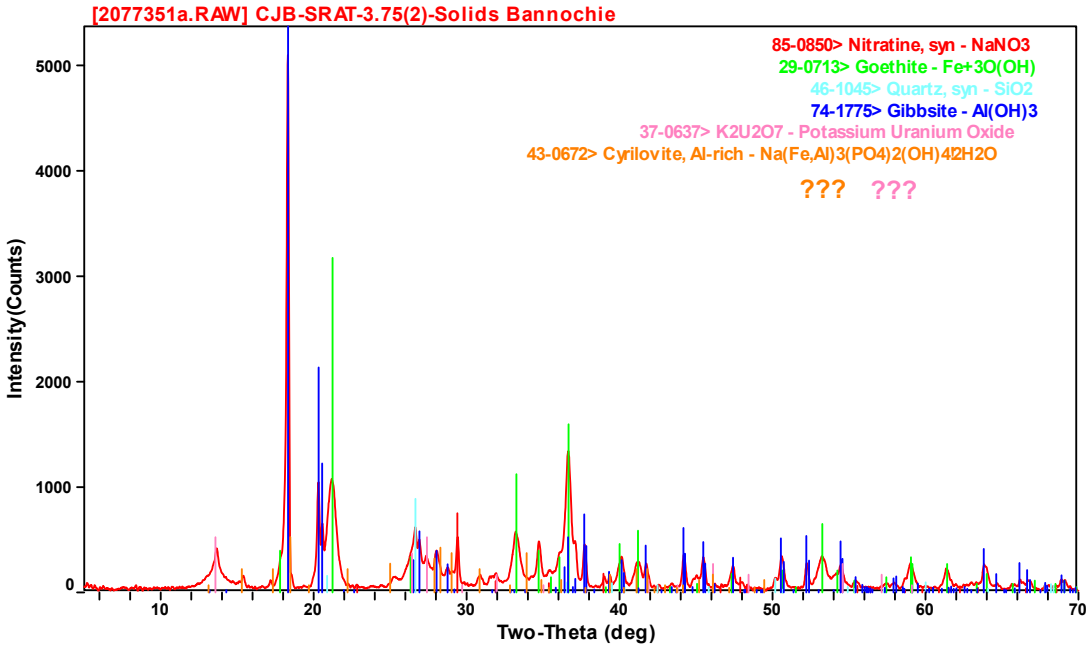

Figure 3-6. XRD Spectra of the Batch 3.75 Uranium SB2 SRAT Product, Run 2

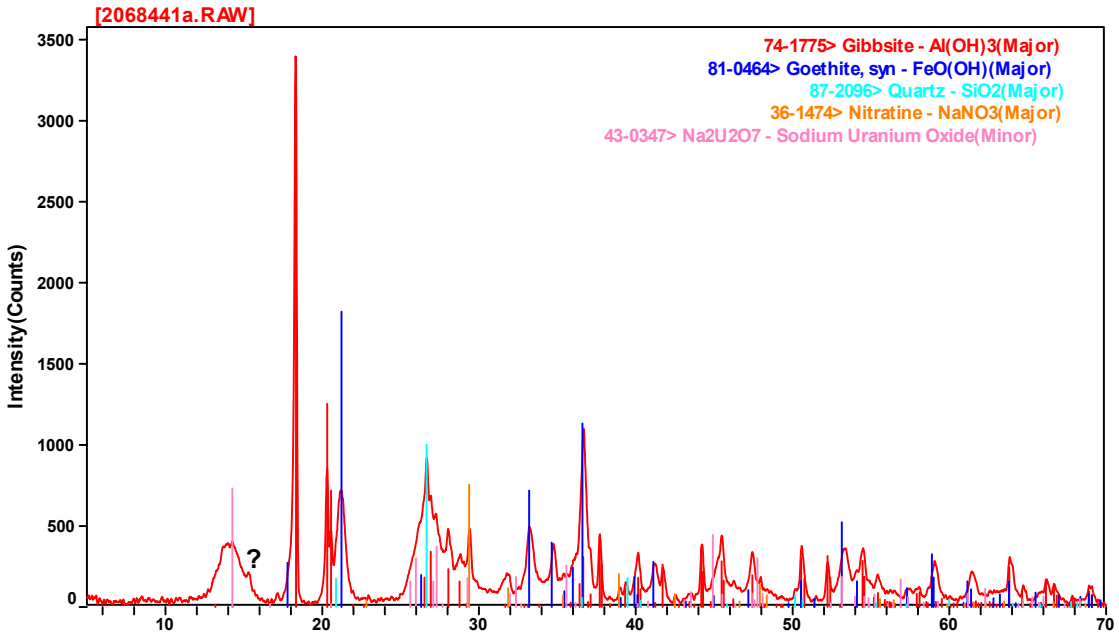

Figure 3-7. XRD Spectra of the Batch 7.5i Uranium SB2 SRAT Product

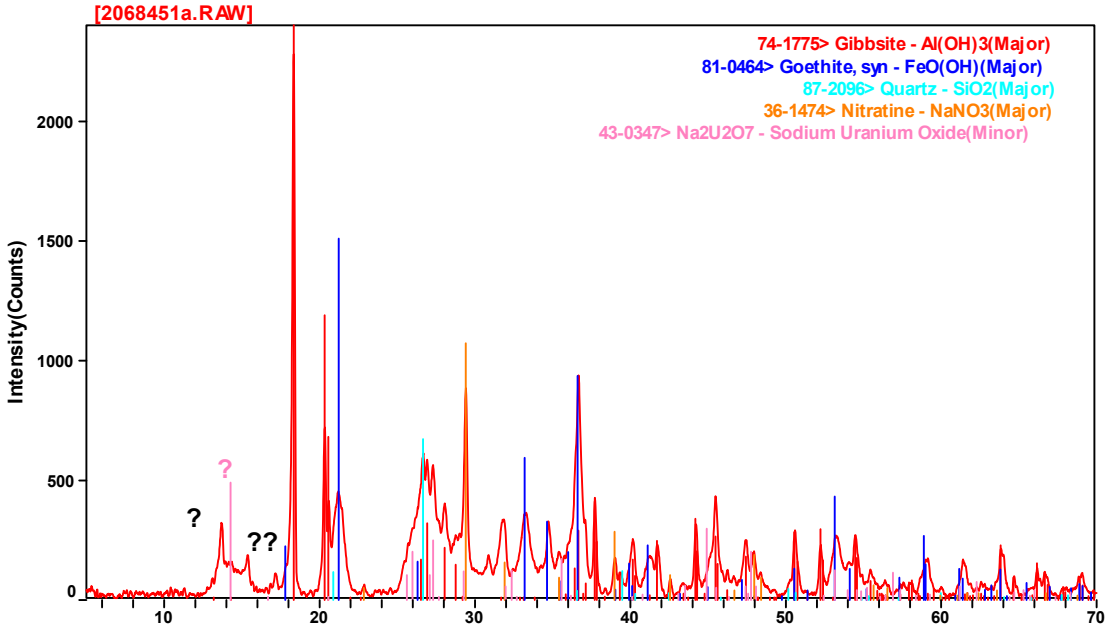

Figure 3-8. XRD Spectra of the Batch 7.5ii Uranium SB2 SRAT Product

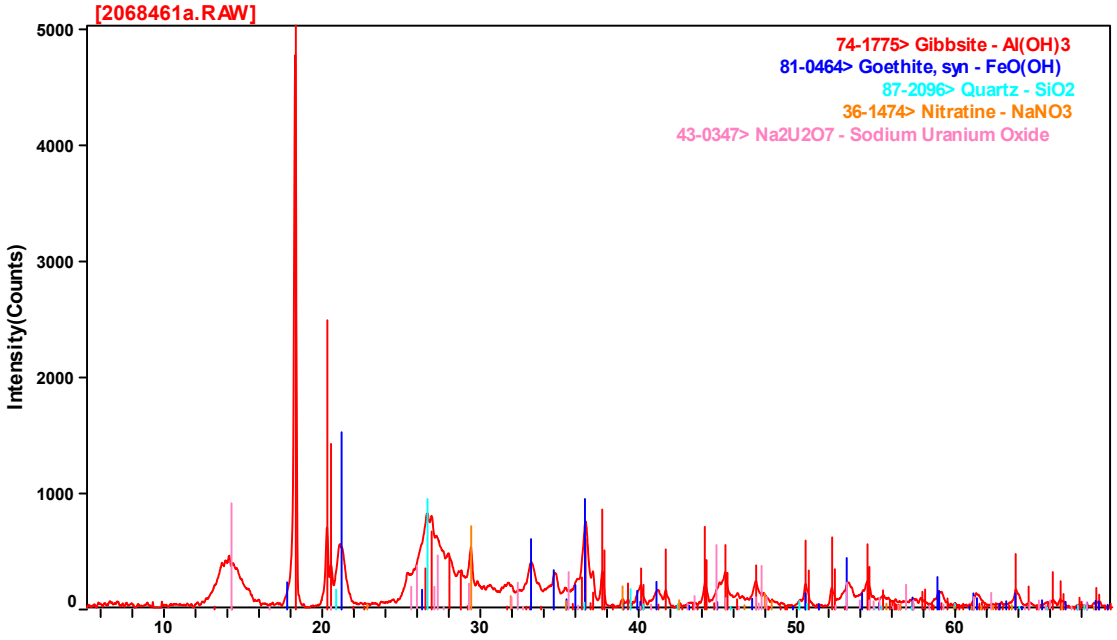

Figure 3-9. XRD Spectra of the Batch 11.25 Uranium SB2 SRAT Product

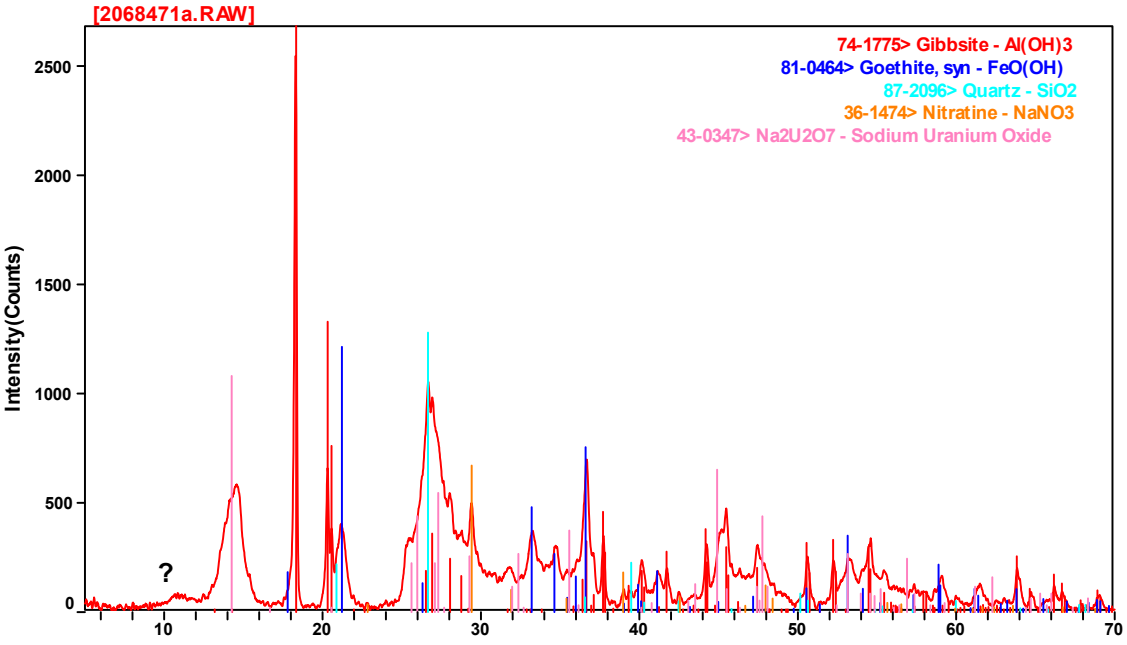

Figure 3-10. XRD Spectra of the Batch 15 Uranium SB2 SRAT Product

Table 3-11 summarizes the post SRAT processing particle parameters run on the solids. Particle size measurements were not run on the second Batch 3.75 SRAT product. There was insufficient supernate

to use as a diluent, so these data were collected from dilution with deionized water. The impact of the deionized water on the insoluble solids is unknown. The full Microtrac volume and number distribution diagrams are provided in Appendix C. The mean diameter of the volume distribution (mv) varies from 14 – 28 μm, essentially the same as in the starting feeds (refer to Table 2-12), though there was a reduction for each sludge individually. The mean diameter of the number distribution (mn) varies from 1.0 – 2.9 μm, a significant reduction from that measured range in the starting feeds (1.9 – 3.9 μm), and again the reduction was reflected in each sludge processed with the percent change varying from 19 – 56% for an individual Batch. The mean diameter value for 95% of the particles was reduced in each sludge following SRAT processing.

Table 3-11. SRAT Cycle Products Particle Size Analyses (values in μm)

Batch No.	mv	mn	95th Percentile
0	28	1.0	≤ 2.6
3.75-1	16	2.4	≤ 5.8
7.5i	14	2.9	≤ 6.2
7.5ii	14	2.9	≤ 5.7
11.25	14	2.1	≤ 5.0
15	23	1.2	≤ 3.2

3.2.5 Product Rheological Results

There were two post-run rheological measurements on each SRAT product. Both measurements were typically made within 24 hours of the completion of the SRAT cycle. The six simulants were each run through one SRAT cycle except for the Batch 3.75 simulant. Two SRAT cycles were run starting with fresh 3.75 simulant, designated 3.75-1 and 3.75-2. The post-run SRAT product rheology measurements occurred on the following days.

Table 3-12. Dates for SRAT Product Rheological Measurements

Batch No.	Date Measured
0	2/19/2004
3.75-1	2/24/2004
3.75-2	4/7/2004
7.5i	2/11/2004
7.5ii	3/5/2004
11.25	2/27/2004
15	3/3/2004

Rheological analyses on the seven SRAT products were identical to those made on the six starting sludges, Appendix G. The seven SRAT products exhibited varying degrees of thixotropy, or thinning with time under shear. This was more pronounced than in most other recent simulant SRAT products. This trait was present in the starting sludges, and appears to have been unaffected by SRAT processing. The seven samples when vigorously shaken showed a negligible tendency to entrain air.

The appearance of typical up ramp flow curves, given in Figure 3-11, is visibly different from that of the starting sludges, compare to Figure 2-8. The Batch 7.5ii SRAT product was still relatively thick compared to Batch 7.5i, but Batch 11.25 and 15 SRAT products were observed to have thickened relative to the 0, 3.75 and 7.5i SRAT products and sludges. The fourteen complete flow curves are given in Appendix F.

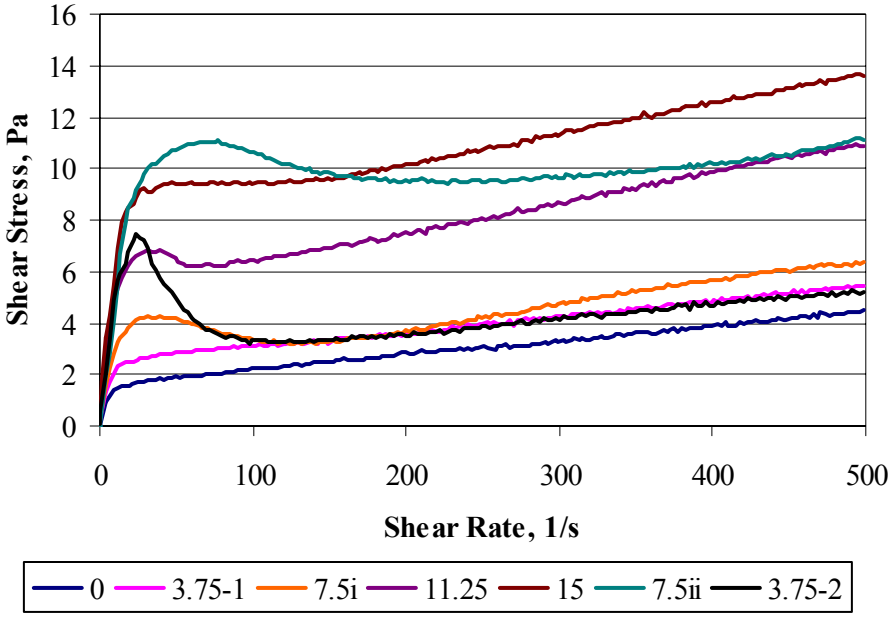

Figure 3-11. Typical Up Ramp Flow Curves of the SRAT Products

The down flow curves, Figure 3-12, were essentially free of abnormal structures.

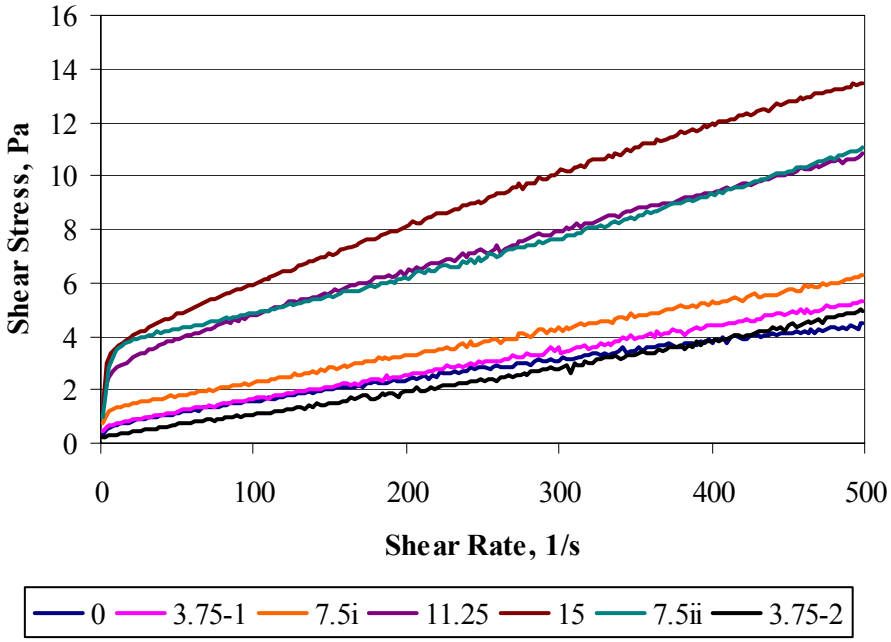

Figure 3-12. Typical Down Ramp Flow Curves of SRAT Products

The SRAT products as a group were more rheologically problematic than the starting sludges. Humps of varying size (Batches 3.75, 7.5, and 11.25) and an elevated plateau (Batch 15) were seen in the up ramp flow curves of the SRAT products. These occurred between 0/s and ~150/s. This limited Bingham plastic model fits to the region beyond the hump (~150/s-500/s). All down ramp flow curves were fit (Appendix G) to the data from 30/s to 500/s shear rate. Fitting data to the Bingham plastic model was

only satisfactory in providing a relative ranking of the SRAT products due to the thixotropic nature of the samples (time independent model being fit to time dependent data). The DWPF target operating region for sludge was taken to be a yield stress between 15 and 50 dynes/cm^2 and a consistency of 5-12 cP[4]. Table 3-13 below summarizes the fitting results. Although the last three up ramp yield stresses were outside the DWPF Operating Region, the samples were still fairly fluid and poured easily.

Table 3-13. SRAT product Bingham plastic model parameters

Batch No.	Yield Stress Up ramp Dynes/cm^2	Yield Stress Down ramp Dynes/cm^2	Consistency Up ramp cP	Consistency Down ramp cP	pH
0	18	11	6.1	7.9	4.81
3.75-1	26	8.0	5.5	9.2	6.62
3.75-2	22	0.5	6.3	9.5	5.79
7.5i	19	12	9.2	10.	6.54
7.5ii	92	44	6.3	16	6.37
11.25	52	33	12	15	6.40
15	82	46	12	19	6.16
DWPF Operating Region	15-50	15-50	5-12	5-12	NA

Two trends are again evident in the data. The yield stress fell, and the consistency increased, between the up ramp and the down ramp in all seven cases. The yield stress fell by roughly 8-50 dynes/cm^2, and the consistency increased by roughly 1-9 cP. This is a consequence of the thixotropic behavior of the SRAT products. The ranges in variations were larger, however, than were seen for the starting sludges.

A trend due to the depleted uranium content was detected in the SRAT products; see Figure 3-13 and Figure 3-14 The Batch 11.25 and 15 SRAT products became relatively thicker as a consequence of SRAT processing. The other four systems did not show much change (analysis of the 7.5ii SRAT product was difficult due to the shape of the curve).

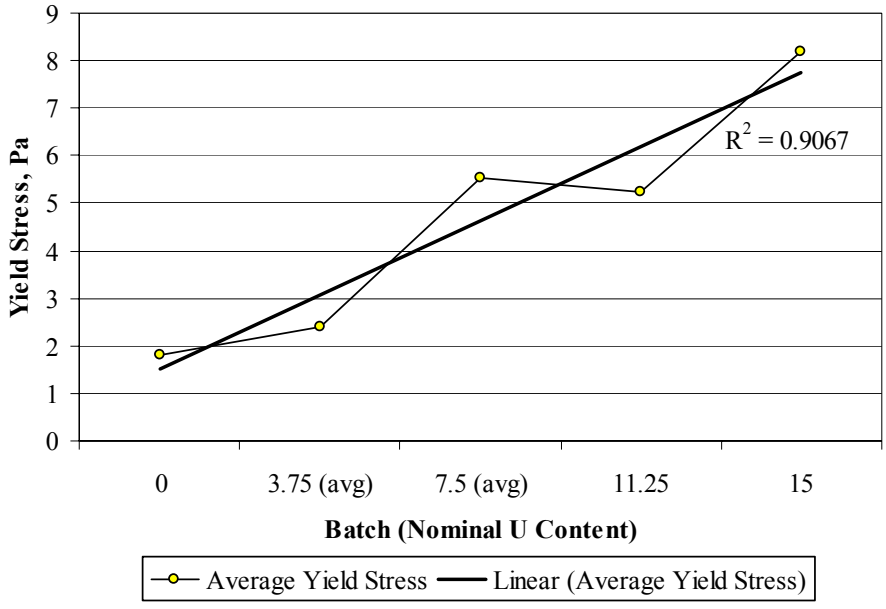

Figure 3-13. SRAT Product Yield Stress versus Nominal Uranium Level (Up Curve Basis)

Yield stresses from the two SRAT products from Batch 3.75 simulant were averaged into a single data point in order to avoid weighting the two runs disproportionately in the regression analysis. Individually, Batch 3.75 SRAT 1 had a yield stress of 2.6 Pa, and SRAT 2 had a yield stress of 2.2 Pa. These measurements are consistent with our understanding of the effect of pH on yield stress, but based upon wt % solids measurements, the effects are possibly reversed. This difference is probably due to the lower pH of SRAT 2 as compared to SRAT 1. Yield stresses from the two SRAT products from the Batch 7.5i and 7.5ii runs were also averaged into a single data point.

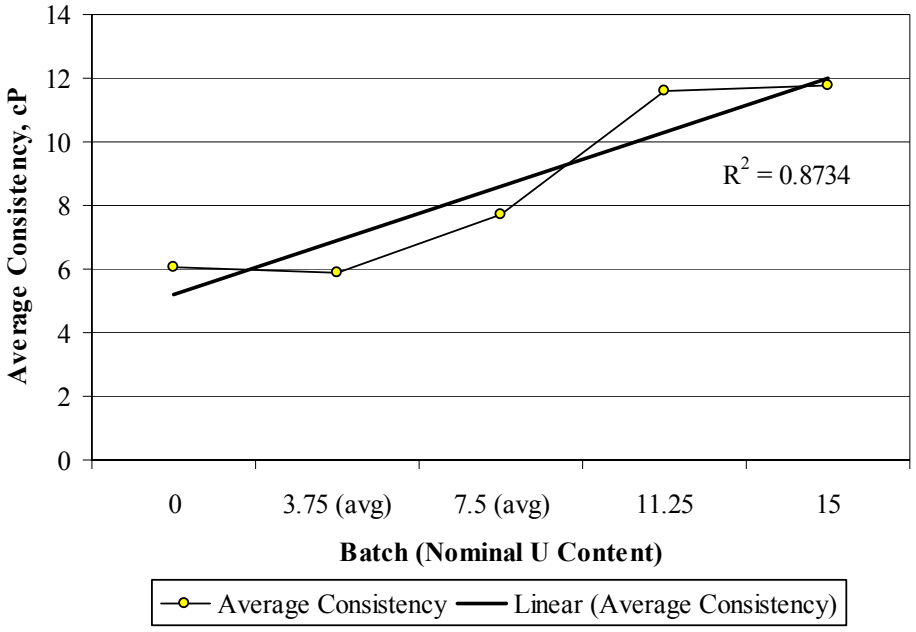

Figure 3-14. SRAT Product Consistency versus Nominal Uranium Level (Up Curve Basis)

Consistencies from the two SRAT products from Batch 3.75 simulant were averaged into a single data point. Consistencies from the SRAT products from the Batch 7.5i and 7.5ii runs were averaged into a single data point. Both the yield stress and the consistency trends with nominal uranium content appear to be statistically significant, i.e. there was greater than a 95% likelihood that both the yield stress and the consistency depended on the uranium content by analysis of variance ($F < 0.02$ in both cases). Due to the large uncertainty in the data from the 7.5i and 7.5ii runs, the R^2 values in Figure 3-13 and Figure 3-14 may not fully reflect the uncertainty in any values derived from these figures.

The down ramp flow curves consistently fell below the up flow curves over the entire range of shear rates. This difference was largest at low shear rates. This thixotropic behavior was investigated further. There were some issues with the manual instrument zero function that impacted some of the early data. Later data are given below for the Batch 7.5ii SRAT product in Figure 3-15, at which point the instrument issues had been resolved.

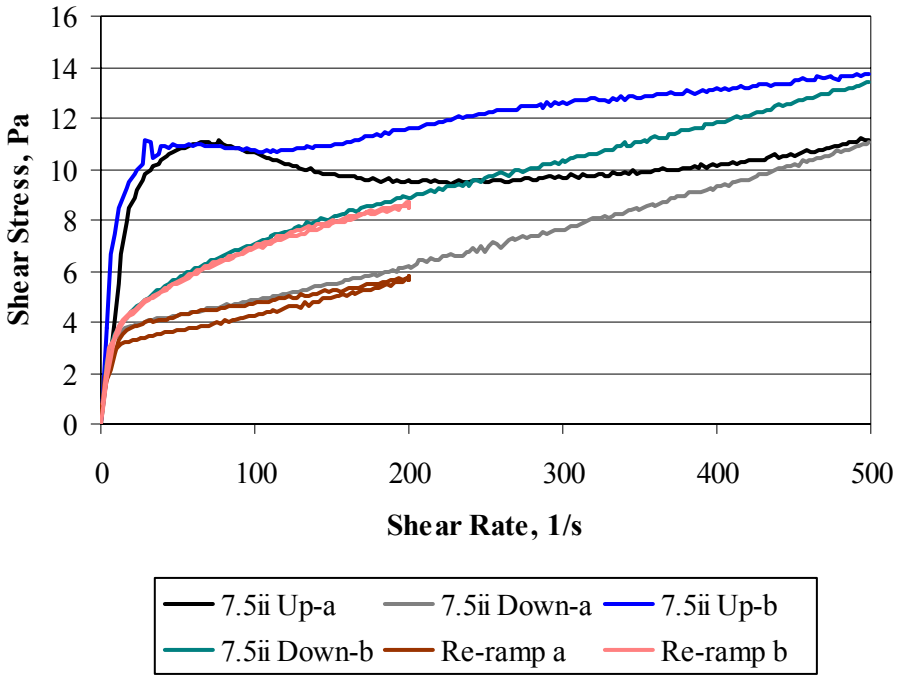

Figure 3-15. Re-Ramping the Batch 7.5ii SRAT Products

Two observations are noteworthy in the re-ramp data. First, there was no hump in the up ramp portion of either flow curve during the re-ramp to 200/s shear rate. Second, there was little further thinning of the flow curve during the re-ramp relative to the down flow curve. In the numerical analyses presented in Table 2-15 and Table 3-13, the Bingham model yield stresses and consistencies were obtained by neglecting the hump in the up ramp data. The justification for this was obtained from data such as that in Figure 3-15. Several samples that were found to have humps were kept in the rheometer after completion of the down ramp portion of the flow curve. These were then re-ramped up through the shear rate range corresponding to the hump. Nothing resembling a hump was observed on the second pass through this range of shear rates. Consequently, the humps were treated as a transient phenomenon that was irrelevant to the relative ranking of the various systems.

Reproducibility of the rheological data, as indicated by the proximity of the second flow curve (-b) to the first flow curve (-a) in Figure 3-15, was better in all other cases (sludges and SRAT products) than that seen here (see Appendices D and F for the entire set of flow curves). The variation seen here is still well within the normal ranges seen in the past.

4.0 DISCUSSION

4.1 SRAT Feeds and Products

The variability in the two Batch 7.5 slurries indicates that there is considerable difficulty in preparing consistent sludges. Additionally, there may be factors in sludge makeup other than starting materials, precipitation temperature, and agitation rate, which need to be controlled more closely if one intends to compare or look for small differences in behavior between sludge batches. Some of these yet unidentified factors may impact particle size distributions. A greater understanding of the factors which impact sludge makeup is the subject of on-going study[16] by Russ Eibling (SRNL, ITS).

The Batch 0 sludge was processed at a different redox target, 0.15, rather than 0.20, due to an excess addition of nitric acid, and was therefore more oxidizing than the other SRAT cycles. The pH was lower, but not necessarily unexpectedly lower since the second Batch 3.75 had a pH intermediate to that of Batches 0 and 7.5i or 7.5ii. While no acid demand due to the presence of U was observed during the room temperature titrations of the SRAT feeds, this does not rule out the possibility of an acid demand by U during the mixed formic and nitric acid addition at elevated temperature, as occurs during a SRAT cycle. If there was such an acid demand at elevated temperature, it may be limited since there was no linear increase in final pH beyond the Batch 7.5 feeds. The nitrate level in Batch 0 was higher, but the measured formate ion levels are essentially constant to ±10% of the mean across the series of SRAT products. The anion data has the highest degree of uncertainty of the measurements made during these experiments, so it is difficult to draw definitive conclusions from it.

The starting form of U was Clarkeite, which contains U(VI). Clarkeite is a uranium species also found in actual SB2 tank waste. A comparison was made between the sludges XRD results obtained in this study and those obtained in the preliminary work with U[5]. The initial work only looked at the final SRAT product solids, hence no spectra were available of the starting SRAT feed materials. Archive samples allowed us to obtain spectra of the starting solids. To ascertain whether or not there had been any changes as a result of aging since the original SRAT product spectra were obtained in July 2003, one sample of the SRAT product was also submitted for analysis. The spectra obtained appear in Figure 4-1 – Figure 4-3. The spectrum of the 15 wt % feed was essentially like that of the 7.5 wt % feed and is not provided here.

The feed materials from the earlier study were not unlike those obtained in this study and contained the expected Gibbsite, Goethite, and Calcite, though no manganese containing species was identified. These results were somewhat surprising in light of the sometimes unusual species previously reported for the SRAT products[5]. The previous study's SRAT products indicated the presence of Hematite, Fe_2O_3, but also the less common Franklinite manganoan, $Zn_{0.6}Mn_{0.4}Fe_2O_4$ containing Mn(II), sodium aluminum silicate, $Na_{1.65}Al_{1.65}Si_{0.35}O_4$, and sodium aluminum iron oxide, $Na_2(Al, Fe)_{12}O_{19}$. The resampled SRAT product from the nominally 7.5 wt % feed indicated none of the previously identified species, but rather the expected Gibbsite, Goethite, and Calcite. All of the Clarkeite was apparently dissolved leaving only a hint of its presence visible in Figure 4-3 with a "?" mark. This is not unexpected due to the low pH of the SRAT product at 4.45; the earlier SRAT cycles were conducted at 170% acid stoichiometry rather than 130% as done in this work. The other species obtained earlier must have resulted from a sampling issue since the samples were not homogenized prior to submission for analysis. In the spectra included here, the solids were collected by vacuum filtration, dried at 105 °C overnight (approximately 15 hrs), crushed to homogenize the sample, and then submitted for analysis. The only Mn containing solid in actual SB2 waste, Desautelsite, $Mg_6Mn_2(OH)_{16}CO_3 \cdot 4H_2O$, was not found in either simulant study. In this work, Manganite, Mn(OH)O, was found, which like Desautelsite contains Mn(III).

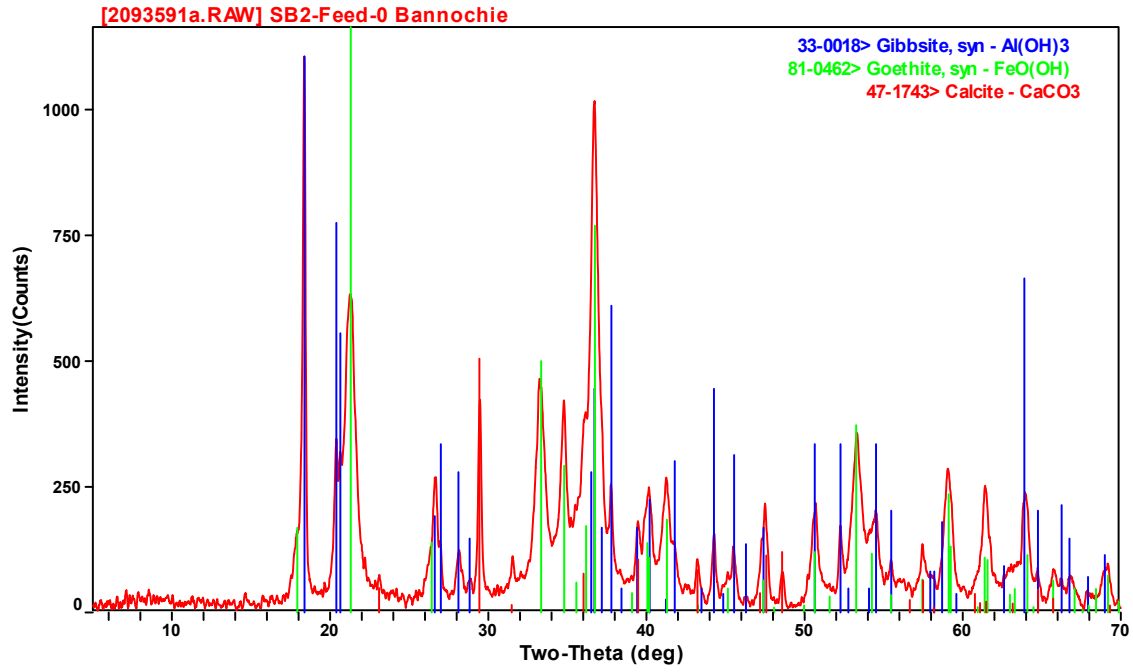

Figure 4-1. XRD Spectra of the CETL SB2 Simulant without Uranium Used in the First Impacts of U on SB2 Processing Study

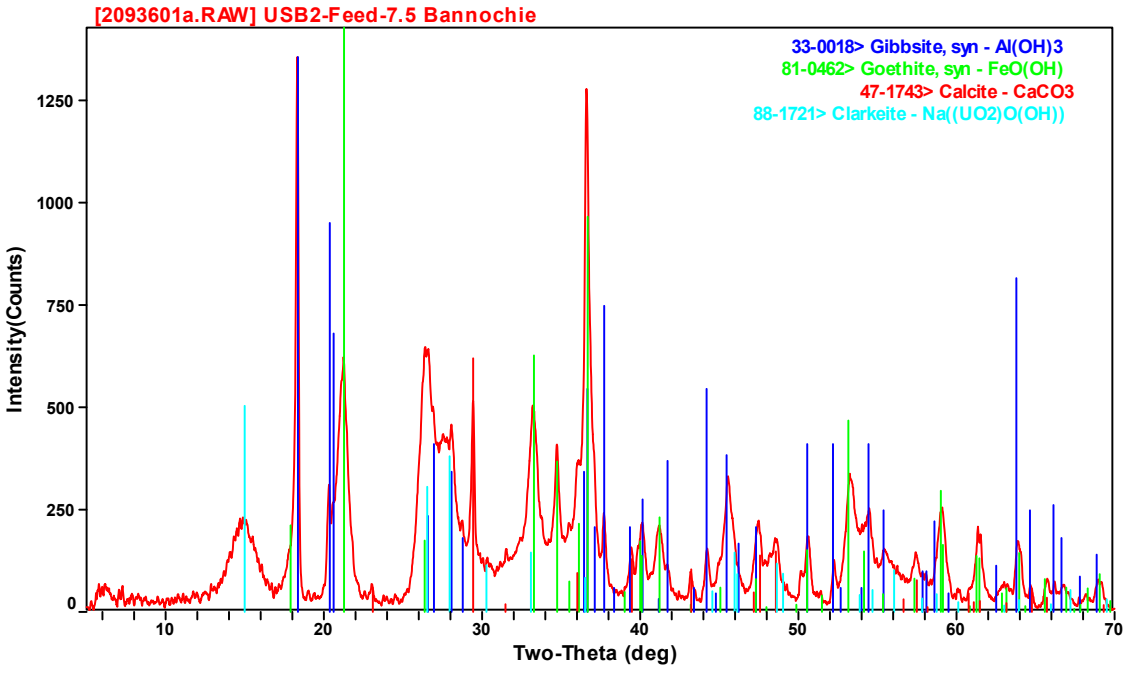

Figure 4-2. XRD Spectra of the CETL SB2 Simulant with Nominally 7.5 wt % Uranium

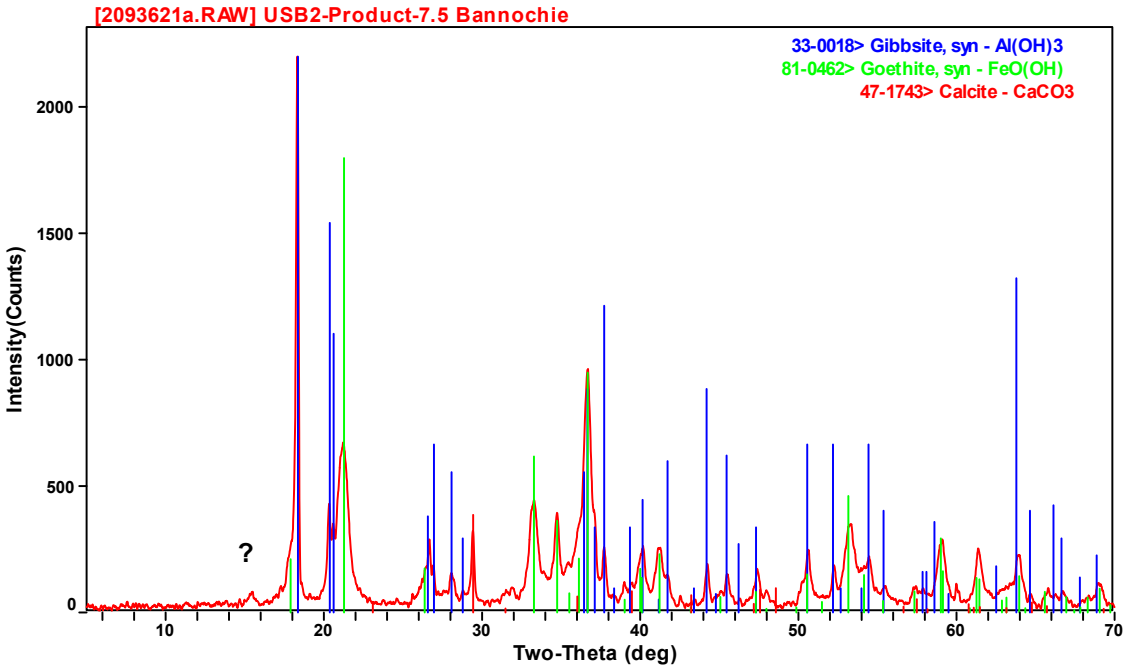

Figure 4-3. XRD Spectra of the CETL SB2 Simulant with Nominally 7.5 wt % Uranium Following SRAT Processing

Essentially no soluble U was found in the SRAT feeds or those products with pH values above 6. Hence the co-precipitation of U during sludge make-up did resolve an uncertainty from the preliminary U work as to how representative the slurries were to actual waste sludges[5]. The observation of soluble U (7.8%) in the Batch 3.75 second SRAT product that had a final pH of 5.79 and the absence of soluble U in the first Batch 3.75 SRAT product with a final pH of 6.62, and all of the other SRAT products with final pH's above 6, would seem to indicate that the lower pH, possibly in conjunction with the elevated temperatures of the SRAT cycle, is the primary factor in solubilizing U.

The first Batch 3.75 SRAT product had a mixed U oxidation state compound, $U_3O_9^{2-}$, which was not seen in any of the other products. This mixed oxidation state species indicates that some of the uranium has likely been reduced from (VI) to (IV). The presence of a mixed oxidation state U compound indicates there is some redox activity in the system that is impacting U. This particular SRAT cycle was repeated to reproduce this mixed oxidation species and to eliminate uncertainties surrounding the higher than anticipated volume of product from the first experiment. Unfortunately, the mixed oxidation state species was not observed in the second product. The fact that it was not repeated may indicate that the factors affecting this equilibrium are not completely defined.

Particle size measurements indicated that each sludge experienced particle size reductions following SRAT cycle processing. Whether these smaller particles have a greater potential for air-entrainment is uncertain. During a review of the pulse jet system for RPP at PNNL, there was a concern over air introduction into the slurry. It was mentioned that the sludge particles could adhere to these fine bubbles (entrained air) which could lead to a foaming problem. XRD analyses of the SRAT product solids indicated the U containing species were very fine, on the order of 100 Å, and not fully crystalline. This observation could indicate that the uranium species are dissolving and then reprecipitating during processing. The final form of the reprecipitated uranium may vary with the redox target for the batch. Therefore, the observation that finer particles result from SRAT processing, combined with the plant

observation of entrained air, leads one to suspect that there may be a connection between the SRAT processing of high uranium containing sludges and the air-entrainment concern.

The observed swelling (refer to Table 3-10) of the SRAT slurry volumes upon heat up from 93 – 100 °C following completion of acid addition, may also be connected to air-entrainment. Since no mass was added to the system during heat up to boiling, the volume change must be due to entrained off-gas released from the system during the increase in temperature. The entrainment of this off-gas was highest in Batch 11.25.

An interesting question has been raised by this work. It is not clear whether the redox target of the SRAT cycle impacts the final uranium oxidation state in the sludge. The partially reduced $U_3O_9^{2-}$ species we observed in only one SRAT product contains two U(VI) and one U(IV). This sludge species would not be expected to liberate oxygen in the melter, and therefore could not result in foaming. From a glass perspective, the uranium staying as U(VI) following the SRAT cycle, as was largely observed in this study, can be assumed to be a worst case scenario. The U species reported in the glass is U_3O_8, or expressed another way, two $U(VI)O_3$ and one $U(IV)O_2$. If all the U is coming to the melter as U(VI), this will result in some oxygen liberation in the melter, and therefore a potential for foaming.

4.2 Rheology

Comparisons of SRAT product to corresponding starting sludge were generated in addition to those limited to either the six sludges or to the seven SRAT products. These looked at each SRAT product relative to its starting sludge at a given U level. They assessed the impact of SRAT processing on the slurry rheology. These comparisons were legitimate for this series, since the SRAT feeds were prepared to essentially identical criteria, and since the SRAT cycle targeted a final volume approximately the same as the volume of the starting sludge.

The seven rheological comparisons are described below in order of increasing depleted uranium content. For consistency, replicate SRAT product flow curves are blue and black, and denoted by “1” and “2”, for the first measurement and the replicate. The pre-run measured flow curves of the sludges are given in red and orange. They are labeled by the date to indicate that they are the pre-run measurements, and denoted by “a” and “b”, for the first measurement and the replicate.

- The Batch 0 SRAT product was qualitatively similar to (or slightly thinner than) the starting sludge.

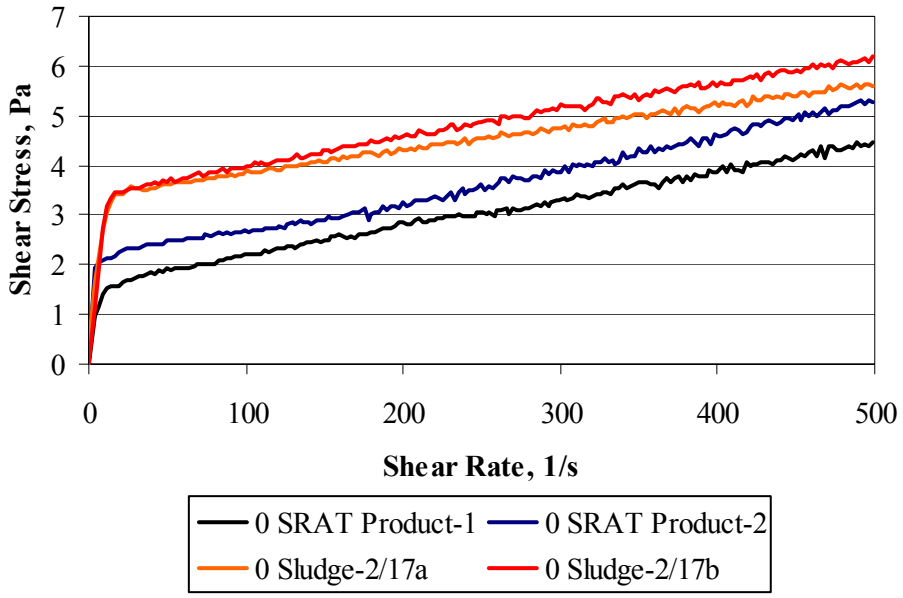

Figure 4-4. Impact of SRAT Processing, Batch 0, Up Ramp Flow Curves

- The Batch 3.75 SRAT product developed a hump in the flow curve and was slightly thicker than the starting sludge for the initial 3.75 SRAT run.

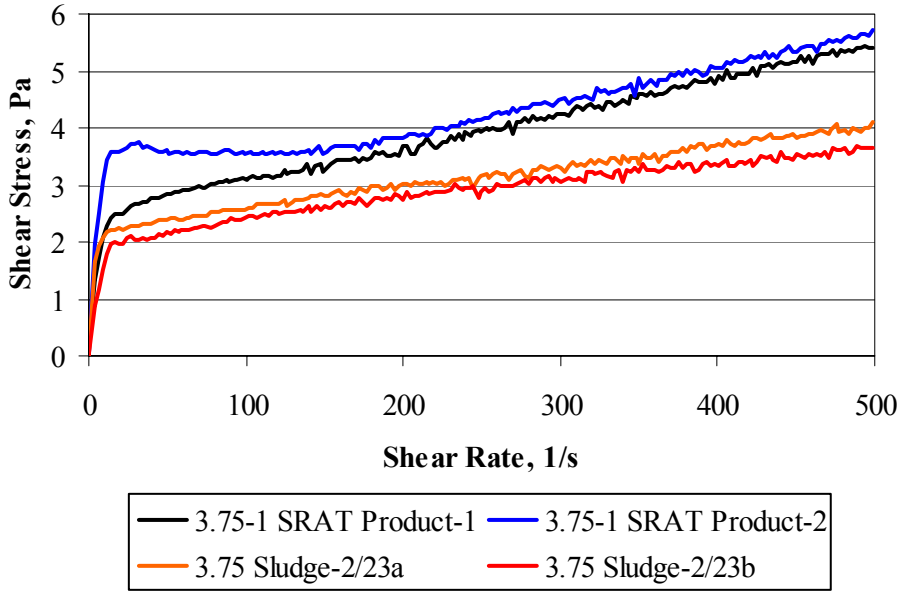

Figure 4-5. Impact of SRAT Processing, Batch 3.75, Run 1, Up Ramp Flow Curves

- The Batch 3.75 SRAT product developed a pronounced hump in the flow curve and was slightly thicker than the starting sludge for the second 3.75 SRAT run.

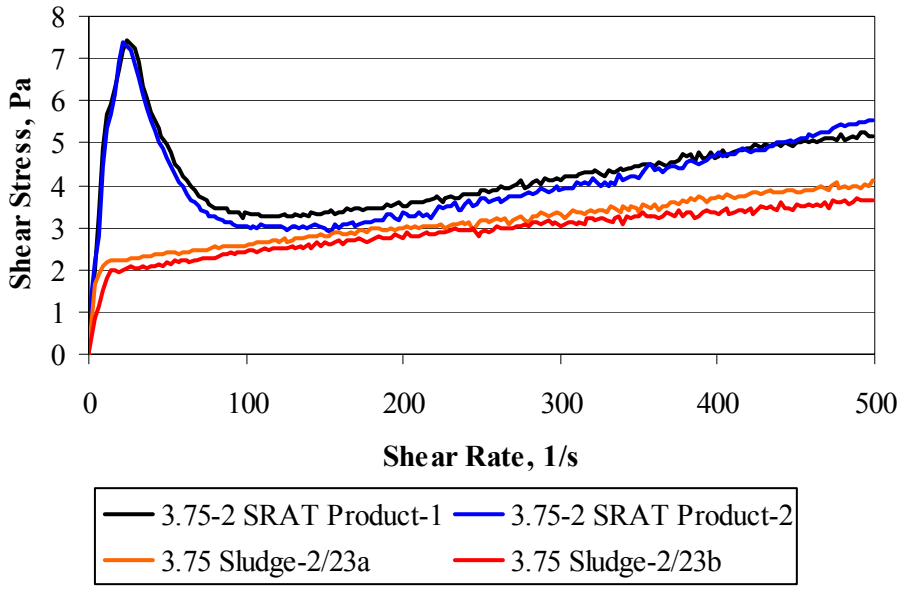

Figure 4-6. Impact of SRAT Processing, Batch 3.75, Run 2, Up Ramp Flow Curves

- The Batch 7.5i SRAT product was nearly identical to the starting sludge in rheology, except for a new hump in the up ramp portion of the flow curve.

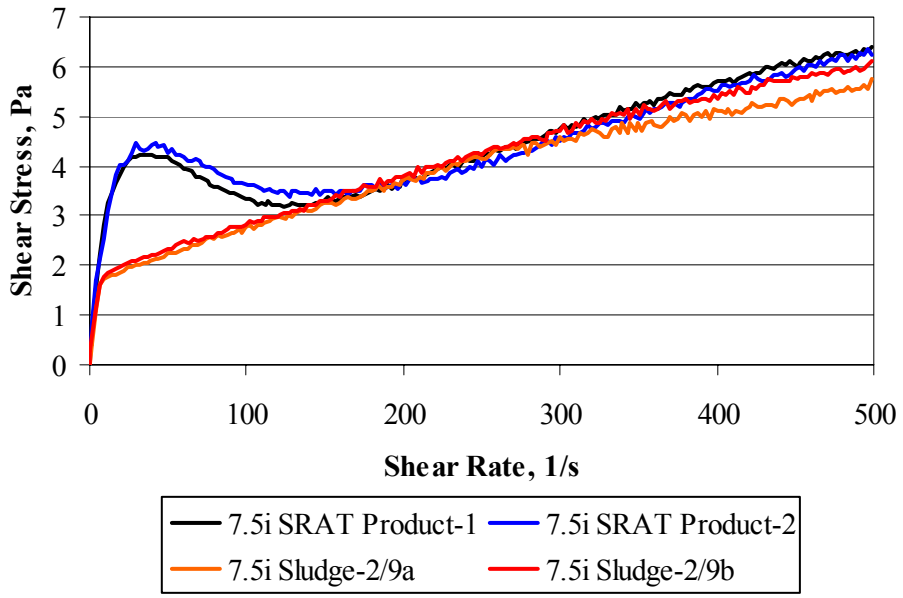

Figure 4-7. Impact of SRAT Processing, Batch 7.5i, Up Ramp Flow Curves

- The Batch 7.5ii SRAT product was nearly identical to the starting sludge except for a new hump in the up ramp portion of the flow curve (similar effect to that seen with Batch 7.5i, although all shear stress data was numerically greater).

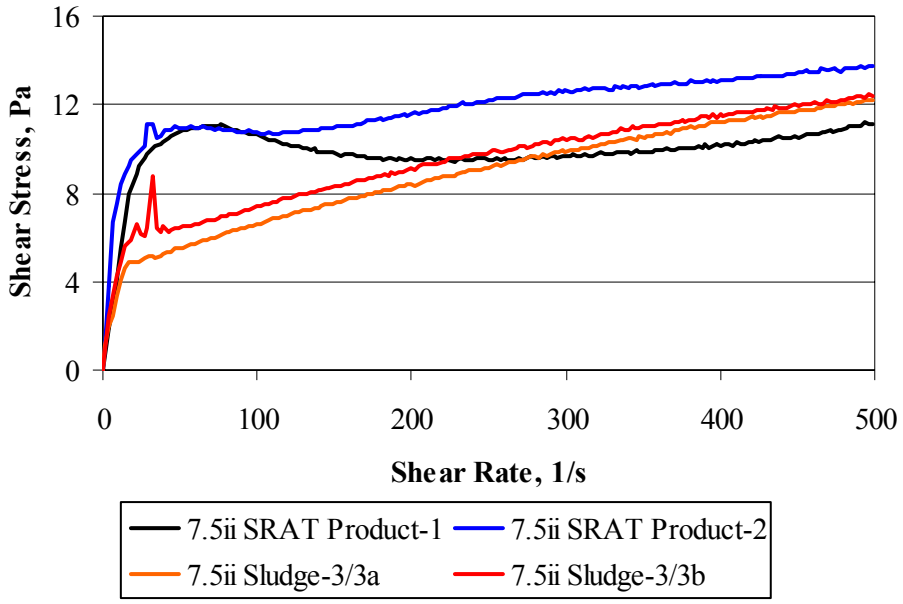

Figure 4-8. Impact of SRAT Processing, Batch 7.5ii, Up Ramp Flow Curves

- The Batch 11.25 SRAT product was considerably thicker than the starting sludge, and also developed a small hump in the up ramp portion of the flow curve.

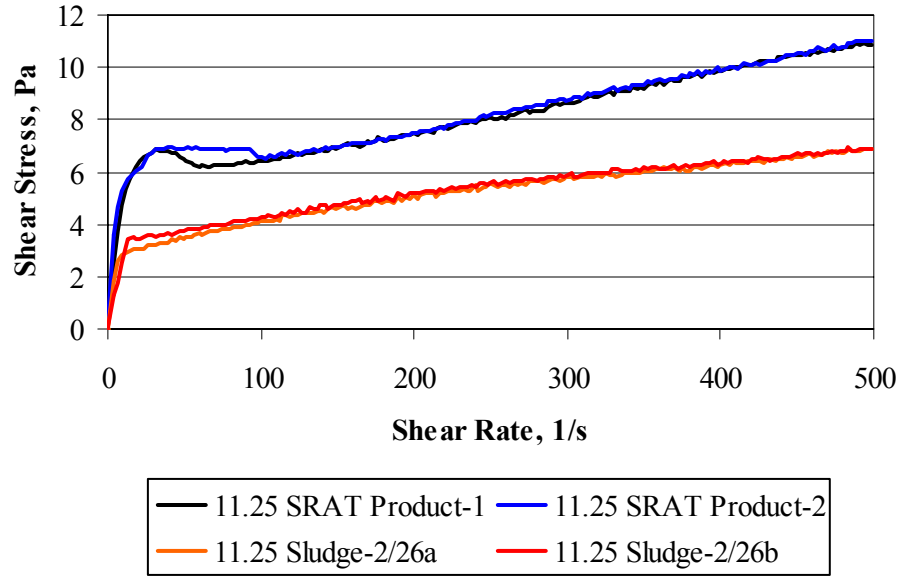

Figure 4-9. Impact of SRAT Processing, Batch 11.25, Up Ramp Flow Curves

- The hump in the Batch 15 sludge survived SRAT processing and was still present in the SRAT product. The SRAT product was considerably thicker, however, than the starting sludge.

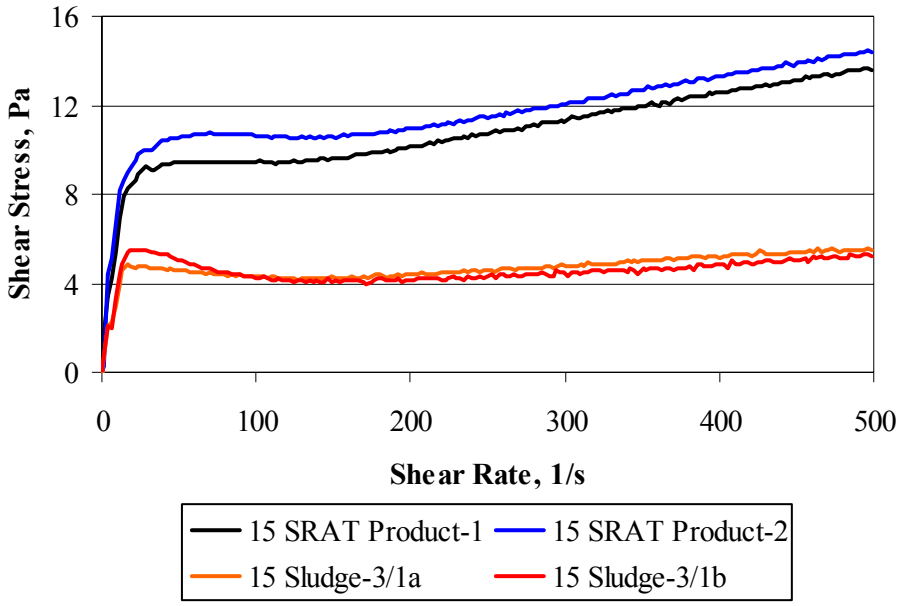

Figure 4-10. Impact of SRAT Processing, Batch 15, Up Ramp Flow Curves

The trend in most prior simulant work has been that the SRAT product was thinner than the starting sludge (implicit in this statement is that the volume of SRAT product is comparable to the volume of starting sludge in the SRAT). This was not observed in any of the six SRAT cycles with U performed as part of this program. Note, the non-uranium containing simulant was thinner, but this was believed to be due to the significantly lower pH of the SRAT product. One possibility is that there is a part of the simulant preparation process that thickens the simulant, but this thickening is somehow reversed in the SRAT cycle. In the case of these six in-house U simulants, perhaps the thickening process did not occur (since the sludge simulants were relatively thin), and the subsequent elimination of the thickening also did not occur (since the thickening never happened). There were obvious differences in scale and mixing between the SRNL simulant preparations and the historic simulant preparations at Optima, USC-Columbia, and CETL that could be responsible. A current program is investigating some of these issues in simulant preparation.

5.0 CONCLUSIONS

5.1 SRAT Feeds and Products

- Co-precipitation of U during simulant sludge makeup results in the formation of Clarkeite, $Na((UO_2)O(OH))$, a hydrated uranate containing U(VI), as the final uranium species. This same species has been identified in actual tank waste for SB2.

- There is no increase in calculated acid demand at room temperature as a result of increasing levels of U in SRAT feed. Whether or not there is an impact on acid demand at elevated temperature or in the presence of mixed acids has not been addressed.

- Essentially no soluble U was found in the SRAT products with pH values above pH 6. This is consistent with observations from SRNL Shielded Cells SRAT cycles with SB2/3 blended waste[17] and SB3 waste[18] which did see soluble U in the SRAT products but which had final pH's below 6. Since DWPF operated SB2 processing at approximately pH 5.5, they should have seen more soluble U and potentially thinner SRAT products.

- Different U species can be produced in the SRAT product suggesting the potential for some U redox activity. The primary species, $U_2O_7^{2-}$ contained fully oxidized U(VI), while one product contained the mixed U oxidation state species $U_3O_9^{2-}$. The impact of redox target on the SRAT product U species could not be addressed since only a single redox target was studied.

- XRD data suggests there was some dissolution and re-precipitation of U as a result of SRAT processing since the SRAT product U-containing species were fine and not fully crystalline.

- SRAT vessel contents entrain gas and the volume increases during processing when the temperature is raised from 93 to 100 °C, and the degree of expansion is greatest at the highest levels of U (Batches 11.25 and 15).

5.2 Rheology

- All six sludges and seven SRAT products were *thixotropic* slurries, i.e. the apparent viscosity decreased with time under shear on a time scale of ten minutes. This produced down ramp flow curves that were always below the up ramp flow curves.

- The six sludges and seven SRAT products were generally *pseudo-plastic* slurries, i.e. the apparent viscosity decreased with increasing shear rate. There were some transient phenomena early in some of the up ramp flow curves during which this was not true.

- The six sludges and seven SRAT products were relatively thin and free-flowing slurries that when shaken vigorously did not retain any significant quantity of air bubbles.

- Rheological properties of the six new simulants were effectively independent of the time since preparation over a time scale of one to six weeks.

- The six new simulants had rheological properties that were bounded by those of the two Batch 7.5 preparations. This indicates that the impact of co-precipitated U on rheology was no more significant than other variations in properties that occur during simulant preparation.

- SRAT product samples showed more anomalous rheological behavior than the starting sludges. This was seen in the occurrence of more transient phenomena in the up ramp flow curves. There was also a greater spread in the rheological results for the seven SRAT products than for the six starting sludges. This indicated that SRAT processing had a variable impact on rheology.

- Both the SRAT product yield stress and consistency were found to increase with an increase in uranium concentration in a statistically significant manner.

- Transient phenomena (humps) in the up flow curves never re-occurred when a sample in the rheometer was run through a second up flow curve.

- The impact of SRAT processing on rheology was most apparent in the results for the Batch 11.25 and 15 slurries. These slurries thickened significantly during SRAT processing. SRAT products have generally been thinner than the starting sludges in previous work.

6.0 RECOMMENDATIONS/PATH FORWARD

The impact of uranium on SRAT cycle processing, and ultimately DWPF processing issues such as air-entrainment, has been studied. There does not appear to be a straightforward relationship between the level of uranium in the feed, at least to the degree we were able to isolate this contribution from other factors such as particle size, and the processing behavior of the sludge. There are still uncertainties related to uranium and the following recommendations may help address these issues.

- Evaluation of the impact of lower pH during the SRAT cycle on the uranium solubility in the SRAT product may help determine if a significant dissolution of uranium has an impact on the rheological properties of the material. This may help us gain a better understanding of the relationship between rheological behavior and plant operational issues.

- Based upon the uranium species produced in the SRAT product ($U_2O_7^{2-}$ and $U_3O_9^{2-}$), it may be useful for melter operations to understand how the redox target (ratio of nitric acid to formic acid) impacts the uranium species formed during SRAT processing. A series of SRAT tests varying the acid ratios may address this issue.

- Evaluate the impact of particle size variations on the starting sludge rheology as well as the resulting SRAT product.

- Begin to characterize the tank waste for particle size distribution to develop an understanding of the impact of this parameter on processing behavior and assess the variability of this parameter in various samples received for qualification and study. Previous methods involving extremely high dilutions into unmatched matrices, i.e. water, for Microtrac analysis may alter the particle size of the sludge solids. Installation of a Lasentek instrument in the SRNL Shielded Cells would address this shortcoming.

- Characterize more actual tank waste solids and SRAT product solids produced from actual tank waste by XRD to develop a better understanding of the species present and formed as a result of processing. This information can then be related back to processing issues as they arise in the plant to help explain what may be causing any given issue.

- The scale of sludge makeup should be larger than the 1L scale used in this study. Samples taken for analyses prior to completion of each slurry represent too large a fraction of the total material and results in unnecessary variability.

- The scale of SRAT cycle simulations should be larger than 300 g. At this level noble metal additions are miniscule and acid addition rates are very low leading to considerable variability and potential error.

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8.0 ACKNOWLEDGEMENTS

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APPENDIX A. SAMPLE SIMULANT MAKEUP PROCEDURE

Uranium Sludge Batch 2 Preparation

Date: December 9, 2003
Activity: LWIIBSF04
Researcher: C. J. Bannochie, 774-42A, 151 / Dave Herman, 735-11A, 119
Manager: S. L. Marra
Technician: John Duvall / Debbie Marsh / Sarah Brown

1.0 - Introduction:

These instructions are for the preparation of DWPF sludge batch 2 simulant with 7.5 wt% uranium.

2.0 - Objectives:

Prepare a sludge solution

3.0 - Safety

Don lab coat and gloves. Work will involve using 50 wt % NaOH. Care should be taken when adding this solution to the bulk solution. This addition will be a neutralization and should be completed in a hood. This addition should take place slowly.

4.0 - Waste Disposal

Any waste produced as part of this work may be hazardous. pH of the solution should be adjusted to 2-4 before disposal in the HLW drainage system.

5.0 - Sludge Preparation

5.1 Obtain the following chemicals. Record the M&TE identifier for the balance and weight set used.

1

Component	FW	Mass (g)	Mass Used	Manufacturer & Lot #
$Mn(NO_3)_2$ [50wt%]		22.164		
NaOH [50 wt%]		252.575		
$KMnO_4$		6.529		
$Fe(NO_3)_3 \cdot 9H_2O$	404.02	403.695		
$Ni(NO_3)_2 \cdot 6H_2O$	290.81	15.901		
$UO_2(NO_3)_2 \cdot 6H_2O$	502.146	41.275		
$CaCO_3$	NA	zero	NA	

See Instructions below (5.2 – 5.11) for preparation of above reagents.
List continued on the page 4.

5.2 Prepare 252.575 g _____of 50 wt% NaOH. Mix 126.288 g _____ of NaOH with 126.275 g _____ of water.

5.3 Prepare 10.8 L of pH 10.5 water (± 0.5 pH unit) (use 0.134 g _____ NaOH).

5.4 Mix 22.164 g _____ of 50 wt % $Mn(NO_3)_2$ with 165.090 g _____ of water in a 6L water jacketed preparation vessel. Adjust the temperature to 35 to 40 °C. Solution is to be stirred continuously.
Label: Solution 1

5.5 In a separate vessel, dissolve 6.529 g _____ of $KMnO_4$ in 227.043 g _____ of water. When the permanganate has dissolved, adjust solution temperature to between 35 to 40°C.
Label: Solution 2

5.6 Add Solution 2 to Solution 1 slowly over 1 hour - Maintain temperature at 35 to 40 °C.

5.7 Dissolve 403.695 g _____ $Fe(NO_3)_3 \cdot 9H_2O$ in 442.341 g _____of water.
Label: Solution 3

5.8 Slowly add Solution 3 to Solution 1. Maintain temperature at 35 to 40 °C.

5.9 Add 15.901 g _____ of $Ni(NO_3)_2 \cdot 6H_2O$ to Solution 1. Mix for at least 15 minutes.

5.10 Add 41.275 g _____ of $UO_2(NO_3)_2 \cdot 6H_2O$ to Solution 1. Mix for at least 15 minutes.

5.11 In a separate vessel add 252.575 g _____of 50% NaOH solution to 42.898 g _____ of water.

5.12 Increase agitation to 600 rpm.

5.13 Slowly add the caustic solution to Solution 1, keeping the temperature between 35 and 40 °C. This step should be done with continuous agitation in a hood.

5.14 Measure pH of aqueous fraction, adjust to ≥ 10.5 (if already > 10.5, take no action).

5.15 Continue agitation for 30 minutes following final chemical addition.

5.16 Pump the sludge from the jacketed preparation vessel in to a settling bottle, set aside. Allow Solution 1 to settle for 12 hours (or longer). Remove aqueous phase and discard.

5.17 Add 3.6 L pH 10.5 adjusted water to Solution 1. Agitate for 30 minutes.

5.18 Allow Solution 1 to settle for 12 hours (or longer). Remove aqueous phase and discard.

5.19 Measure pH, adjust to ≥ 10.5 (if already > 10.5, take no action).

5.20 Add 3.6 L pH 10.5 adjusted water to Solution 1. Agitate for 30 minutes.

5.21 Allow Solution 1 to settle for 12 hours (or longer). Remove aqueous phase and discard.

5.22 Measure pH, adjust to ≥ 10.5 (if already > 10.5, take no action).

5.23 Add 3.6 L pH 10.5 adjusted water to Solution 1. Agitate for 30 minutes.

5.24 Allow Solution 1 to settle for 12 hours (or longer). Remove aqueous phase and discard.

5.25 Measure pH, adjust to ≥ 10.5 (if already > 10.5, take no action).

5.26 Confirm soluble solids concentration in the aqueous fraction of the slurry is between 0.15 - 0.20 wt %.

5.27 Determine concentration of Fe, Mn, and Ni in sludge solids and concentration of Na in supernatant liquid by ICP-AES.

5.28 Add all remaining chemicals. Each chemical is to be added separately with at least 15 minutes between additions.

NOTE: The following reagent concentrations need to be adjusted based on the size of the sample removed for analyses listed in 5.26 and 5.27. See researcher for adjustment calculation prior to preparing these reagents.

Component†	FW	Mass (g)	Adj. Mass(g)	Mass Used	Manufacturer & Lot #
$Al(OH)_3 \bullet nH_2O$ [32-35 wt% water]*		74.855			
$BaSO_4$	233.40	0.778			
$1.5Ca_3(PO_4)_2 \bullet 0.5Ca(OH)_2$*	502.32	0.456			
$CaCO_3$	100.09	11.360			
$CaSO_4$ [anhydrous]*	136.15	1.205			
Cr_2O_3	151.99	0.715			
$CsNO_3$	NA	zero		NA	
CuO	79.54	0.366			
KNO_3	101.10	0.352			
KOH	NA	zero		NA	
MgO	40.31	0.438			
Na_2CO_3	124.00	4.767			
Na_2SO_4	142.04	0.666			
$Na_3PO_4 \bullet 12H_2O$	380.12	0.408			
NaCl	58.44	4.672			
NaF	41.99	0.078			
NaI	149.89	0.079			
$NaNO_2$	69.00	16.467			
$NaNO_3$	84.99	5.947			
NaOH	40.00	9.681			
Nd_2O_3	NA	zero		NA	
$PbSO_4$	303.25	0.822			
SiO_2	60.09	3.746			
$SrCO_3$	147.63	0.273			
Zeolite	NA	Zero		NA	
ZnO	81.37	0.742			
ZrO_2	123.22	1.479			

* specified mass assumes given component, if hydration level or other change occurs, mass needed must be recalculated.
† particle size must be less than 40 µm

5.29 Agitate for 1 hour.

5.30 Determine wt % solids in triplicate using 5 g samples. Submit sample for total cationic and anionic analysis.

	Sludge Batch 2 Simulant		
Filter Paper mass (g)			
g of sludge			
Dried (115°C) filter paper & sludge			
Wt. of dried sludge			
Wt % solids			

5.30.1 Weigh a filter paper.

5.30.2 Filter a 5.00 mL sample.

5.30.3 Wash filtered sample with water. Discard wash water.

5.30.4 Dry sample overnight at ~ 115 °C.

5.30.5 Weigh dried filter paper.

5.31 Store and label: DWPF Sludge Batch 2 Simulant w/ 7.5 wt % uranium.

6.0 - Housekeeping

Restore area to acceptable housekeeping standards.

7.0 - Documentation

Initial Instructions and return completed copy for placement in the Laboratory notebook.

APPENDIX B. SIMULANT RECIPES

Table B- 1. Recipe Calculation for 0 wt % Uranium Sludge Batch 2 Simulant

Recipe for Tank 40 + Tank 8 Blend
For 1.2 liter batch sludge simulant
Keyed to [2]-rev. for Bannochie, 11/2003 (solids boosted x 1.16)

Phase 1

[A]	25.172	gms	50% $Mn(NO_3)_2$
[B]	187.495	mL	Water
[C]	7.415	gms	$KMnO_4$
[D]	257.857	mL	Water
[E]	55.680	mL	Water
[F]	905.179	gms	7% Fe as Ferric Nitrate
[G]	18.059	gms	$Ni(NO_3)_2 \cdot 6H_2O$
[H]	286.294	gms	50% NaOH
[I]	48.720	mL	Water
[J]	0.000	gms	$CaCO_3$

This converts to these solids (iron phase must be guessed)

	gms	My check:	elements:	Total in sludge solids		
MnO_2	10.193	10.19	6.44	2.47%	0.1017	Mn
Fe_2O_3	104.513	44.32				
$Fe(OH)_3$	121.251	121.25	63.36	24.30%	1.0000	Fe
$Ni(OH)_2$	5.752	5.76	3.65	1.40%	0.0575	Ni
$CaCO_3$		0.00	0.00	-	see below	

The soluble portion must be removed by thorough washing.

Phase 4

Chemicals	gms					
$Al(OH)_3$	55.260	55.26	19.114	7.33%	0.3017	Al
$BaSO_4$	0.884	0.88	0.520	0.20%	0.0082	Ba
$Ca_3(PO4)_2$	0.479	0.48	5.755	2.21%	0.0908	total Ca
$CaCO_3$	12.902	12.90				
$CaSO_4$	1.368	1.37				
Cr_2O_3	0.812	0.81	0.556	0.21%	0.0088	Cr
$CsNO_3$	0.000	0.00				
CuO	0.416	0.42	0.332	0.13%	0.0052	Cu
KNO_3	0.399	0.40	0.154	0.06%	0.0024	K
KOH	0.000	0.00				
MgO	0.498	0.50	0.300	0.12%	0.0047	Mg
Na_2CO_3	4.767	4.77	16.910	6.48%	0.2669	total Na
Na_2SO_4	0.666	0.67				
Na_3PO_4	0.176	0.18				
NaCl	4.672	4.67				
NaF	0.078	0.08				
NaI	0.079	0.08				
$NaNO_2$	16.467	16.47				
$NaNO_3$	5.947	5.95				
NaOH	9.681	9.68				
Nd_2O_3	0.000	0.00				
$PbSO_4$	0.934	0.93	0.638	0.24%	0.0101	Pb
SiO_2	4.254	4.25	1.988	0.76%	0.0314	Si
$SrCO_3$	0.310	0.31	0.184	0.07%	0.0029	Sr
Zeolite	0.000	0.00				
ZnO	0.843	0.84	0.677	0.26%	0.0107	Zn
ZrO_2	1.679	1.68	1.243	0.48%	0.0196	Zr
	260.77	gms. (using $Fe(OH)_3$)				
Dry Solids	260.8	Includes Sludge + Supernate.				
		Sludge Solids				
	19.6%	Total Solids				
	3.0%	Soluble Solids				
Dry Solids	244.0	gms. (using Fe_2O_3)				
	18.3%	Total Solids				

Total	Anions:	Total, gms	%	Na Salts, gm	%
SO_4^{2-}		2.08	0.796%	0.45	0.173%
PO_4^{3-}		0.40	0.152%	0.10	0.039%
CO_3^{2-}		10.56	4.050%	2.70	1.035%
NO_3^-		4.58	1.758%	4.34	1.664%
Cl^-		2.83	1.087%	2.83	1.087%
F^-		0.04	0.013%	0.04	0.013%
I^-		0.07	0.026%	0.07	0.026%
NO_2^-		10.98	4.211%	10.98	4.211%
OH^- (tot)		100.26	38.449%	4.12	1.579%
O^{2-}		7.33	2.811%		
SUM=		139.12 gms		42.53	16.310%
Noble Metals, Mercury and Silver					
To Be Added On-Site				42.531	

Table B- 2. Recipe Calculation for 3.75 wt % Uranium Sludge Batch 2 Simulant

Recipe for Tank 40 + Tank 8 Blend
For 1.2 liter batch sludge simulant
Keyed to [2]-rev. for Bannochie, 11/2003 (solids boosted x 1.16)
reduce insolubles for U incorporation, constant Na 0.94

Phase 1

[A]	23.662	gms	50% $Mn(NO_3)_2$ in water
[B]	176.246	mL	Water
[C]	6.970	gms	$KMnO_4$
[D]	242.386	mL	Water
[E]	52.339	mL	Water
[F]	850.868	gms	7% Fe as Ferric Nitrate in water
[G]	16.976	gms	$Ni(NO_3)_2 6H_2O$
[-]	16.200	gms	$UO_2(NO_3)_2$
[H]	269.363	gms	50% NaOH in water
[I]	45.797	mL	Water
[J]	0.000	gms	$CaCO_3$

This converts to these solids (iron phase must be guessed)

	gms	My check:	elements:	Total in sludge solids		
MnO_2	9.582	9.58	6.06	2.32%	0.1017	Mn
Fe_2O_3	98.242	41.66				
$Fe(OH)_3$	113.976	113.98	59.56	22.85%	1.0000	Fe
$Ni(OH)_2$	5.407	5.41	3.43	1.31%	0.0575	Ni
$Na_2U_2O_7$	13.035	13.04	9.79	3.75%	0.1643	U
$CaCO_3$		0.00	0.00	-	see below	

The soluble portion must be removed by thorough washing.

Phase 4

Chemicals	gms					
$Al(OH)_3$	51.944	51.94	17.968	6.89%	0.3017	Al
$BaSO_4$	0.831	0.83	0.489	0.19%	0.0082	Ba
$Ca_3(PO4)_2$	0.451	0.45	5.410	2.08%	0.0908	total Ca
$CaCO_3$	12.128	12.13				
$CaSO_4$	1.286	1.29				
Cr_2O_3	0.763	0.76	0.522	0.20%	0.0088	Cr
$CsNO_3$	0.000	0.00				
CuO	0.391	0.39	0.312	0.12%	0.0052	Cu
KNO_3	0.375	0.38	0.145	0.06%	0.0024	K
KOH	0.000	0.00				
MgO	0.468	0.47	0.282	0.11%	0.0047	Mg
Na_2CO_3	4.767	4.77	16.910	6.49%	0.2839	total Na
Na_2SO_4	0.666	0.67		6.85%	0.2998	Na+U.Na
Na_3PO_4	0.176	0.18				
NaCl	4.672	4.67				
NaF	0.078	0.08				
NaI	0.079	0.08				
$NaNO_2$	16.467	16.47				
$NaNO_3$	5.947	5.95				
NaOH	9.681	9.68				
Nd_2O_3	0.000	0.00				
$PbSO_4$	0.878	0.88	0.600	0.23%	0.0101	Pb
SiO_2	3.999	4.00	1.869	0.72%	0.0314	Si
$SrCO_3$	0.292	0.29	0.173	0.07%	0.0029	Sr
Zeolite	0.000	0.00				
ZnO	0.792	0.79	0.636	0.24%	0.0107	Zn
ZrO_2	1.578	1.58	1.169	0.45%	0.0196	Zr
	260.71	gms. (using $Fe(OH)_3$)				
Dry Solids	260.7	Includes Sludge + Supernate.				
		Sludge Solids				
	19.6%	Total Solids				
	2.8%	Soluble Solids				
Dry Solids	231.9	gms. (using Fe_2O_3)				
	17.4%	Total Solids				

Total Anions:	Total, gms	%	Na Salts, gm	%
SO_4^{2-}	1.98	0.759%	0.45	0.173%
PO_4^{3-}	0.38	0.145%	0.10	0.039%
CO_3^{2-}	10.09	3.870%	2.70	1.035%
NO_3^-	4.57	1.752%	4.34	1.664%
Cl^-	2.83	1.087%	2.83	1.087%
F^-	0.04	0.013%	0.04	0.013%
I^-	0.07	0.026%	0.07	0.026%
NO_2^-	10.98	4.212%	10.98	4.212%
OH^- (tot)	94.49	36.245%	4.12	1.579%
O^{2-}	9.19	3.526%	0.95	
SUM=	134.61	gms	43.48	16.314%

Noble Metals, Mercury and Silver
To Be Added On-Site

Table B- 3. Recipe Calculation for 7.5 wt % Uranium Sludge Batch 2 Simulant

Recipe for Tank 40 + Tank 8 Blend
For 1.2 liter batch sludge simulant
Keyed to [2]-rev. for Bannochie, 11/2003 (solids boosted x 1.16)
reduce insolubles for U incorporation, constant Na 0.8805

Phase 1

[A]	22.164	gms	50% $Mn(NO_3)_2$ in water
[B]	165.090	mL	Water
[C]	6.529	gms	$KMnO_4$
[D]	227.043	mL	Water
[E]	49.026	mL	Water
[F]	797.010	gms	7% Fe as Ferric Nitrate in water
[G]	15.901	gms	$Ni(NO_3)_2 \cdot 6H_2O$
[-]	32.390	gms	$UO_2(NO_3)_2$
[H]	252.575	gms	50% NaOH in water
[I]	42.898	mL	Water
[J]	0.000	gms	$CaCO_3$

This converts to these solids (iron phase must be guessed)

	gms	My check:	elements:	Total in sludge solids		
MnO_2	8.975	8.98	5.67	2.18%	0.1017	Mn
Fe_2O_3	92.024	39.02				
$Fe(OH)_3$	106.761	106.76	55.79	21.40%	1.0000	Fe
$Ni(OH)_2$	5.064	5.07	3.21	1.23%	0.0575	Ni
$Na_2U_2O_7$	26.062	26.06	19.57	7.50%	0.3508	U
$CaCO_3$		0.00	0.00	-	see below	

The soluble portion must be removed by thorough washing.

Phase 4

Chemicals	gms					
$Al(OH)_3$	48.656	48.66	16.830	6.45%	0.3017	Al
$BaSO_4$	0.778	0.78	0.458	0.18%	0.0082	Ba
$Ca_3(PO4)_2$	0.422	0.42	5.068	1.94%	0.0908	total Ca
$CaCO_3$	11.360	11.36				
$CaSO_4$	1.205	1.20				
Cr_2O_3	0.715	0.71	0.489	0.19%	0.0088	Cr
$CsNO_3$	0.000	0.00				
CuO	0.366	0.37	0.293	0.11%	0.0052	Cu
KNO_3	0.352	0.35	0.136	0.05%	0.0024	K
KOH	0.000	0.00				
MgO	0.438	0.44	0.264	0.10%	0.0047	Mg
Na_2CO_3	4.767	4.77	16.910	6.49%	0.3031	total Na
Na_2SO_4	0.666	0.67		7.21%	0.3370	Na+U.Na
Na_3PO_4	0.176	0.18				
NaCl	4.672	4.67				
NaF	0.078	0.08				
NaI	0.079	0.08				
$NaNO_2$	16.467	16.47				
$NaNO_3$	5.947	5.95				
NaOH	9.681	9.68				
Nd_2O_3	0.000	0.00				
$PbSO_4$	0.822	0.82	0.562	0.22%	0.0101	Pb
SiO_2	3.746	3.75	1.751	0.67%	0.0314	Si
$SrCO_3$	0.273	0.27	0.162	0.06%	0.0029	Sr
Zeolite	0.000	0.00				
ZnO	0.742	0.74	0.596	0.23%	0.0107	Zn
ZrO_2	1.479	1.48	1.095	0.42%	0.0196	Zr
	260.75	gms. (using $Fe(OH)_3$)				
Dry Solids	260.7	Includes Sludge + Supernate.				
		Sludge Solids				
	19.6%	Total Solids				
	2.7%	Soluble Solids				
Dry Solids	219.9	gms. (using Fe_2O_3)				
	16.5%	Total Solids				

Total Anions:	Total, gms	%	Na Salts, gm	%
SO_4^{2-}	1.88	0.721%	0.45	0.173%
PO_4^{3-}	0.36	0.138%	0.10	0.039%
CO_3^{2-}	9.62	3.690%	2.70	1.035%
NO_3^-	4.55	1.747%	4.34	1.664%
Cl^-	2.83	1.087%	2.83	1.087%
F^-	0.04	0.013%	0.04	0.013%
I^-	0.07	0.026%	0.07	0.026%
NO_2^-	10.98	4.211%	10.98	4.211%
OH^- (tot)	88.77	34.045%	4.12	1.579%
O^{2-}	11.06	4.241%	1.89	
SUM=	130.16	gms	44.42	16.311%

Noble Metals, Mercury and Silver
To Be Added On-Site

Table B- 4. Recipe Calculation for 11.25 wt % Uranium Sludge Batch 2 Simulant

Recipe for Tank 40 + Tank 8 Blend
For 1.2 liter batch sludge simulant
Keyed to [2]-rev. for Bannochie, 11/2003 (solids boosted x 1.16)
reduce insolubles for U incorporation, constant Na 0.821

Phase 1

[A]	20.667	gms	50% $Mn(NO_3)_2$ in water
[B]	153.934	mL	Water
[C]	6.088	gms	$KMnO_4$
[D]	211.701	mL	Water
[E]	45.713	mL	Water
[F]	743.152	gms	7% Fe as Ferric Nitrate in water
[G]	14.827	gms	$Ni(NO_3)_2 \cdot 6H_2O$
[-]	48.550	gms	$UO_2(NO_3)_2$
[H]	235.787	gms	50% NaOH in water
[I]	39.999	mL	Water
[J]	0.000	gms	$CaCO_3$

This converts to these solids (iron phase must be guessed)

	gms	My check:	elements:	Total in sludge solids		
MnO_2	8.369	8.37	5.29	2.03%	0.1017	Mn
Fe_2O_3	85.805	36.38				
$Fe(OH)_3$	99.547	99.55	52.02	19.95%	1.0000	Fe
$Ni(OH)_2$	4.722	4.73	2.99	1.15%	0.0575	Ni
$Na_2U_2O_7$	39.065	39.07	29.33	11.25%	0.5639	U
$CaCO_3$		0.00	0.00	-	see below	

The soluble portion must be removed by thorough washing.

Phase 4

Chemicals	gms					
$Al(OH)_3$	45.368	45.37	15.693	6.02%	0.3017	Al
$BaSO_4$	0.725	0.73	0.427	0.16%	0.0082	Ba
$Ca_3(PO4)_2$	0.394	0.39	4.725	1.81%	0.0908	total Ca
$CaCO_3$	10.593	10.59				
$CaSO_4$	1.123	1.12				
Cr_2O_3	0.667	0.67	0.456	0.17%	0.0088	Cr
$CsNO_3$	0.000	0.00				
CuO	0.342	0.34	0.273	0.10%	0.0052	Cu
KNO_3	0.328	0.33	0.127	0.05%	0.0024	K
KOH	0.000	0.00				
MgO	0.408	0.41	0.246	0.09%	0.0047	Mg
Na_2CO_3	4.767	4.77	16.910	6.48%	0.3251	total Na
Na_2SO_4	0.666	0.67		7.57%	0.3795	Na+U.Na
Na_3PO_4	0.176	0.18				
NaCl	4.672	4.67				
NaF	0.078	0.08				
NaI	0.079	0.08				
$NaNO_2$	16.467	16.47				
$NaNO_3$	5.947	5.95				
NaOH	9.681	9.68				
Nd_2O_3	0.000	0.00				
$PbSO_4$	0.767	0.77	0.524	0.20%	0.0101	Pb
SiO_2	3.492	3.49	1.633	0.63%	0.0314	Si
$SrCO_3$	0.255	0.25	0.151	0.06%	0.0029	Sr
Zeolite	0.000	0.00				
ZnO	0.692	0.69	0.556	0.21%	0.0107	Zn
ZrO_2	1.379	1.38	1.021	0.39%	0.0196	Zr
	260.77	gms. (using $Fe(OH)_3$)				
Dry Solids	260.8	Includes Sludge + Supernate.				
		Sludge Solids				
	19.6%	Total Solids				
	2.5%	Soluble Solids				
Dry Solids	208.0	gms. (using Fe_2O_3)				
	15.6%	Total Solids				

Total Anions:	Total, gms	%	Na Salts, gm	%
SO_4^{2-}	1.78	0.684%	0.45	0.173%
PO_4^{3-}	0.34	0.131%	0.10	0.039%
CO_3^{2-}	9.15	3.510%	2.70	1.035%
NO_3^-	4.54	1.741%	4.34	1.664%
Cl^-	2.83	1.087%	2.83	1.087%
F^-	0.04	0.013%	0.04	0.013%
I^-	0.07	0.026%	0.07	0.026%
NO_2^-	10.98	4.211%	10.98	4.211%
OH^- (tot)	83.05	31.849%	4.12	1.579%
O^{2-}	12.92	4.954%	2.83	
SUM=	125.71 gms		45.37	16.310%

Noble Metals, Mercury and Silver
To Be Added On-Site

Table B- 5. Recipe Calculation for 15 wt % Uranium Sludge Batch 2 Simulant

Recipe for Tank 40 + Tank 8 Blend
For 1.2 liter batch sludge simulant
Keyed to [2]-rev. for Bannochie, 11/2003 (solids boosted x 1.16)
reduce insolubles for U incorporation, constant Na 0.7615

Phase 1

[A]	19.169	gms	50% $Mn(NO_3)_2$ in water
[B]	142.778	mL	Water
[C]	5.647	gms	$KMnO_4$
[D]	196.358	mL	Water
[E]	42.400	mL	Water
[F]	689.294	gms	7% Fe as Ferric Nitrate in water
[G]	13.752	gms	$Ni(NO_3)_2 6H_2O$
[-]	64.730	gms	$UO_2(NO_3)_2$
[H]	218.999	gms	50% NaOH in water
[I]	37.100	mL	Water
[J]	0.000	gms	$CaCO_3$

This converts to these solids (iron phase must be guessed)

	gms	My check:	elements:	Total in sludge solids		
MnO_2	7.762	7.76	4.91	1.88%	0.1017	Mn
Fe_2O_3	79.587	33.75				
$Fe(OH)_3$	92.333	92.33	48.25	18.50%	1.0000	Fe
$Ni(OH)_2$	4.380	4.38	2.78	1.06%	0.0575	Ni
$Na_2U_2O_7$	52.084	52.08	39.10	15.00%	0.8105	U
$CaCO_3$		0.00	0.00	-	see below	

The soluble portion must be removed by thorough washing.

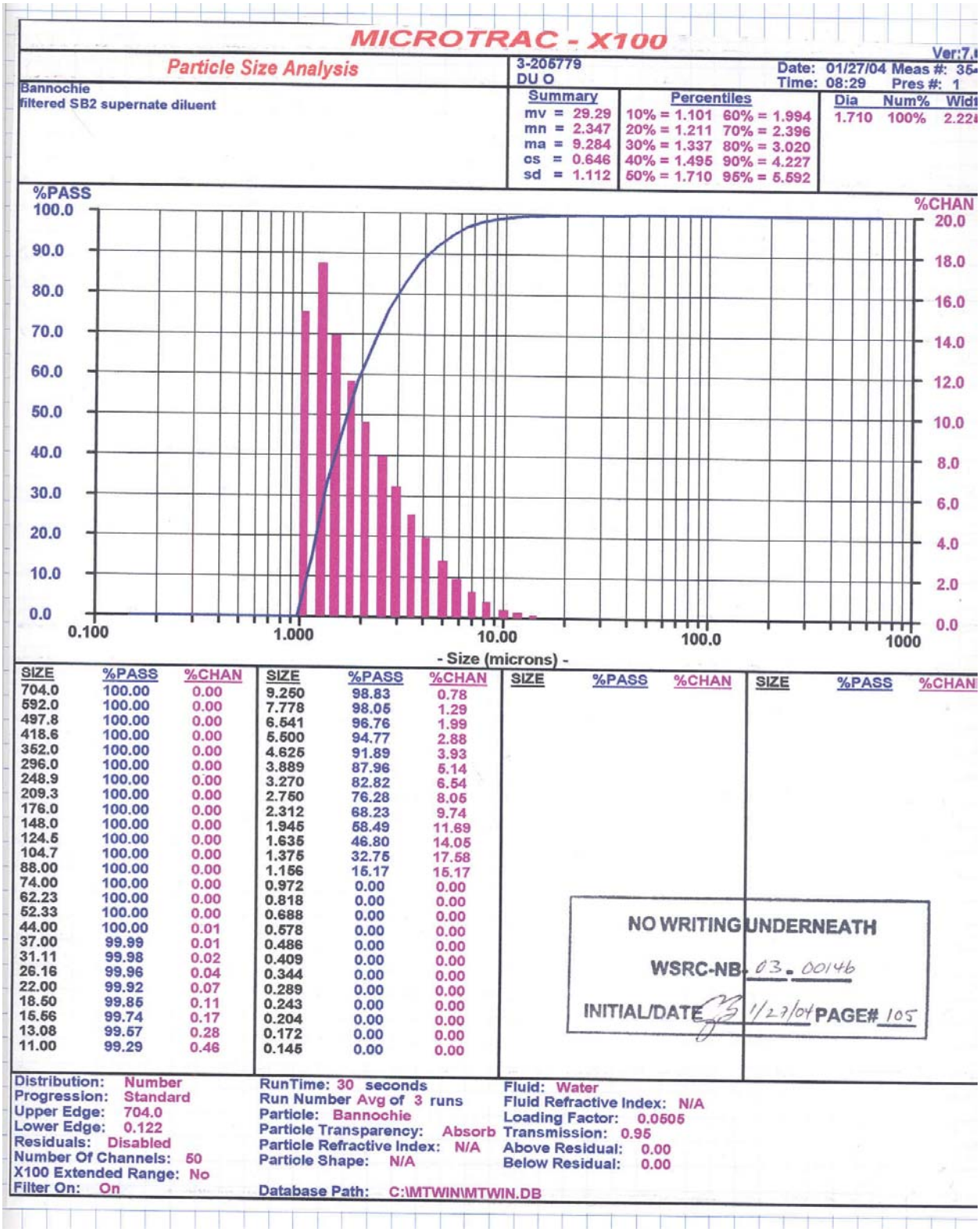
Phase 4

Chemicals	gms					
$Al(OH)_3$	42.080	42.08	14.556	5.58%	0.3017	Al
$BaSO_4$	0.673	0.67	0.396	0.15%	0.0082	Ba
$Ca_3(PO4)_2$	0.365	0.36	4.383	1.68%	0.0908	total Ca
$CaCO_3$	9.825	9.83				
$CaSO_4$	1.042	1.04				
Cr_2O_3	0.618	0.62	0.423	0.16%	0.0088	Cr
$CsNO_3$	0.000	0.00				
CuO	0.317	0.32	0.253	0.10%	0.0052	Cu
KNO_3	0.304	0.30	0.118	0.05%	0.0024	K
KOH	0.000	0.00				
MgO	0.379	0.38	0.228	0.09%	0.0047	Mg
Na_2CO_3	4.767	4.77	16.910	6.48%	0.3505	total Na
Na_2SO_4	0.666	0.67		7.93%	0.4288	Na+U.Na
Na_3PO_4	0.176	0.18				
NaCl	4.672	4.67				
NaF	0.078	0.08				
NaI	0.079	0.08				
$NaNO_2$	16.467	16.47				
$NaNO_3$	5.947	5.95				
NaOH	9.681	9.68				
Nd_2O_3	0.000	0.00				
$PbSO_4$	0.711	0.71	0.486	0.19%	0.0101	Pb
SiO_2	3.239	3.24	1.514	0.58%	0.0314	Si
$SrCO_3$	0.236	0.24	0.140	0.05%	0.0029	Sr
Zeolite	0.000	0.00				
ZnO	0.642	0.64	0.516	0.20%	0.0107	Zn
ZrO_2	1.279	1.28	0.947	0.36%	0.0196	Zr
	260.80	gms. (using $Fe(OH)_3$)				
Dry Solids	260.8	Includes Sludge + Supernate.				
		Sludge Solids				
	19.6%	Total Solids				
	2.4%	Soluble Solids				
Dry Solids	196.0	gms. (using Fe_2O_3)				
	14.7%	Total Solids				

Total Anions:	Total, gms	%	Na Salts, gm	%
SO_4^{2-}	1.69	0.647%	0.45	0.173%
PO_4^{3-}	0.33	0.125%	0.10	0.039%
CO_3^{2-}	8.69	3.330%	2.70	1.035%
NO_3^-	4.52	1.735%	4.34	1.664%
Cl^-	2.83	1.087%	2.83	1.087%
F^-	0.04	0.013%	0.04	0.013%
I^-	0.07	0.026%	0.07	0.026%
NO_2^-	10.98	4.210%	10.98	4.210%
OH^- (tot)	77.33	29.652%	4.12	1.578%
O^{2-}	14.78	5.668%	3.78	
SUM=	121.25 gms		46.31	16.308%

Noble Metals, Mercury and Silver
To Be Added On-Site

APPENDIX C. PARTICLE SIZE MEASUREMENTS



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
704.0	100.00	0.00	9.250	98.83	0.78
592.0	100.00	0.00	7.778	98.05	1.29
497.8	100.00	0.00	6.541	96.76	1.99
418.6	100.00	0.00	5.500	94.77	2.88
352.0	100.00	0.00	4.625	91.89	3.93
296.0	100.00	0.00	3.889	87.96	5.14
248.9	100.00	0.00	3.270	82.82	6.54
209.3	100.00	0.00	2.750	76.28	8.05
176.0	100.00	0.00	2.312	68.23	9.74
148.0	100.00	0.00	1.945	58.49	11.69
124.5	100.00	0.00	1.635	46.80	14.05
104.7	100.00	0.00	1.375	32.75	17.58
88.00	100.00	0.00	1.156	15.17	15.17
74.00	100.00	0.00	0.972	0.00	0.00
62.23	100.00	0.00	0.818	0.00	0.00
52.33	100.00	0.00	0.688	0.00	0.00
44.00	100.00	0.01	0.578	0.00	0.00
37.00	99.99	0.01	0.486	0.00	0.00
31.11	99.98	0.02	0.409	0.00	0.00
26.16	99.96	0.04	0.344	0.00	0.00
22.00	99.92	0.07	0.289	0.00	0.00
18.50	99.85	0.11	0.243	0.00	0.00
15.56	99.74	0.17	0.204	0.00	0.00
13.08	99.57	0.28	0.172	0.00	0.00
11.00	99.29	0.46	0.145	0.00	0.00

Figure C- 1. Particle size number distribution for SB2 simulant without uranium

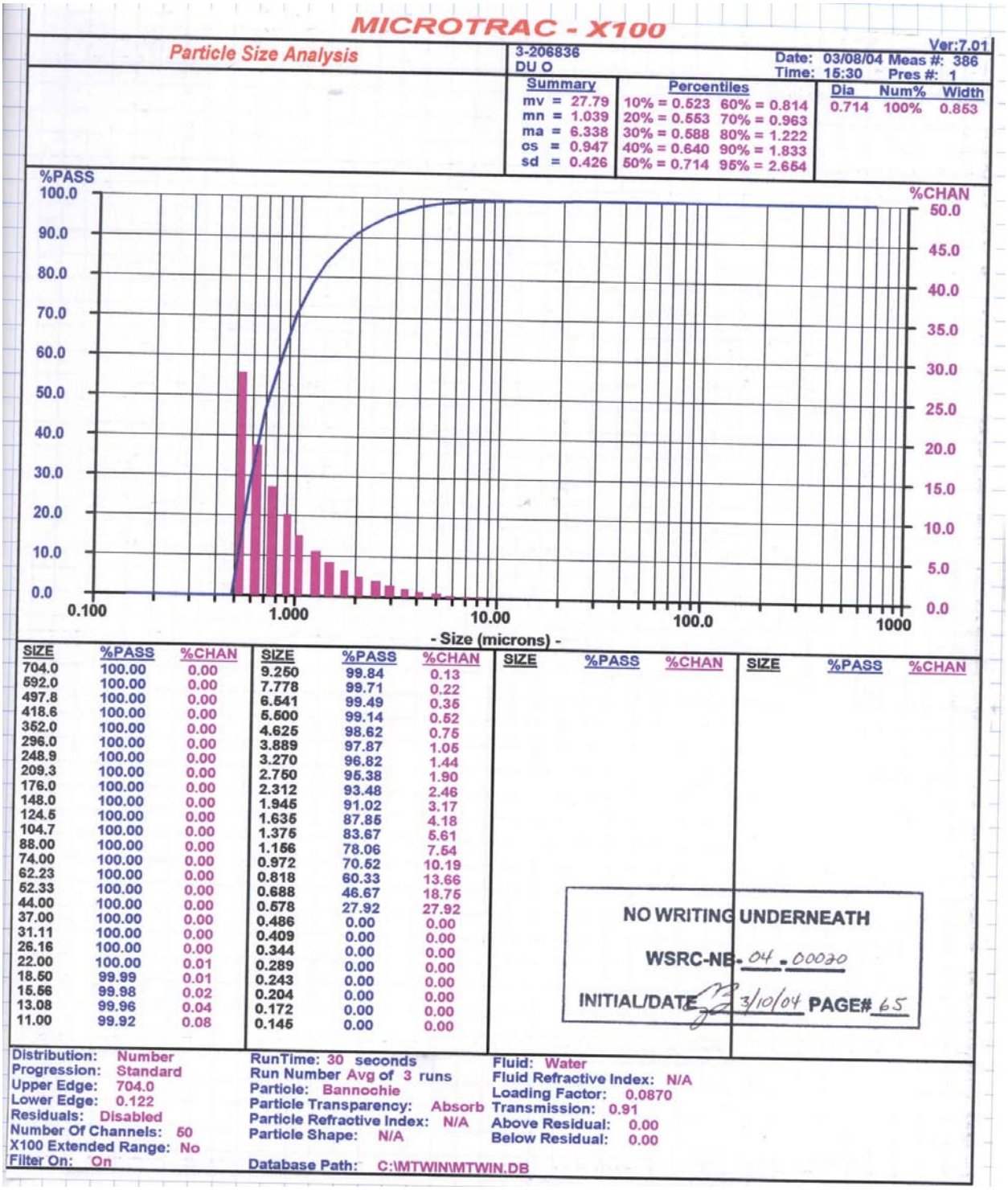


Figure C- 2. Particle size number distribution for SB2 simulant without uranium following SRAT cycle processing

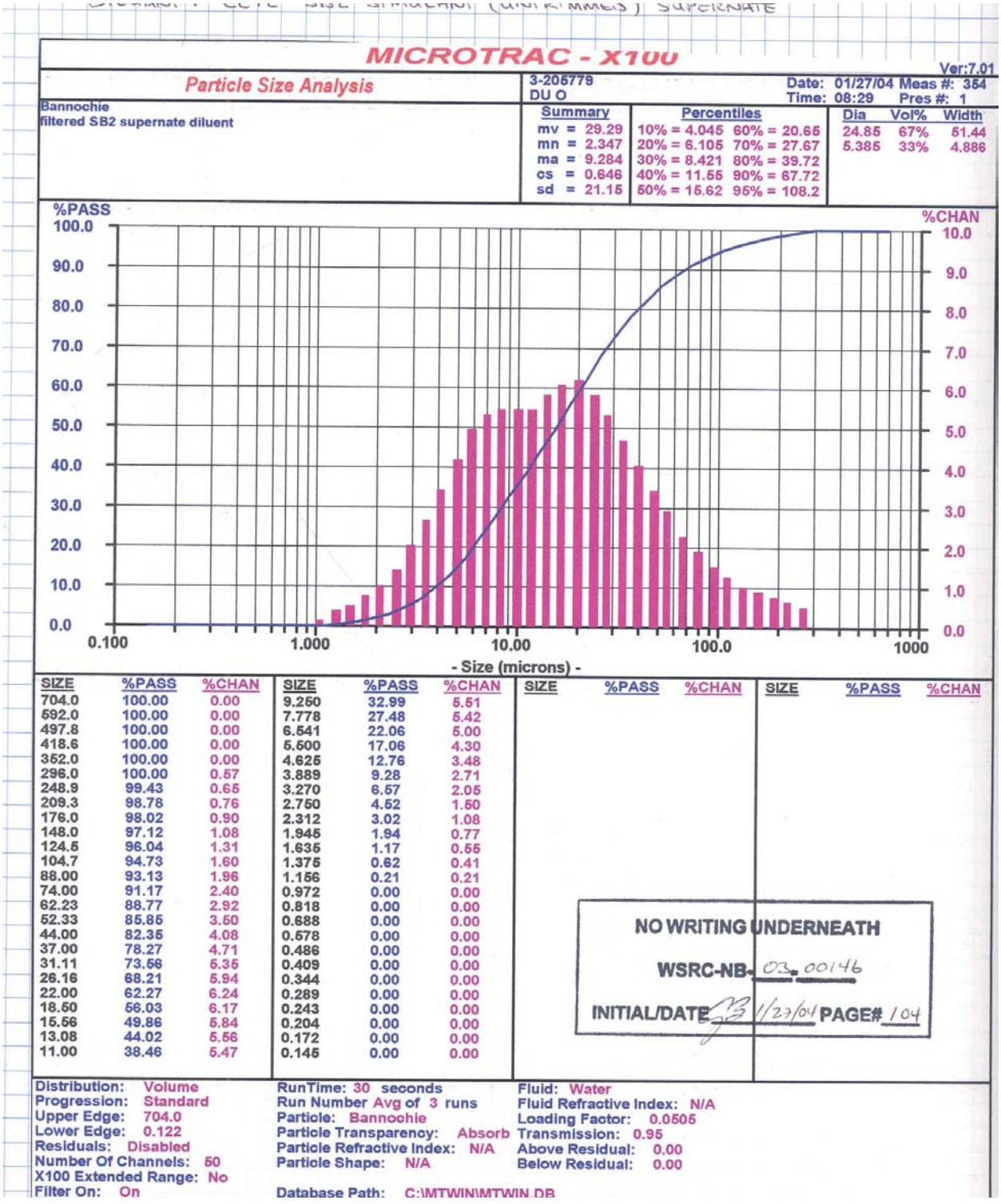


Figure C- 3. Particle size volume distribution for SB2 simulant without uranium

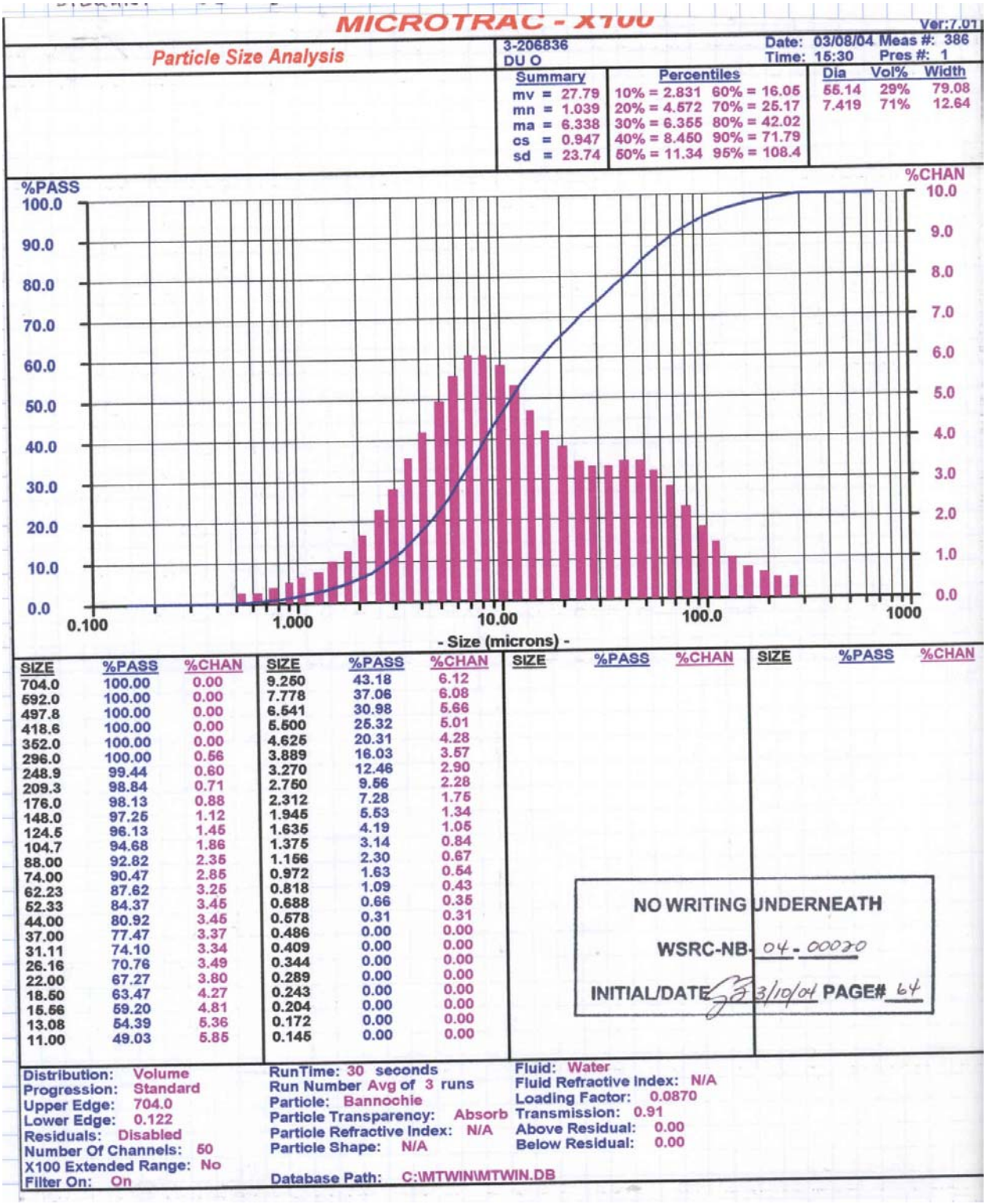
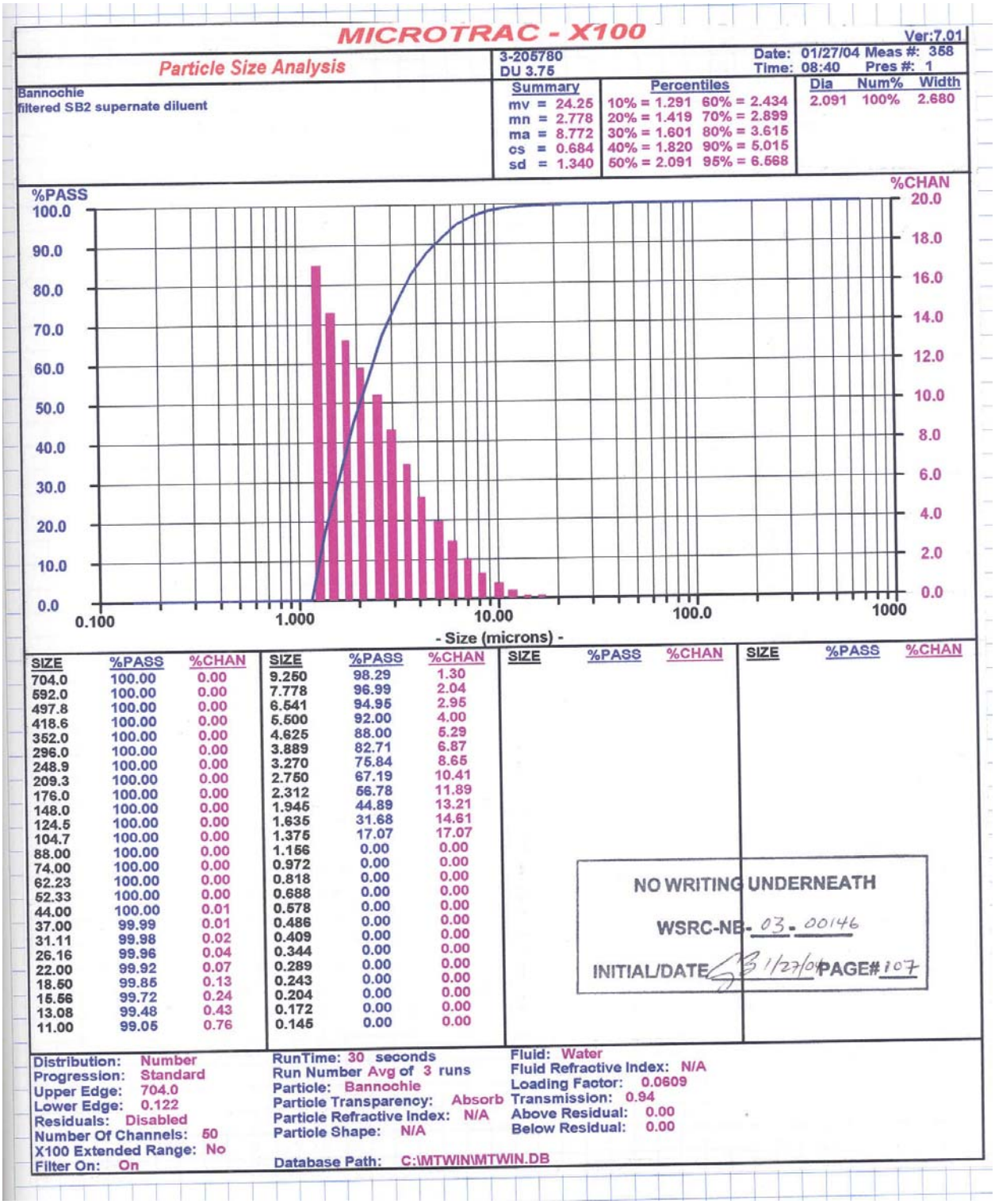


Figure C- 4. Particle size volume distribution for SB2 simulant without uranium following SRAT cycle processing



SIZE	%PASS	%CHAN
704.0	100.00	0.00
592.0	100.00	0.00
497.8	100.00	0.00
418.6	100.00	0.00
352.0	100.00	0.00
296.0	100.00	0.00
248.9	100.00	0.00
209.3	100.00	0.00
176.0	100.00	0.00
148.0	100.00	0.00
124.5	100.00	0.00
104.7	100.00	0.00
88.00	100.00	0.00
74.00	100.00	0.00
62.23	100.00	0.00
52.33	100.00	0.00
44.00	100.00	0.01
37.00	99.99	0.01
31.11	99.98	0.02
26.16	99.96	0.04
22.00	99.92	0.07
18.50	99.85	0.13
15.56	99.72	0.24
13.08	99.48	0.43
11.00	99.05	0.76

SIZE	%PASS	%CHAN
9.250	98.29	1.30
7.778	96.99	2.04
6.541	94.95	2.95
5.500	92.00	4.00
4.625	88.00	5.29
3.889	82.71	6.87
3.270	75.84	8.65
2.750	67.19	10.41
2.312	56.78	11.89
1.945	44.89	13.21
1.635	31.68	14.61
1.375	17.07	17.07
1.156	0.00	0.00
0.972	0.00	0.00
0.818	0.00	0.00
0.688	0.00	0.00
0.578	0.00	0.00
0.486	0.00	0.00
0.409	0.00	0.00
0.344	0.00	0.00
0.289	0.00	0.00
0.243	0.00	0.00
0.204	0.00	0.00
0.172	0.00	0.00
0.145	0.00	0.00

SIZE	%PASS	%CHAN

SIZE	%PASS	%CHAN

Figure C- 5. Particle size number distribution for SB2 simulant with 3.75 wt % uranium

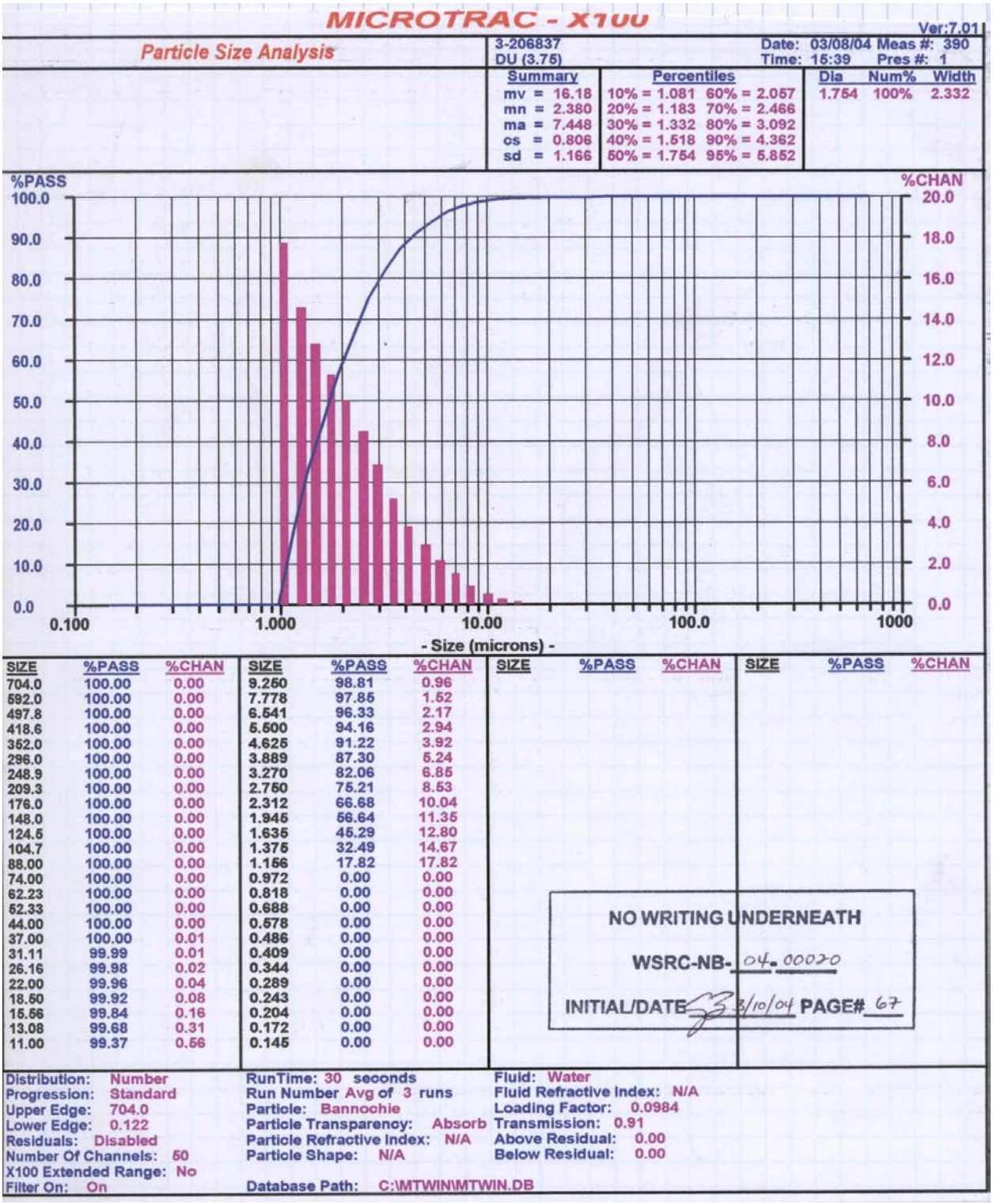


Figure C- 6. Particle size number distribution for SB2 simulant with 3.75 wt % uranium following SRAT cycle processing

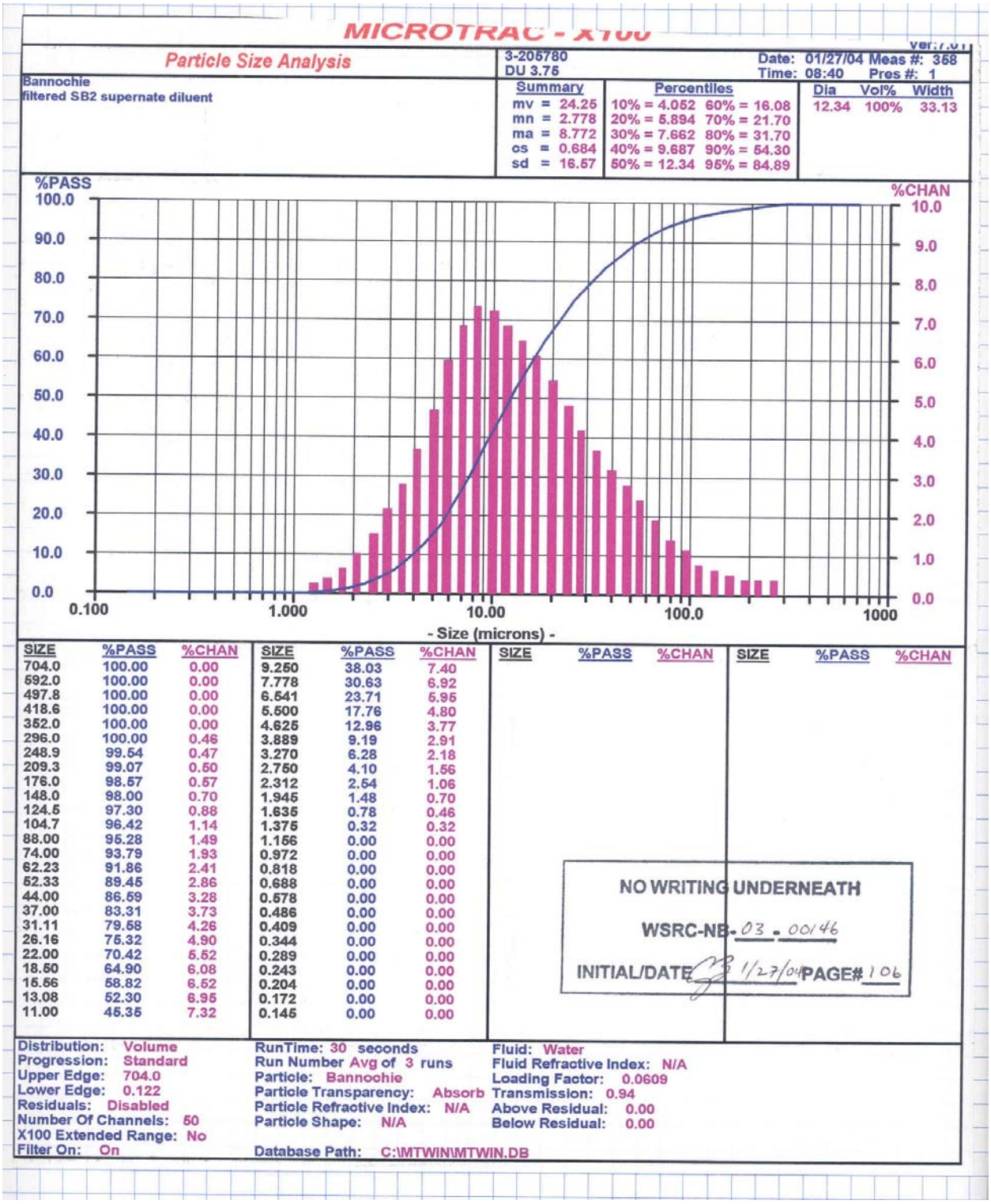


Figure C- 7. Particle size volume distribution for SB2 simulant with 3.75 wt % uranium

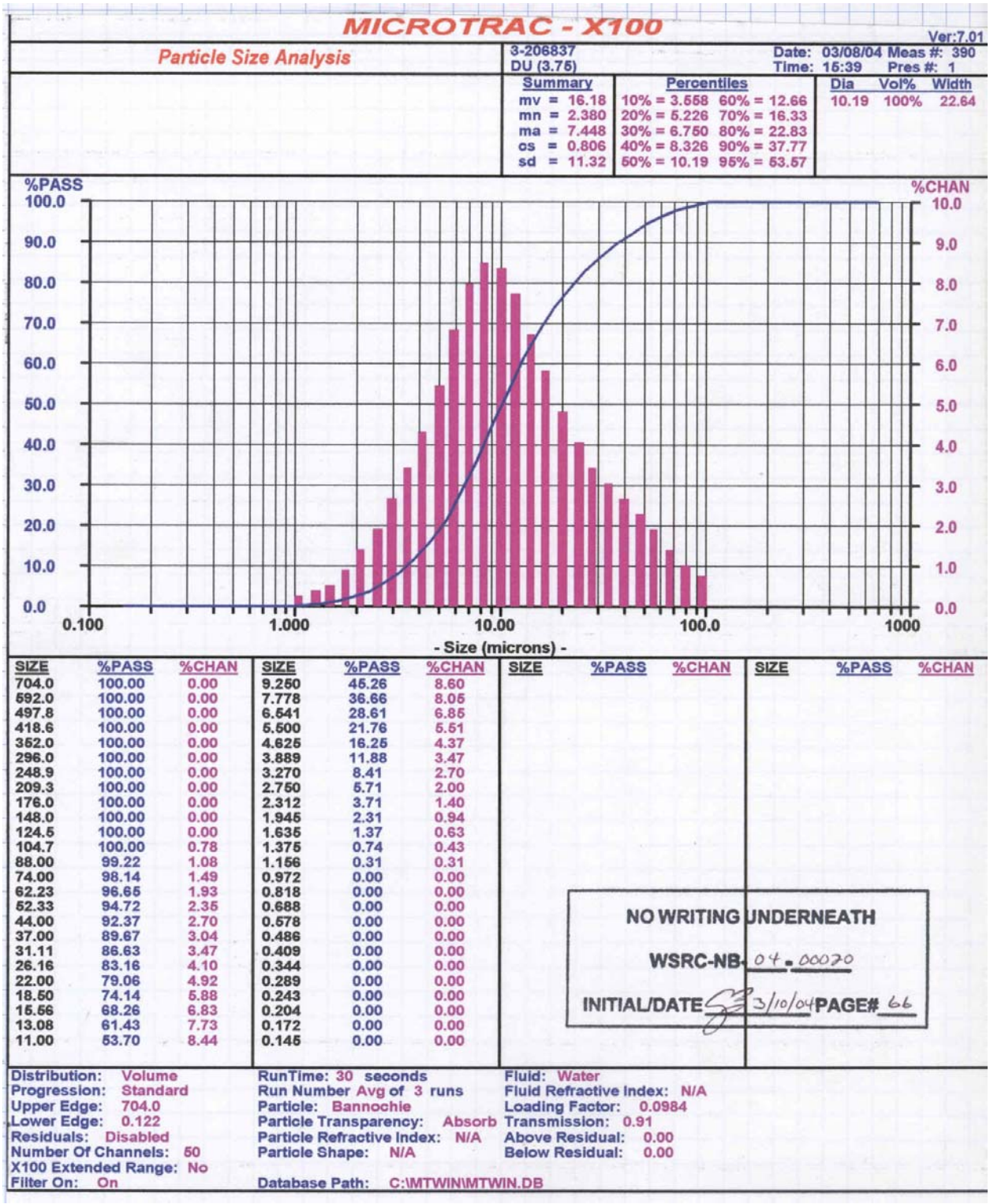


Figure C- 8. Particle size volume distribution for SB2 simulant with 3.75 wt % uranium following SRAT cycle processing

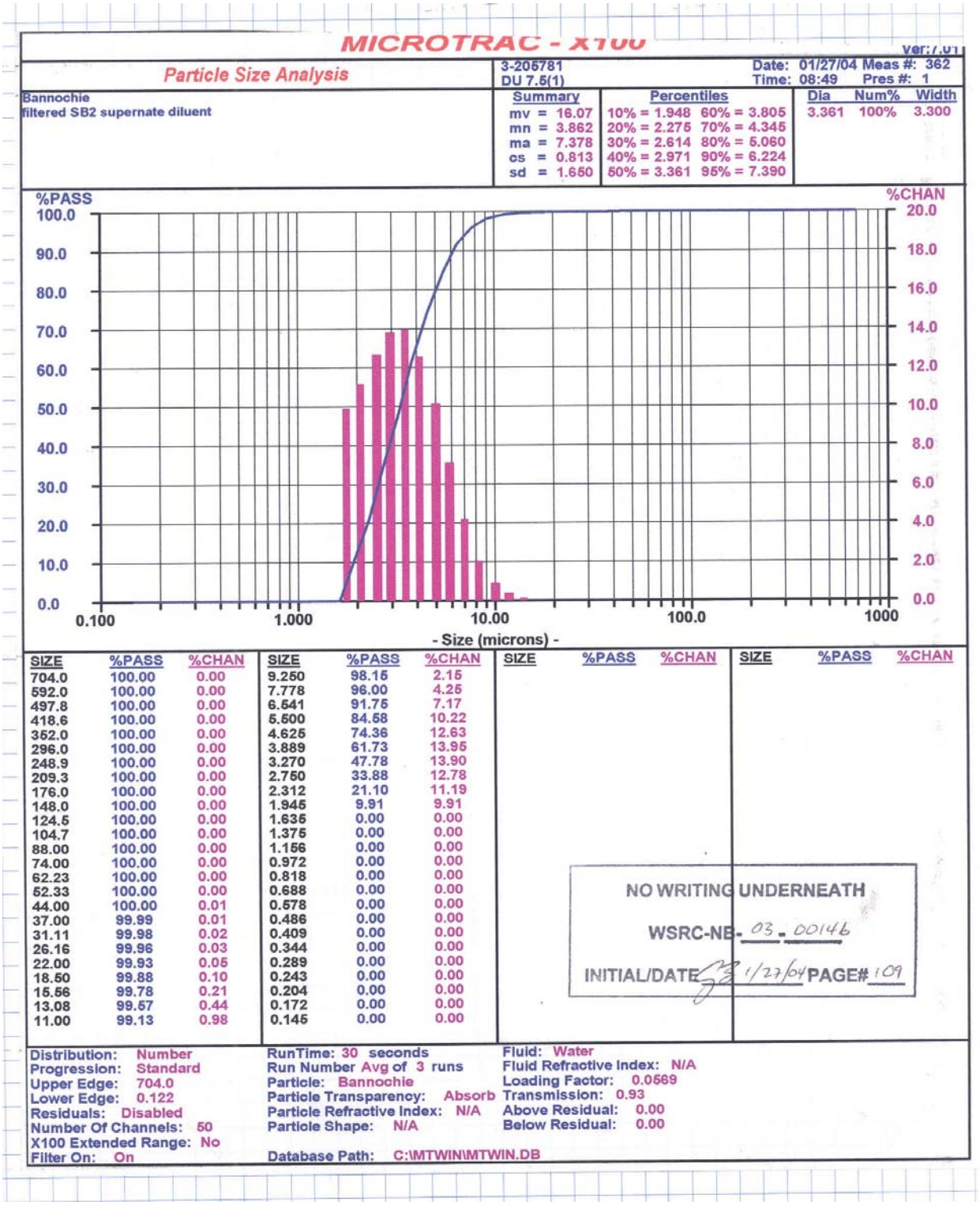


Figure C- 9. Particle size number distribution for SB2 simulant with 7.5i wt % uranium

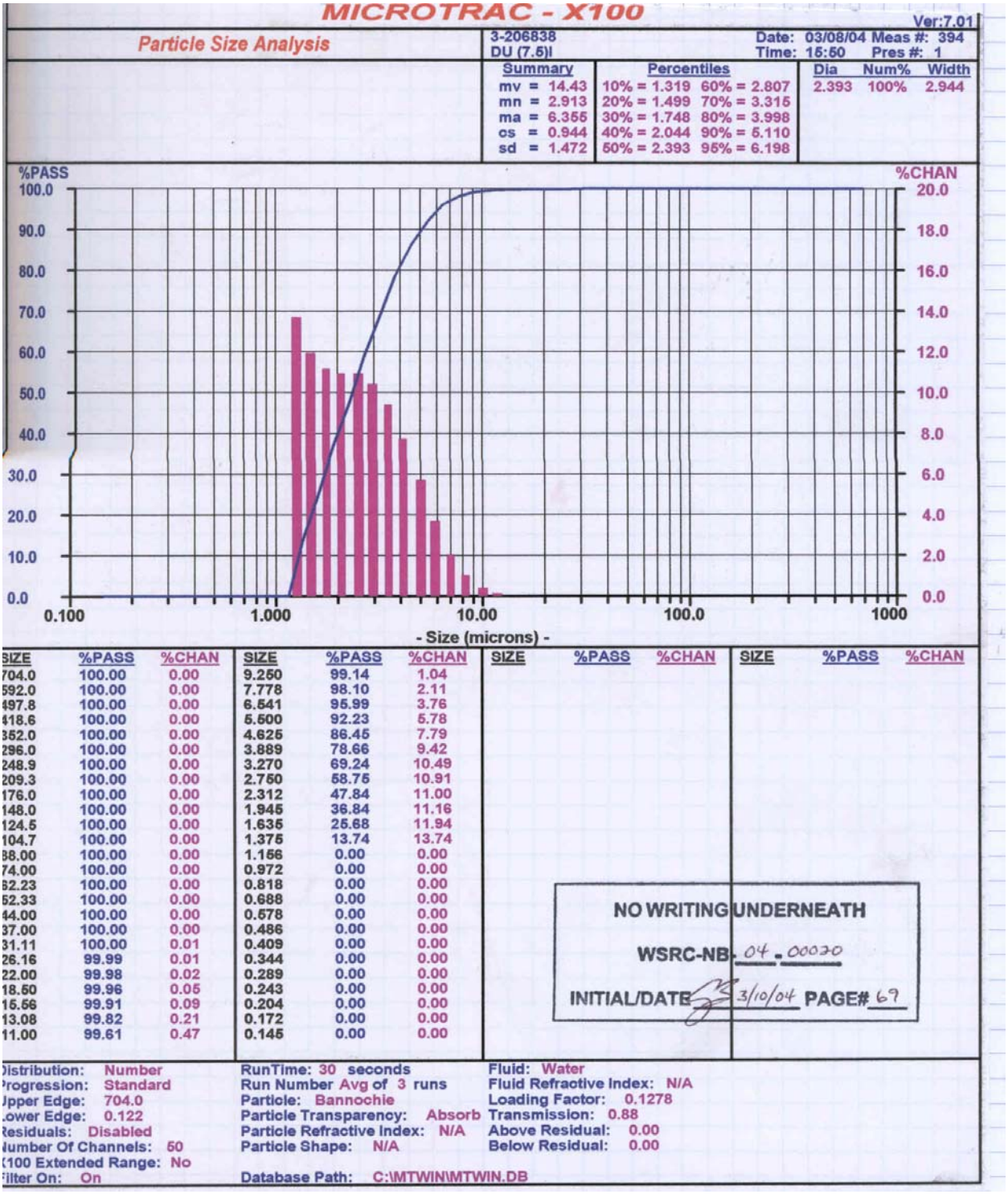
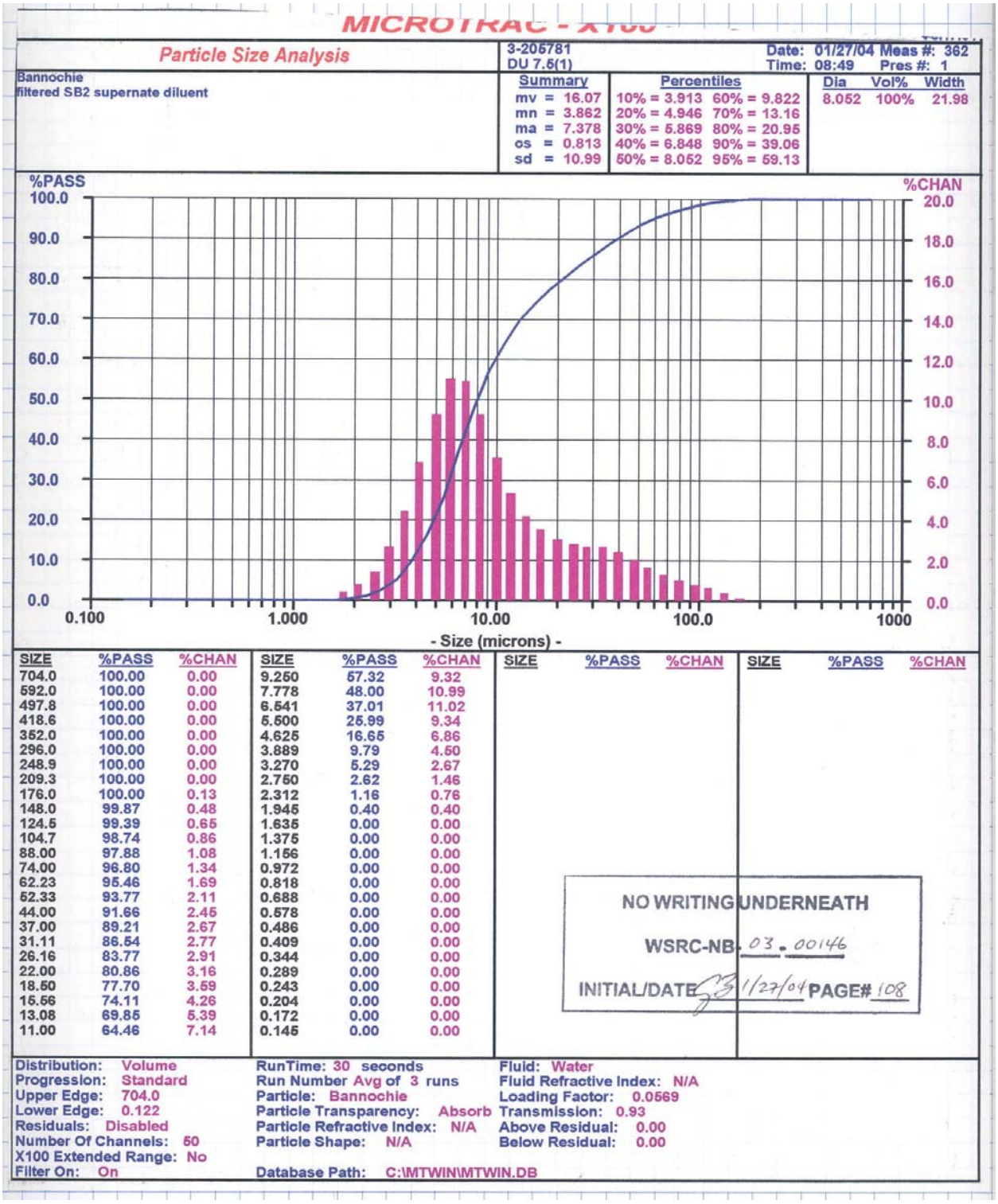


Figure C- 10. Particle size number distribution for SB2 simulant with 7.5i wt % uranium following SRAT cycle processing



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
704.0	100.00	0.00	9.250	57.32	9.32						
592.0	100.00	0.00	7.778	48.00	10.99						
497.8	100.00	0.00	6.541	37.01	11.02						
418.6	100.00	0.00	5.500	25.99	9.34						
352.0	100.00	0.00	4.625	16.65	6.86						
296.0	100.00	0.00	3.889	9.79	4.50						
248.9	100.00	0.00	3.270	5.29	2.67						
209.3	100.00	0.00	2.750	2.62	1.46						
176.0	100.00	0.13	2.312	1.16	0.76						
148.0	99.87	0.48	1.945	0.40	0.40						
124.5	99.39	0.65	1.635	0.00	0.00						
104.7	98.74	0.86	1.375	0.00	0.00						
88.00	97.88	1.08	1.156	0.00	0.00						
74.00	96.80	1.34	0.972	0.00	0.00						
62.23	95.46	1.69	0.818	0.00	0.00						
52.33	93.77	2.11	0.688	0.00	0.00						
44.00	91.66	2.45	0.578	0.00	0.00						
37.00	89.21	2.67	0.486	0.00	0.00						
31.11	86.54	2.77	0.409	0.00	0.00						
26.16	83.77	2.91	0.344	0.00	0.00						
22.00	80.86	3.16	0.289	0.00	0.00						
18.50	77.70	3.59	0.243	0.00	0.00						
15.56	74.11	4.26	0.204	0.00	0.00						
13.08	69.85	5.39	0.172	0.00	0.00						
11.00	64.46	7.14	0.145	0.00	0.00						

Figure C- 11. Particle size volume distribution for SB2 simulant with 7.5i wt % uranium

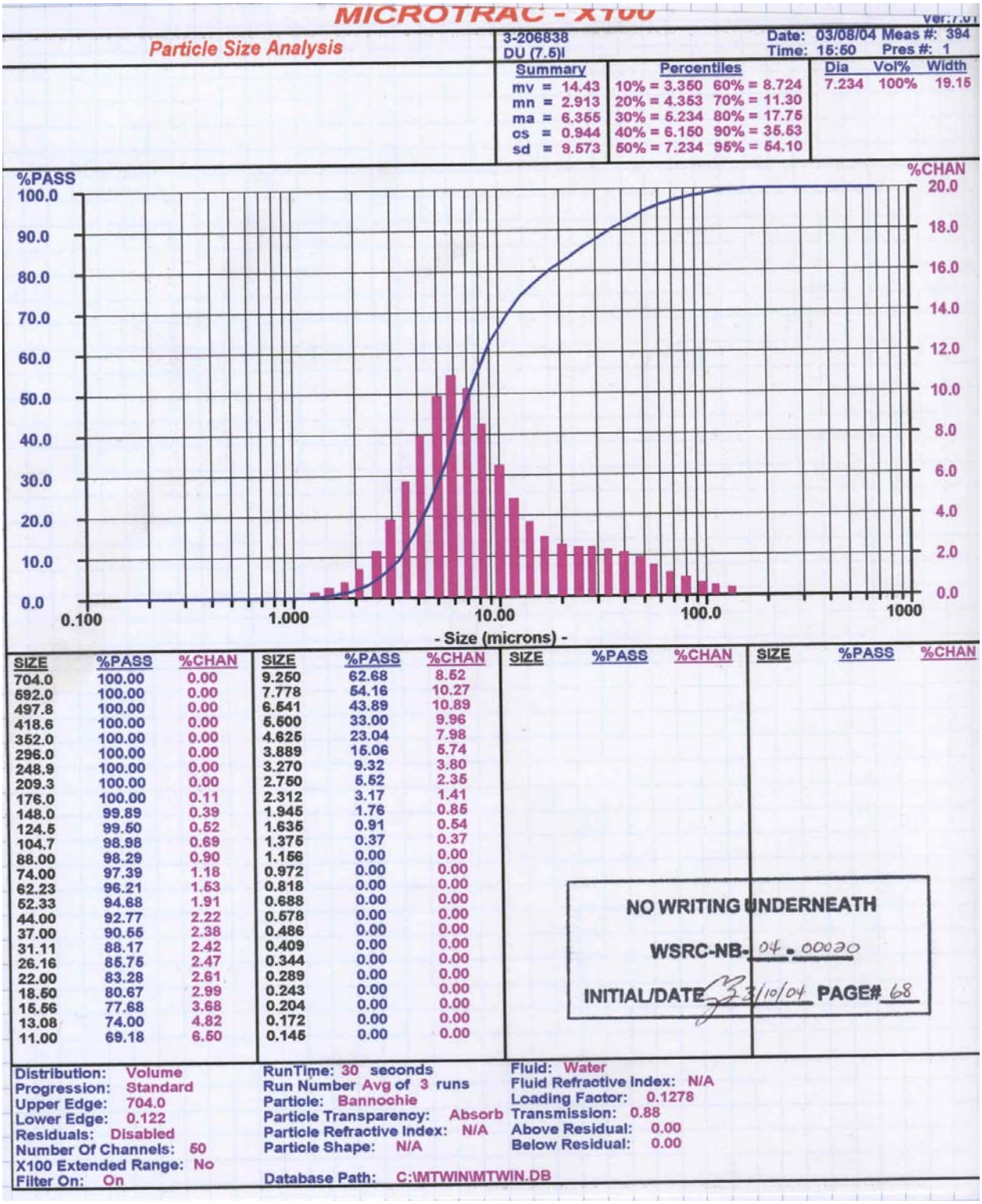


Figure C- 12. Particle size volume distribution for SB2 simulant with 7.5i wt % uranium following SRAT cycle processing

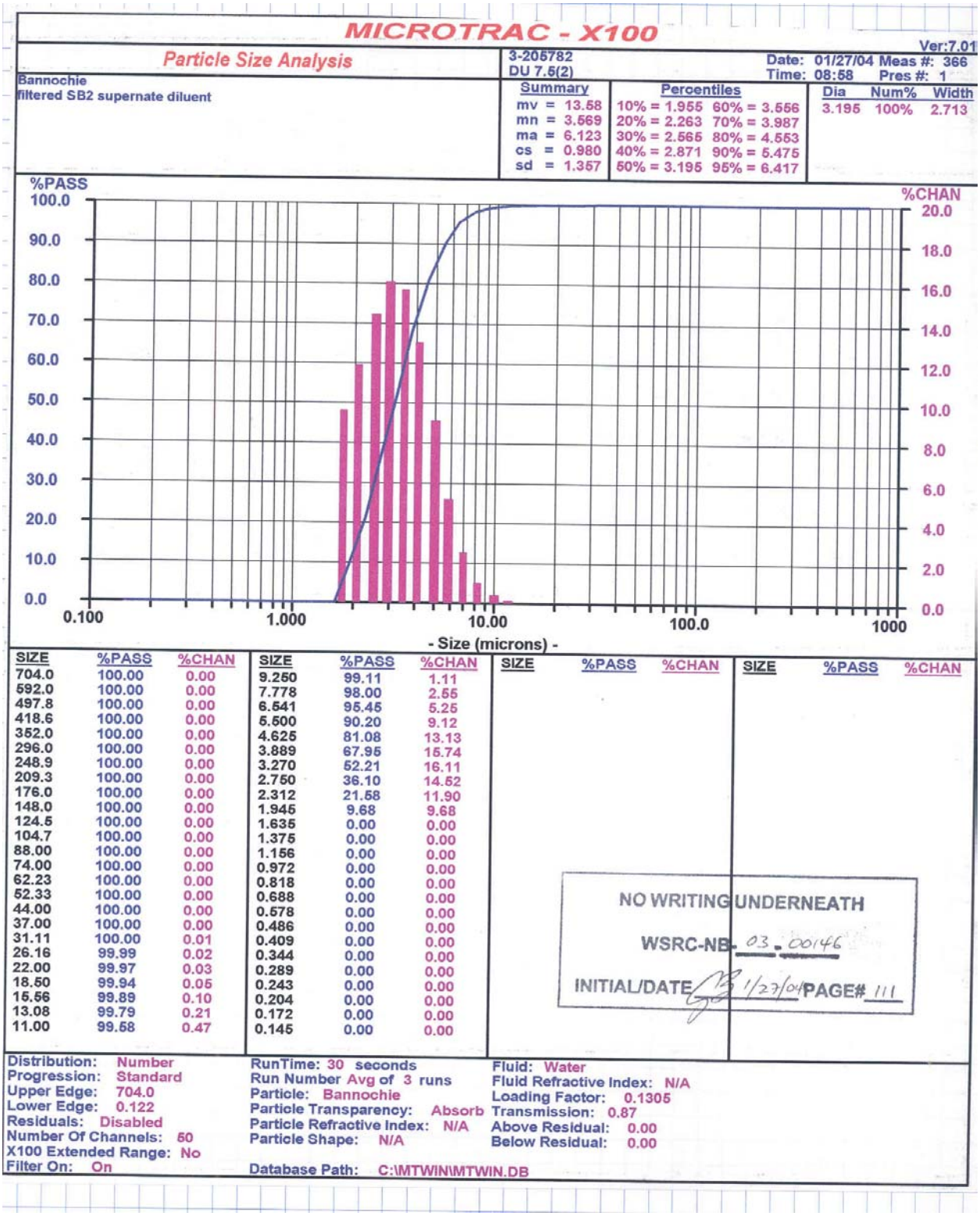


Figure C- 13. Particle size number distribution for SB2 simulant with 7.5ii wt % uranium

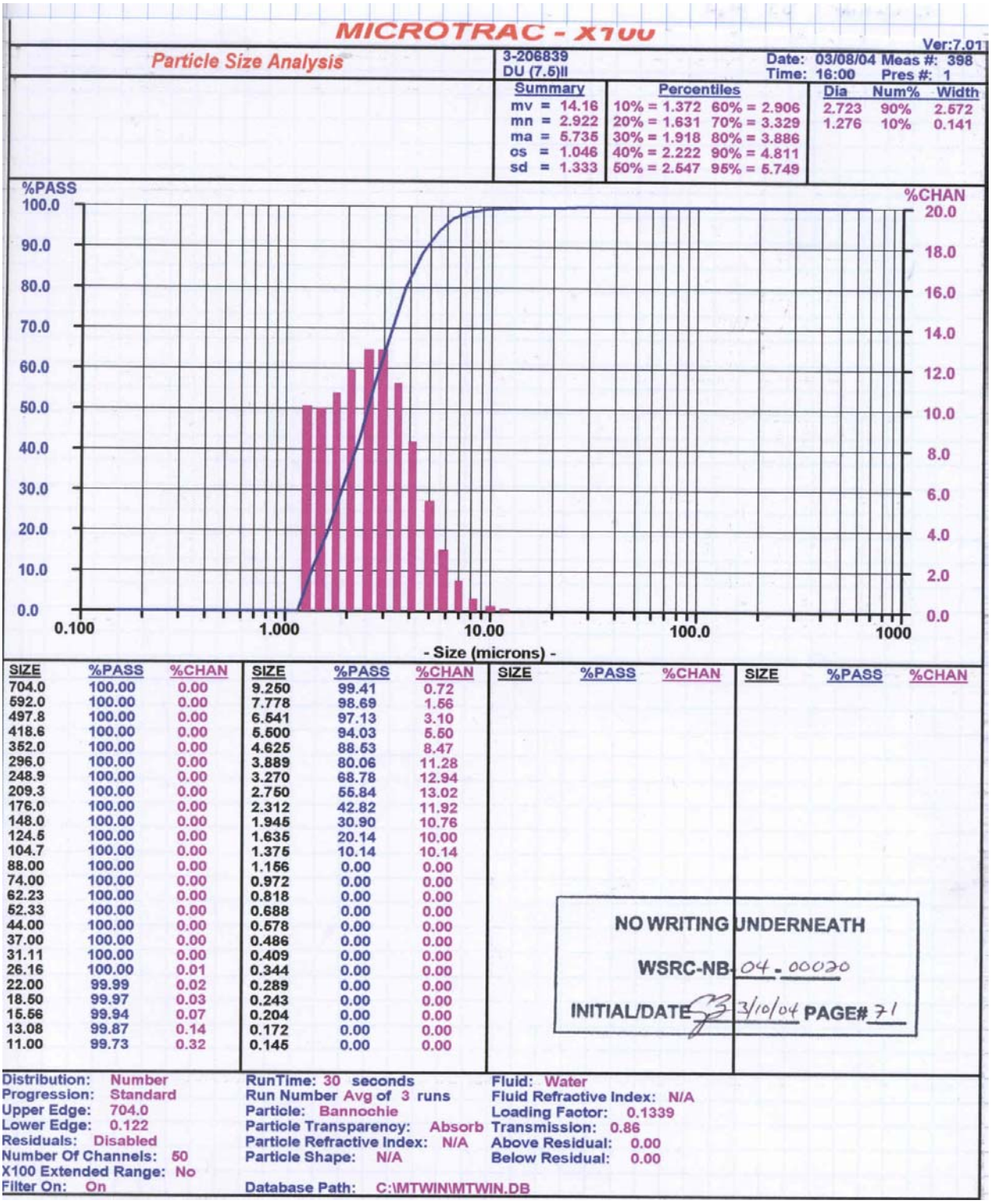


Figure C- 14. Particle size number distribution for SB2 simulant with 7.5ii wt % uranium following SRAT cycle processing

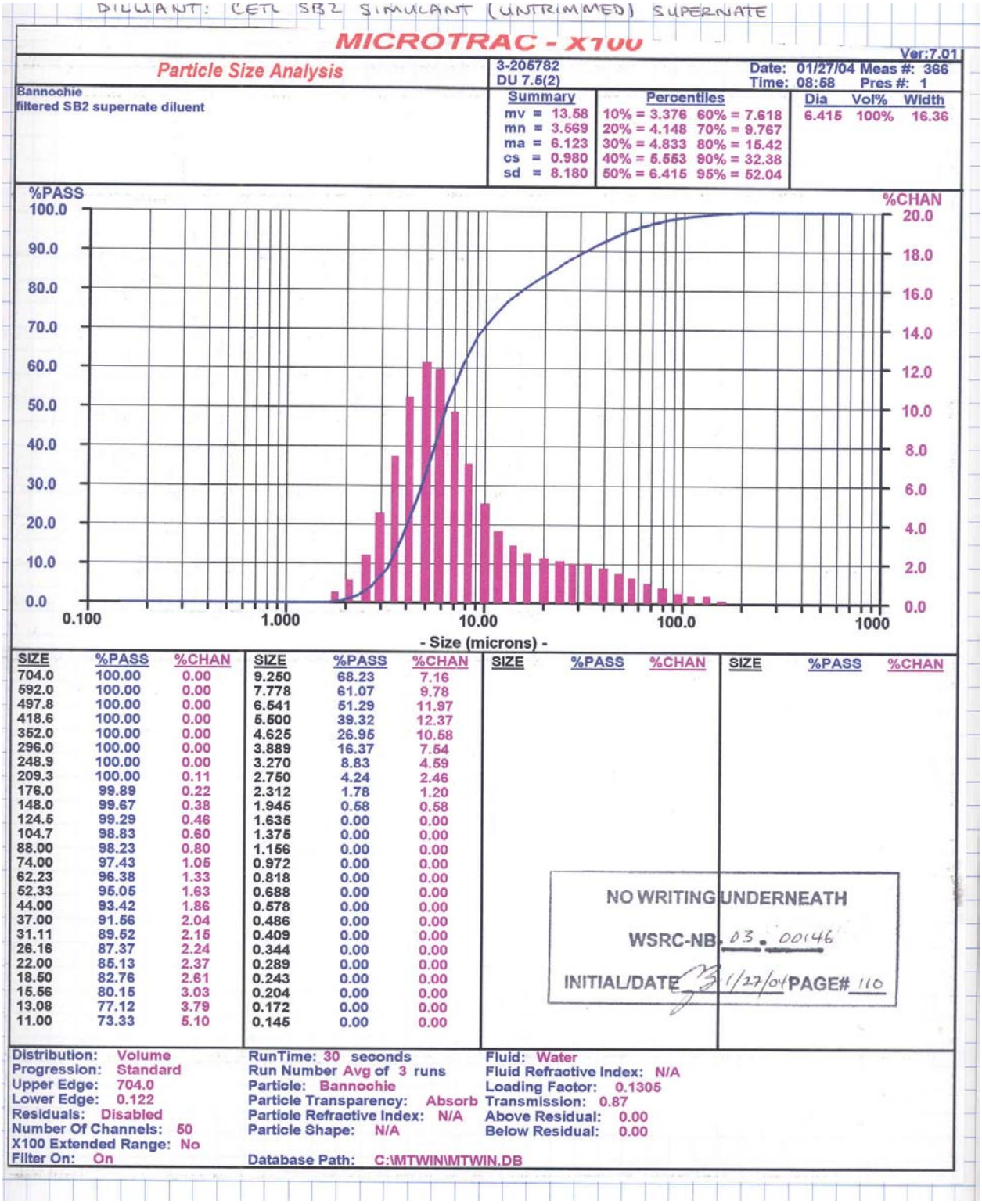
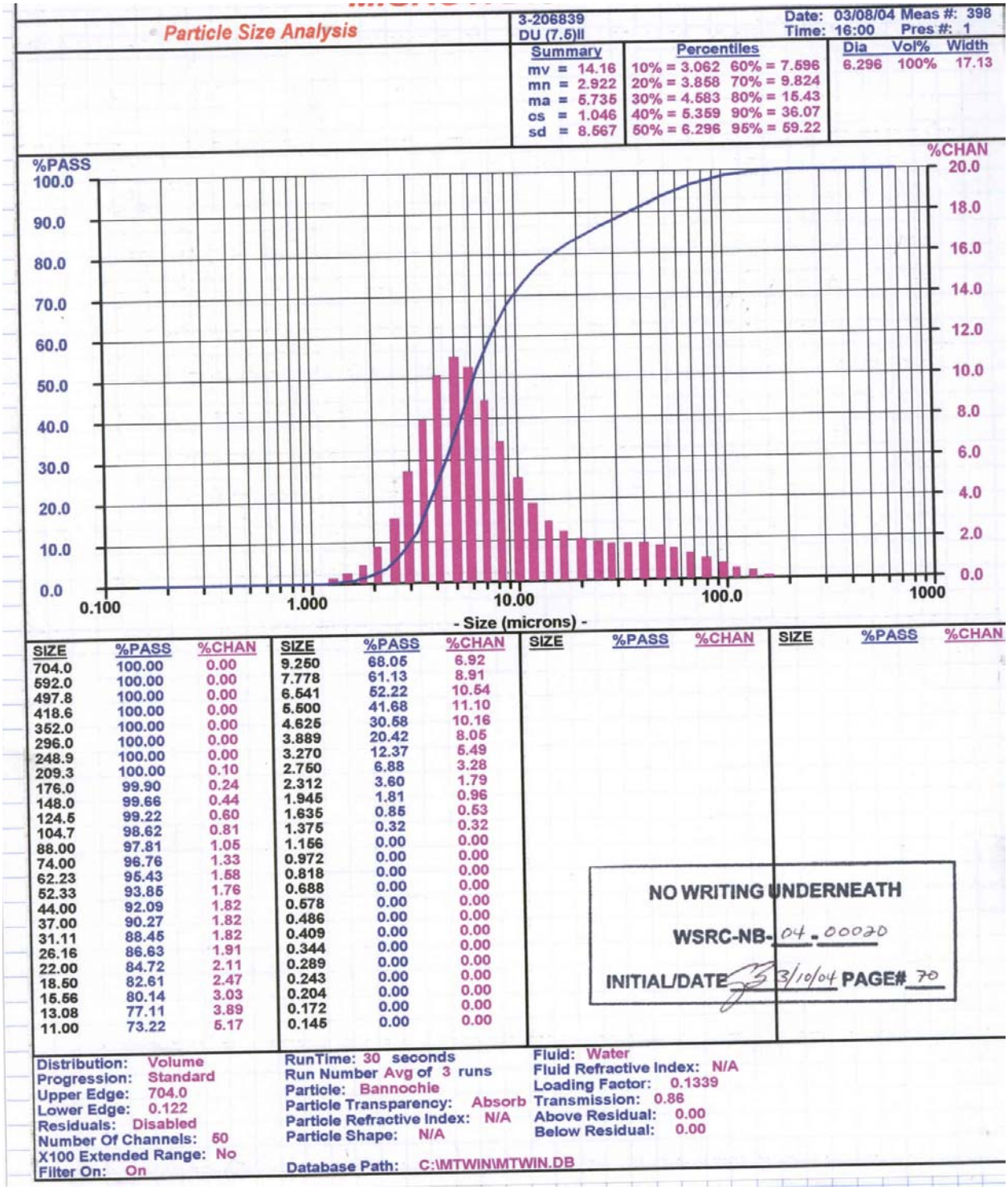


Figure C- 15. Particle size volume distribution for SB2 simulant with 7.5ii wt % uranium



SIZE	%PASS	%CHAN
704.0	100.00	0.00
592.0	100.00	0.00
497.8	100.00	0.00
418.6	100.00	0.00
352.0	100.00	0.00
296.0	100.00	0.00
248.9	100.00	0.00
209.3	100.00	0.10
176.0	99.90	0.24
148.0	99.66	0.44
124.5	99.22	0.60
104.7	98.62	0.81
88.00	97.81	1.05
74.00	96.76	1.33
62.23	95.43	1.58
52.33	93.85	1.76
44.00	92.09	1.82
37.00	90.27	1.82
31.11	88.45	1.82
26.16	86.63	1.91
22.00	84.72	2.11
18.50	82.61	2.47
15.56	80.14	3.03
13.08	77.11	3.89
11.00	73.22	5.17
9.250	68.05	6.92
7.778	61.13	8.91
6.541	52.22	10.54
5.500	41.68	11.10
4.625	30.58	10.16
3.889	20.42	8.05
3.270	12.37	6.49
2.750	6.88	3.28
2.312	3.60	1.79
1.945	1.81	0.96
1.635	0.85	0.53
1.375	0.32	0.32
1.156	0.00	0.00
0.972	0.00	0.00
0.818	0.00	0.00
0.688	0.00	0.00
0.578	0.00	0.00
0.486	0.00	0.00
0.409	0.00	0.00
0.344	0.00	0.00
0.289	0.00	0.00
0.243	0.00	0.00
0.204	0.00	0.00
0.172	0.00	0.00
0.145	0.00	0.00

Figure C- 16. Particle size volume distribution for SB2 simulant with 7.5ii wt % uranium following SRAT cycle processing

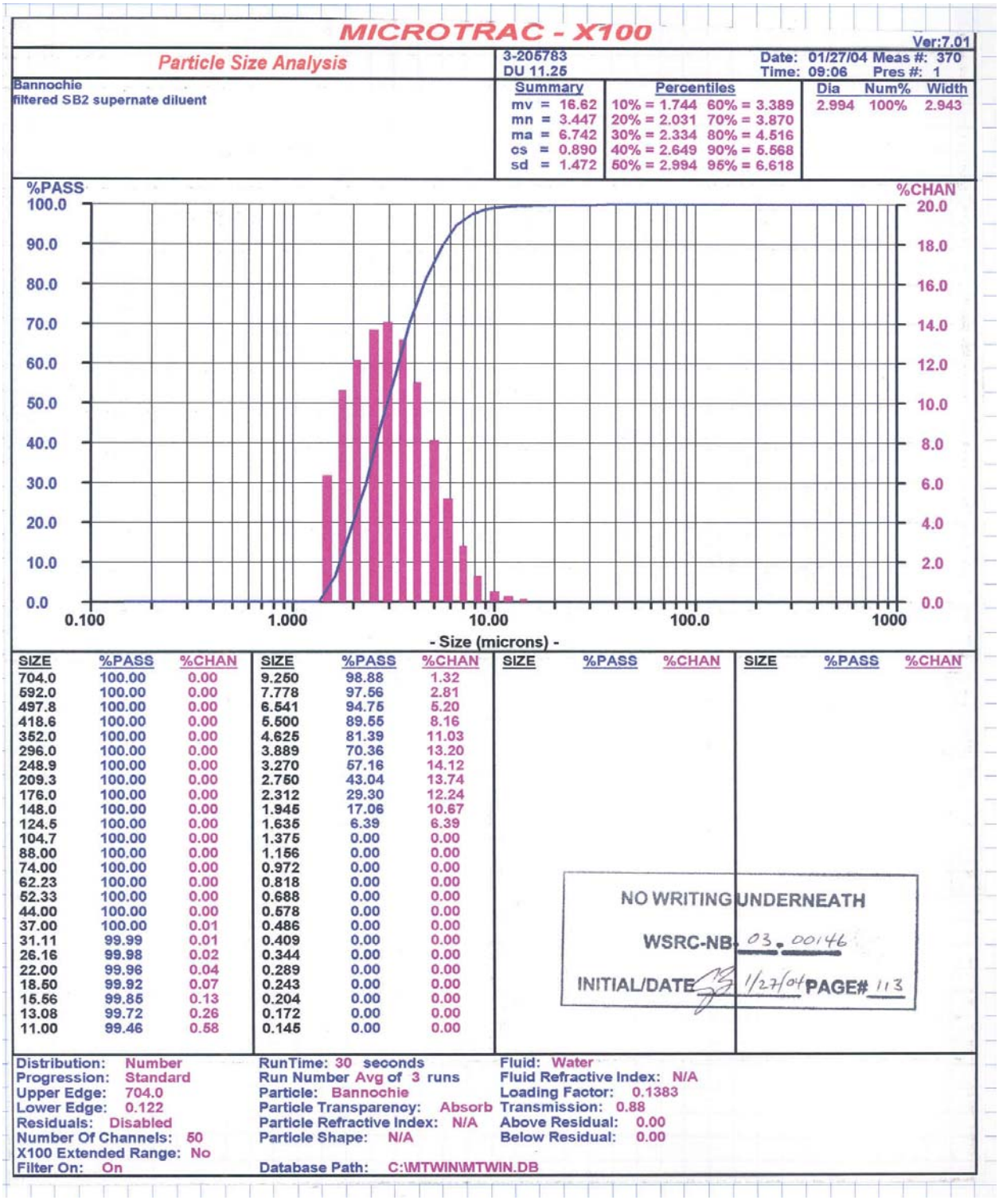


Figure C- 17. Particle size number distribution for SB2 simulant with 11.25 wt % uranium

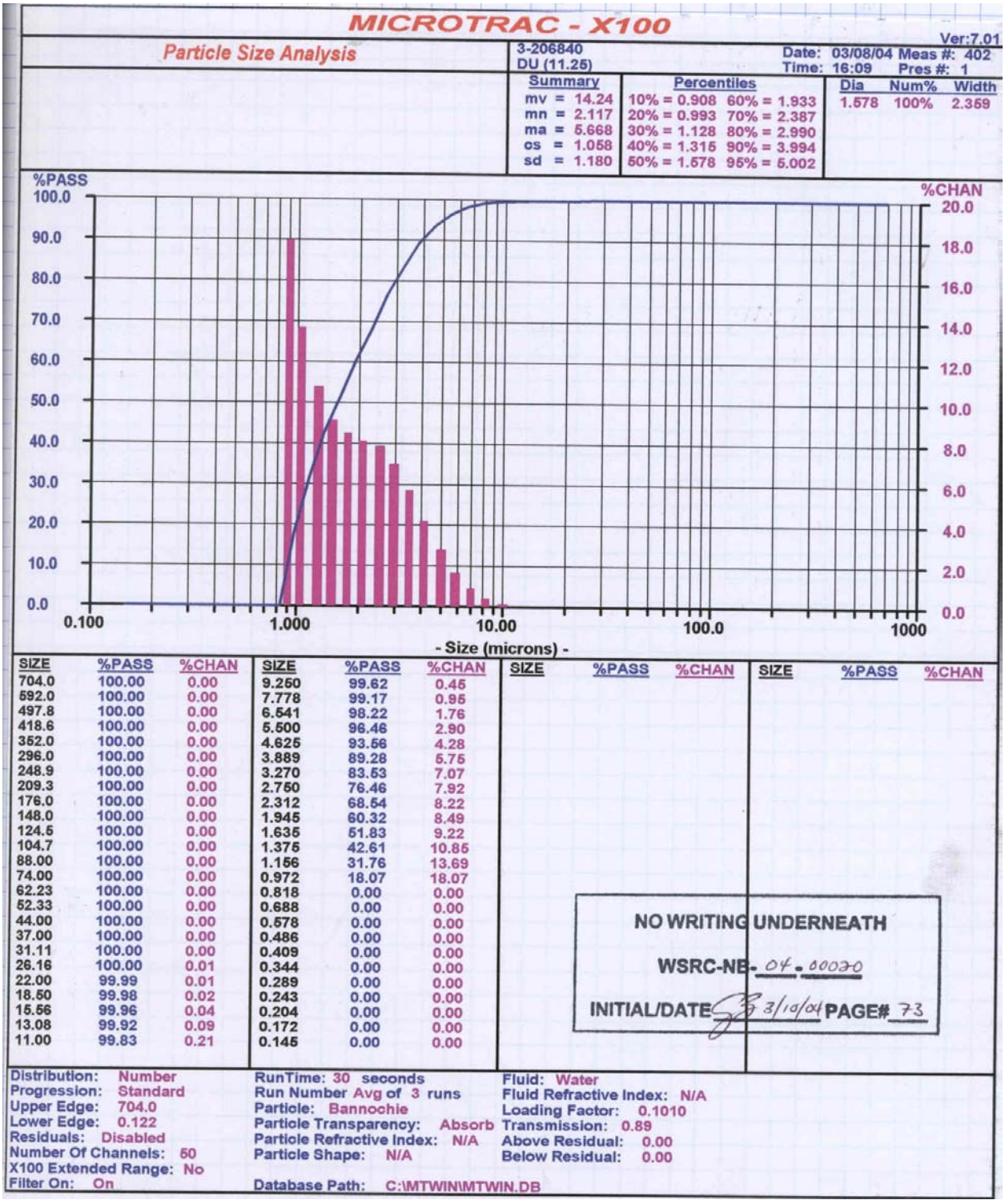


Figure C- 18. Particle size number distribution for SB2 simulant with 11.25 wt % uranium following SRAT cycle processing

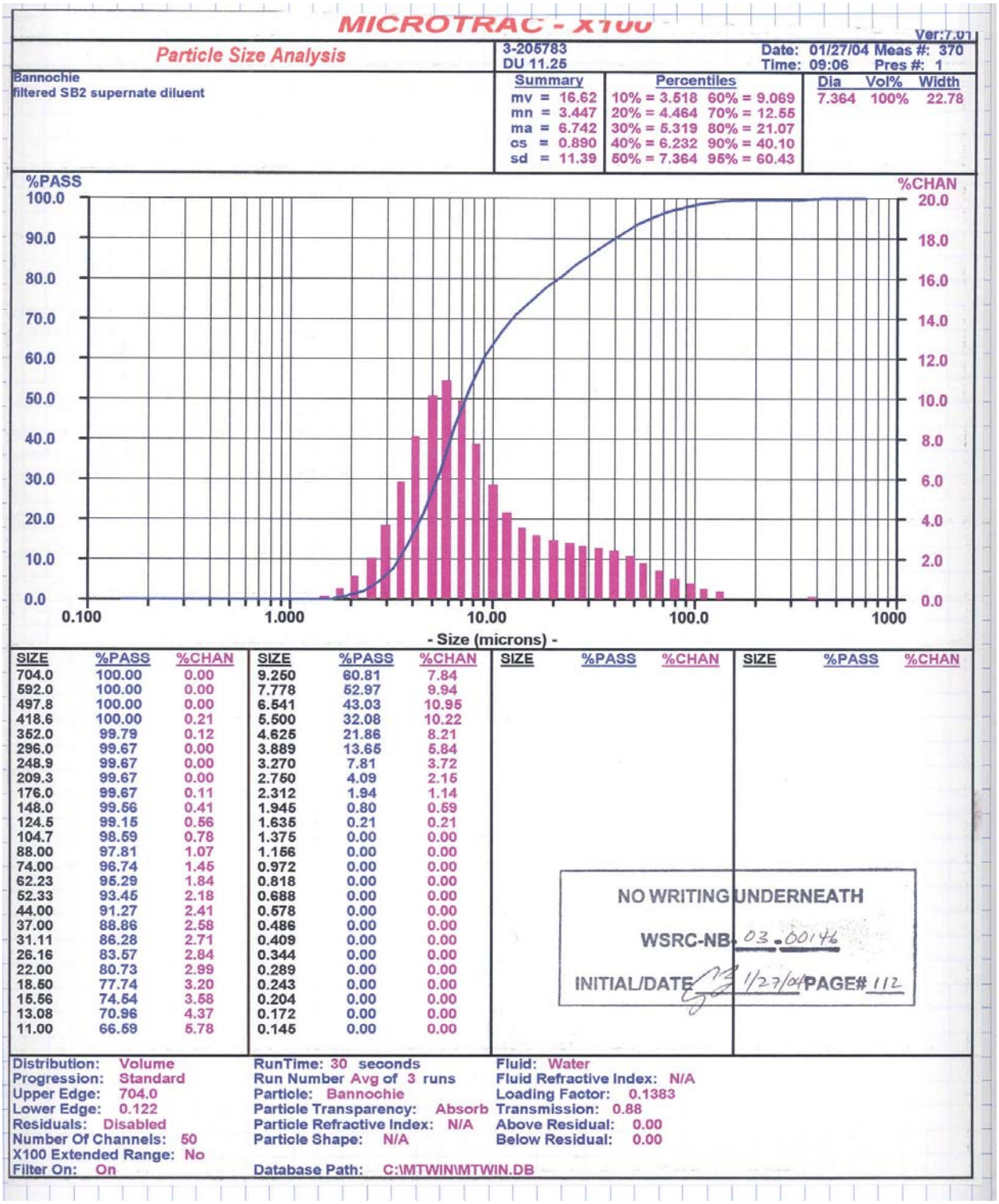
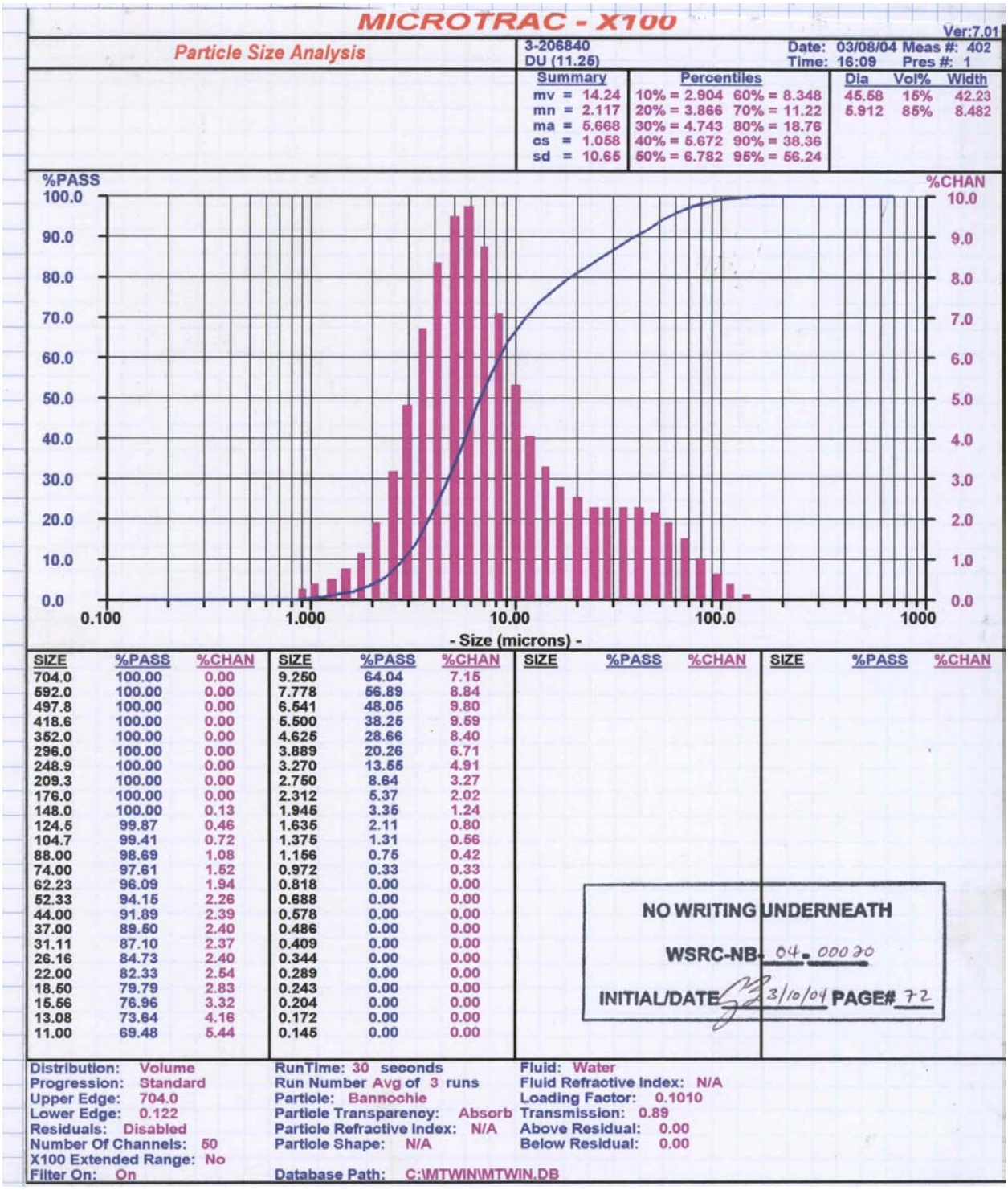


Figure C- 19. Particle size volume distribution for SB2 simulant with 11.25 wt % uranium



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
704.0	100.00	0.00	9.250	64.04	7.15						
592.0	100.00	0.00	7.778	56.89	8.84						
497.8	100.00	0.00	6.541	48.05	9.80						
418.6	100.00	0.00	5.500	38.25	9.59						
352.0	100.00	0.00	4.625	28.66	8.40						
296.0	100.00	0.00	3.889	20.26	6.71						
248.9	100.00	0.00	3.270	13.55	4.91						
209.3	100.00	0.00	2.750	8.64	3.27						
176.0	100.00	0.00	2.312	5.37	2.02						
148.0	100.00	0.13	1.945	3.35	1.24						
124.5	99.87	0.46	1.635	2.11	0.80						
104.7	99.41	0.72	1.375	1.31	0.56						
88.00	98.69	1.08	1.156	0.75	0.42						
74.00	97.61	1.52	0.972	0.33	0.33						
62.23	96.09	1.94	0.818	0.00	0.00						
52.33	94.15	2.26	0.688	0.00	0.00						
44.00	91.89	2.39	0.578	0.00	0.00						
37.00	89.50	2.40	0.486	0.00	0.00						
31.11	87.10	2.37	0.409	0.00	0.00						
26.16	84.73	2.40	0.344	0.00	0.00						
22.00	82.33	2.54	0.289	0.00	0.00						
18.50	79.79	2.83	0.243	0.00	0.00						
15.56	76.96	3.32	0.204	0.00	0.00						
13.08	73.64	4.16	0.172	0.00	0.00						
11.00	69.48	5.44	0.145	0.00	0.00						

Figure C- 20. Particle size volume distribution for SB2 simulant with 11.25 wt % uranium following SRAT cycle processing

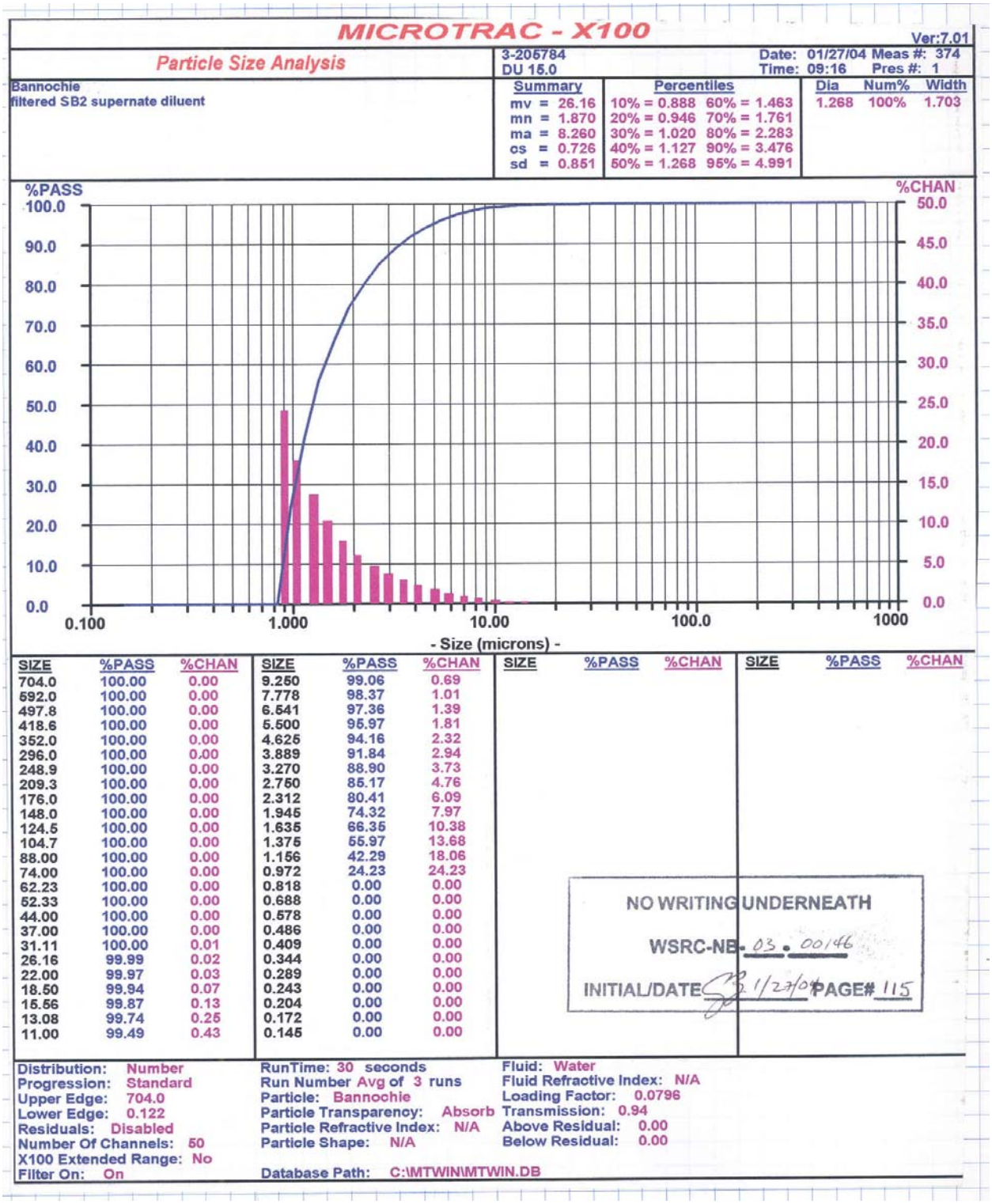


Figure C- 21. Particle size number distribution for SB2 simulant with 15 wt % uranium

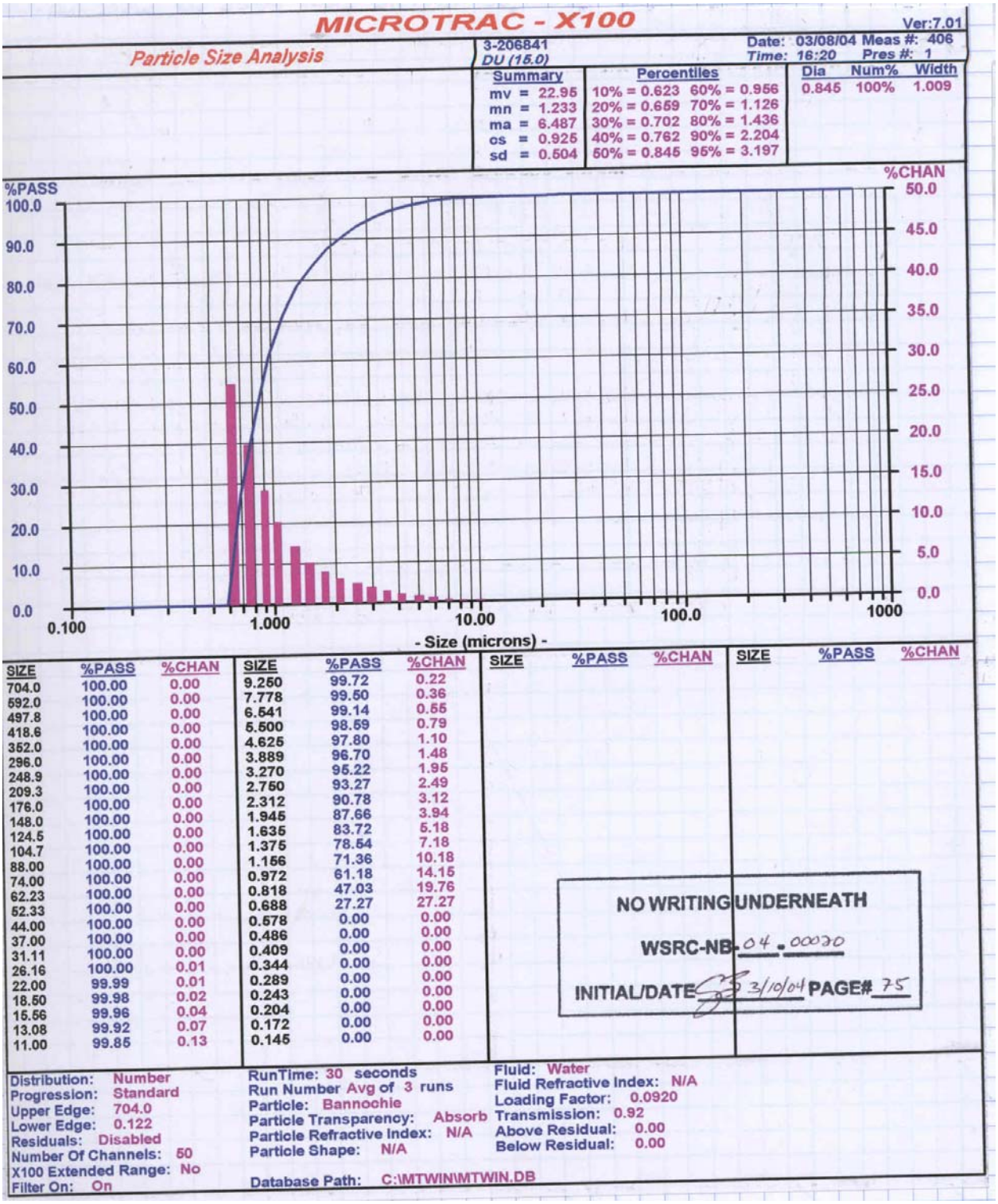


Figure C- 22. Particle size number distribution for SB2 simulant with 15 wt % uranium following SRAT cycle processing

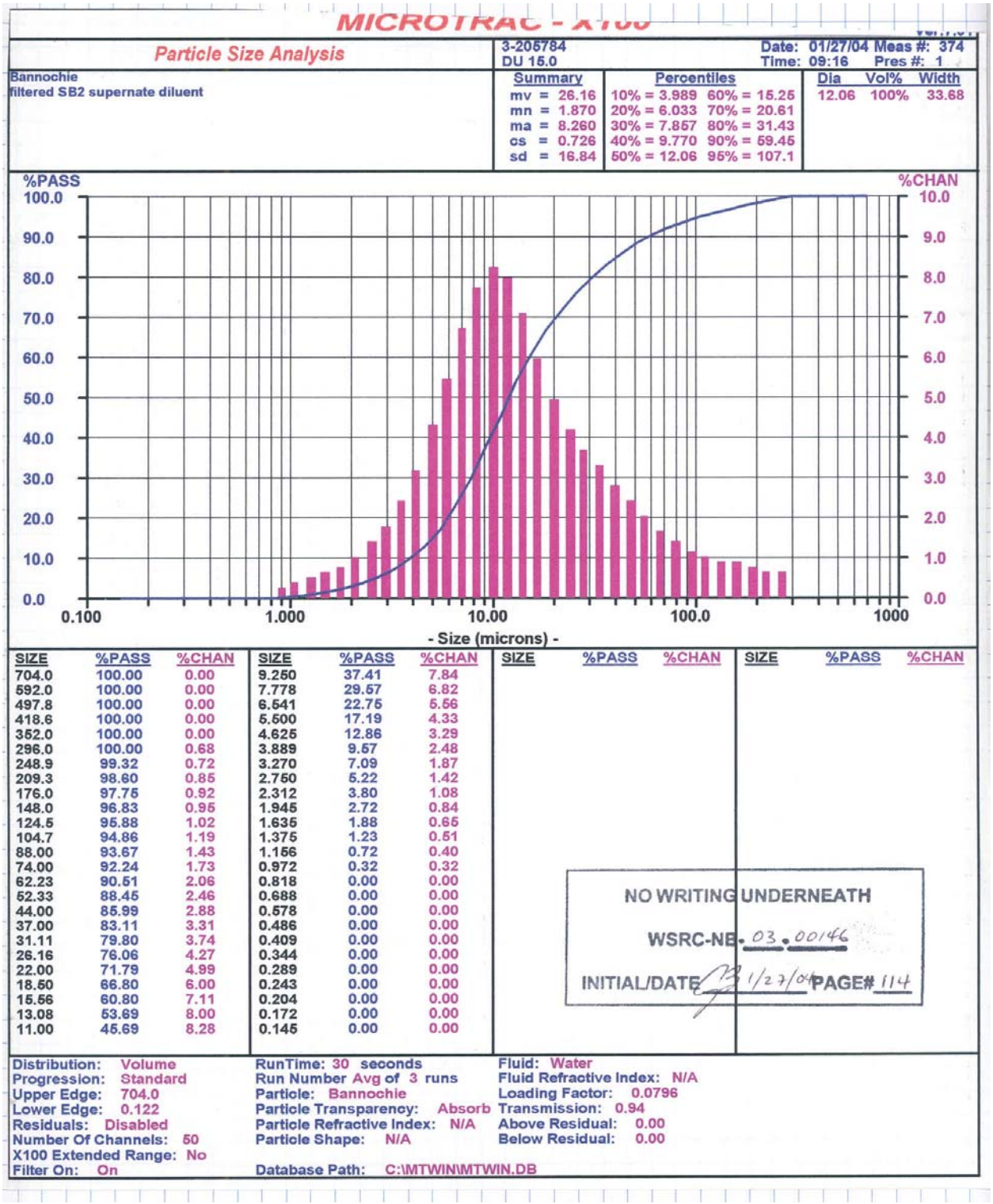
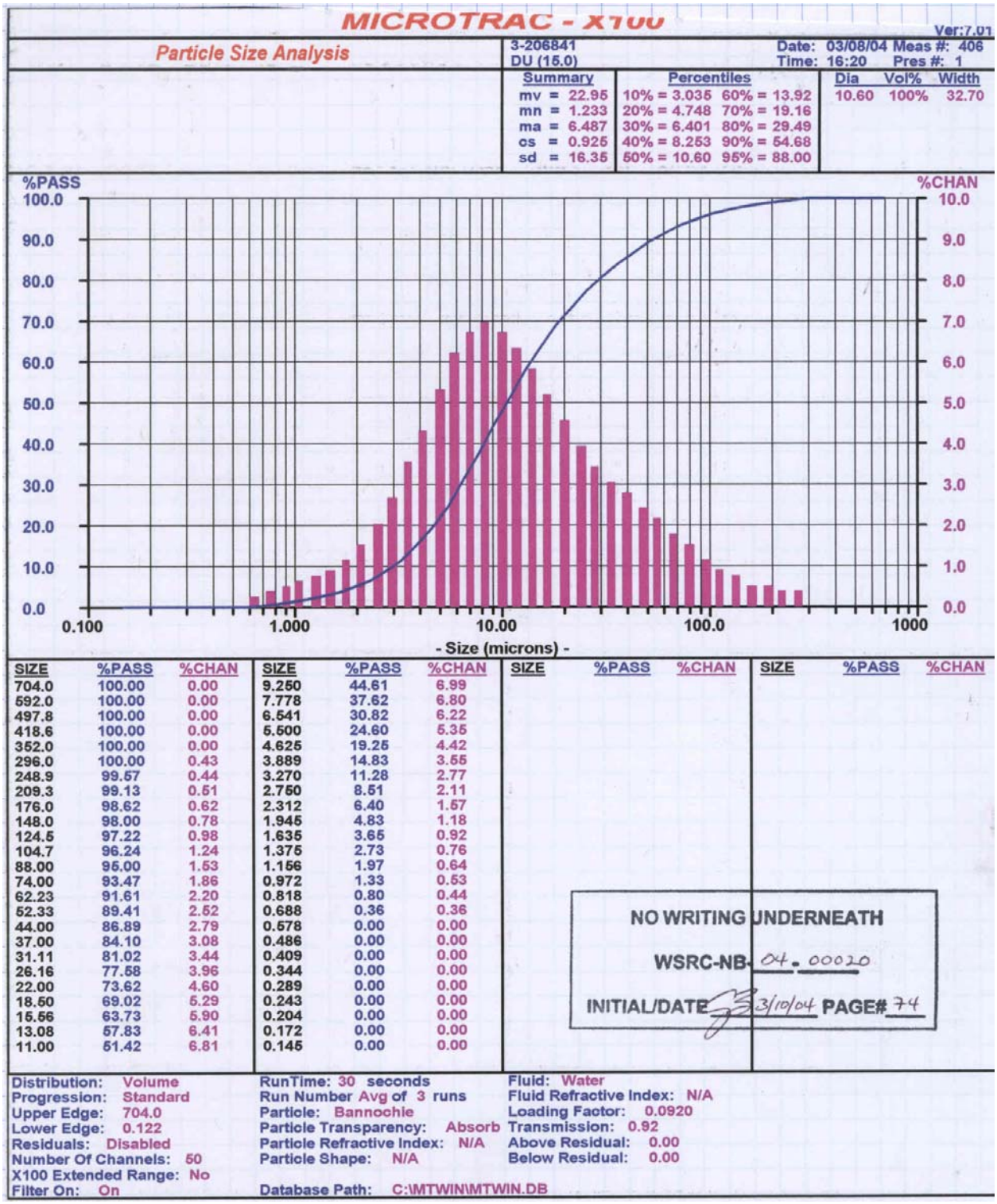


Figure C- 23. Particle size volume distribution for SB2 simulant with 15 wt % uranium



SIZE	%PASS	%CHAN	SIZE	%PASS	%CHAN
704.0	100.00	0.00	9.250	44.61	6.99
592.0	100.00	0.00	7.778	37.62	6.80
497.8	100.00	0.00	6.541	30.82	6.22
418.6	100.00	0.00	5.500	24.60	5.35
352.0	100.00	0.00	4.625	19.25	4.42
296.0	100.00	0.43	3.889	14.83	3.55
248.9	99.57	0.44	3.270	11.28	2.77
209.3	99.13	0.51	2.750	8.51	2.11
176.0	98.62	0.62	2.312	6.40	1.57
148.0	98.00	0.78	1.945	4.83	1.18
124.5	97.22	0.98	1.635	3.65	0.92
104.7	96.24	1.24	1.375	2.73	0.76
88.00	95.00	1.53	1.156	1.97	0.64
74.00	93.47	1.86	0.972	1.33	0.53
62.23	91.61	2.20	0.818	0.80	0.44
52.33	89.41	2.52	0.688	0.36	0.36
44.00	86.89	2.79	0.578	0.00	0.00
37.00	84.10	3.08	0.486	0.00	0.00
31.11	81.02	3.44	0.409	0.00	0.00
26.16	77.58	3.96	0.344	0.00	0.00
22.00	73.62	4.60	0.289	0.00	0.00
18.50	69.02	5.29	0.243	0.00	0.00
15.56	63.73	5.90	0.204	0.00	0.00
13.08	57.83	6.41	0.172	0.00	0.00
11.00	51.42	6.81	0.145	0.00	0.00

Figure C- 24. Particle size volume distribution for SB2 simulant with 15 wt % uranium following SRAT cycle processing

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APPENDIX D. SRAT FEED RHEOGRAMS

Key:
Black/gray = initial up/down ramp flow curves
Blue/Teal = replicate up/down ramp flow curves

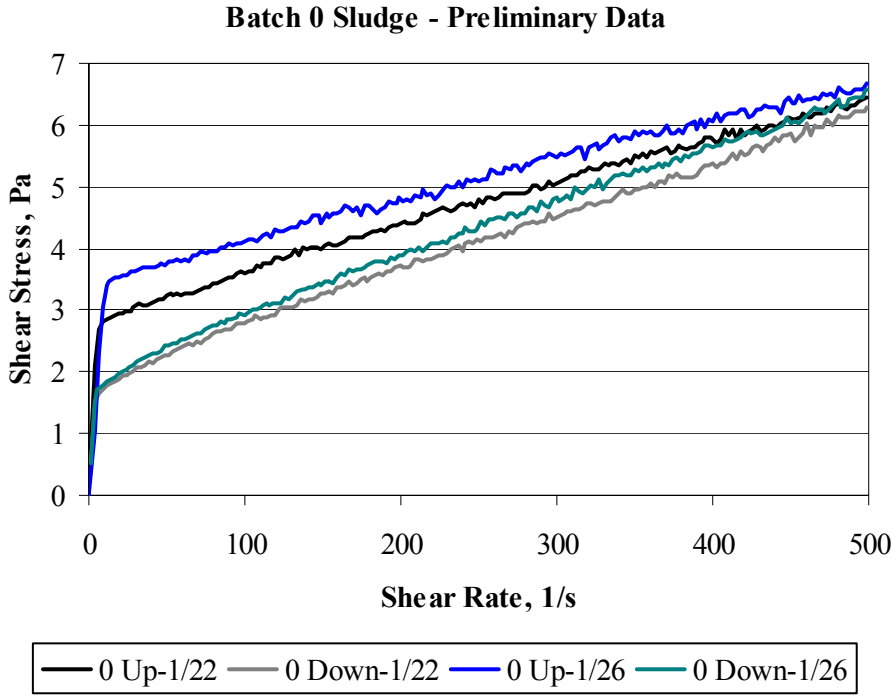

Figure D- 1. Preliminary Batch 0 Sludge Rheology Data

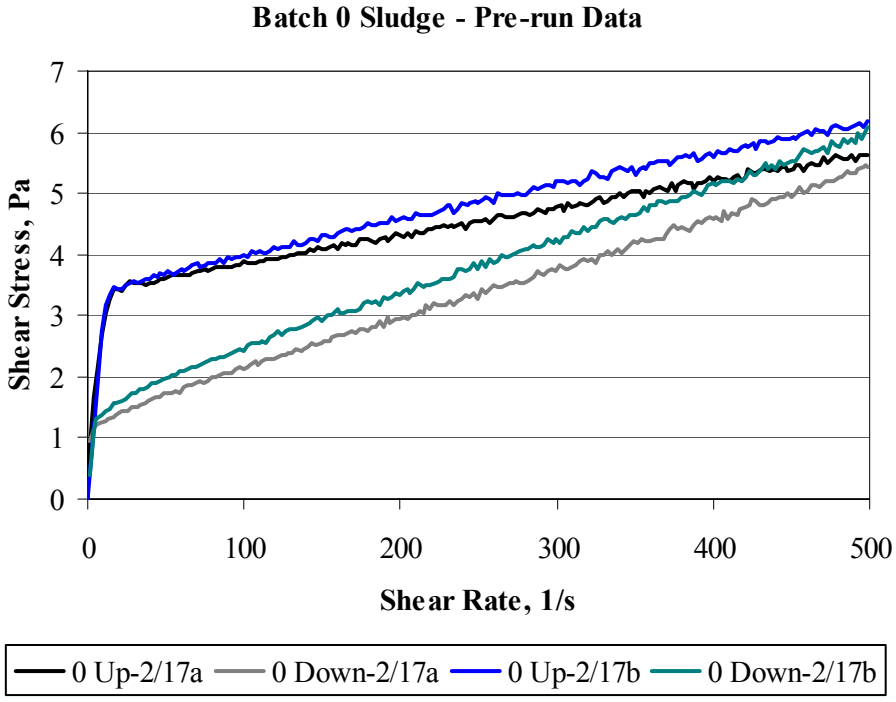

Figure D- 2. Pre-Run Batch 0 Sludge Rheology Data

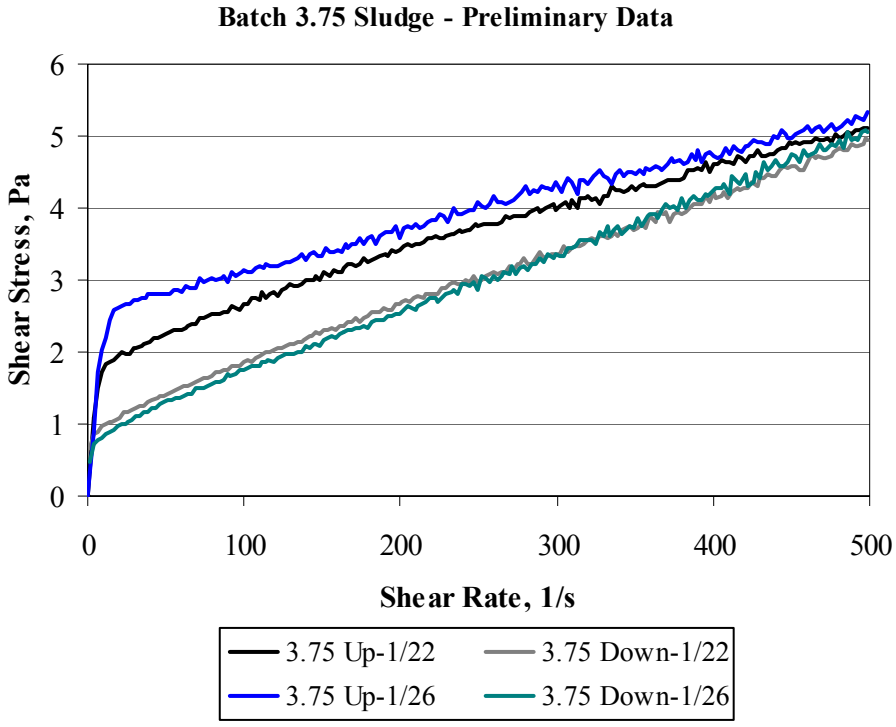

Figure D- 3. Preliminary Batch 3.75 Sludge Rheology Data

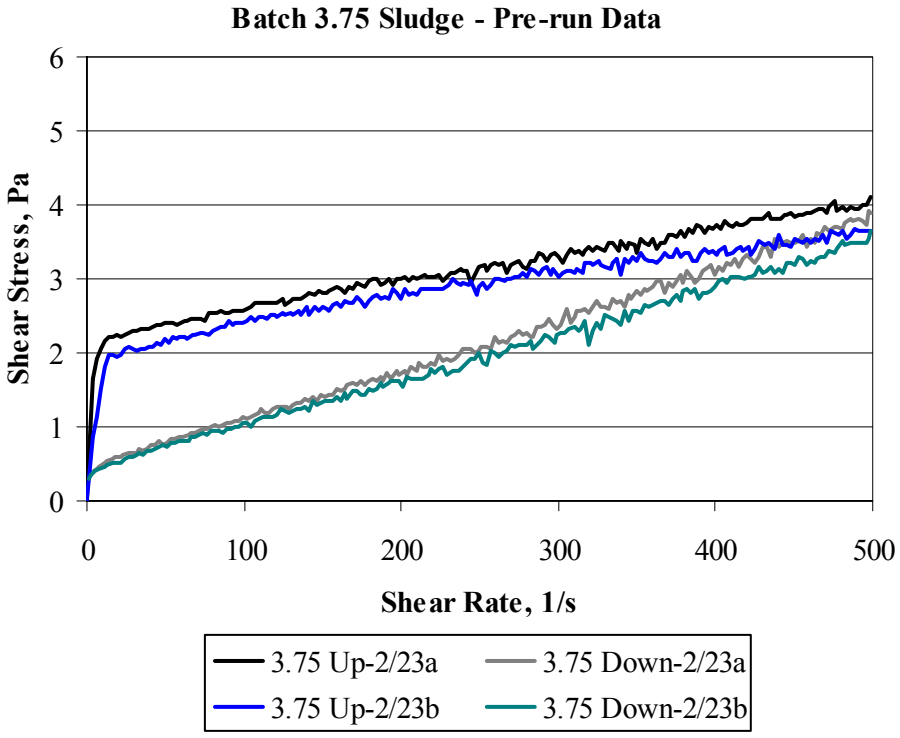

Figure D- 4. Pre-Run Batch 3.75 Sludge Rheology Data

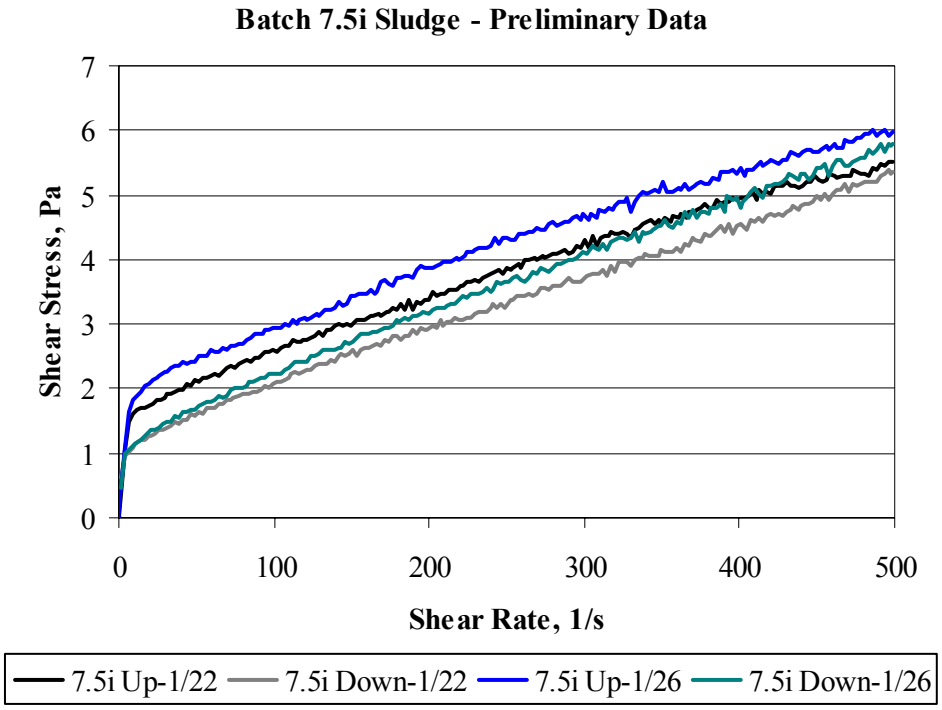

Figure D- 5. Preliminary Batch 7.5i Sludge Rheology Data

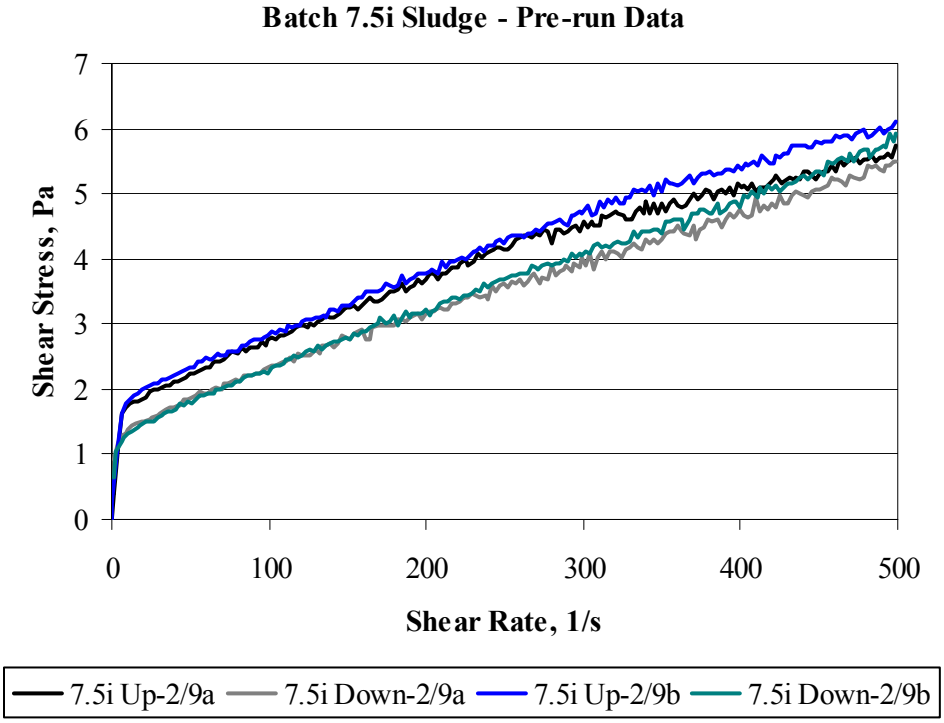

Figure D- 6. Pre-Run Batch 7.5i Sludge Rheology Data

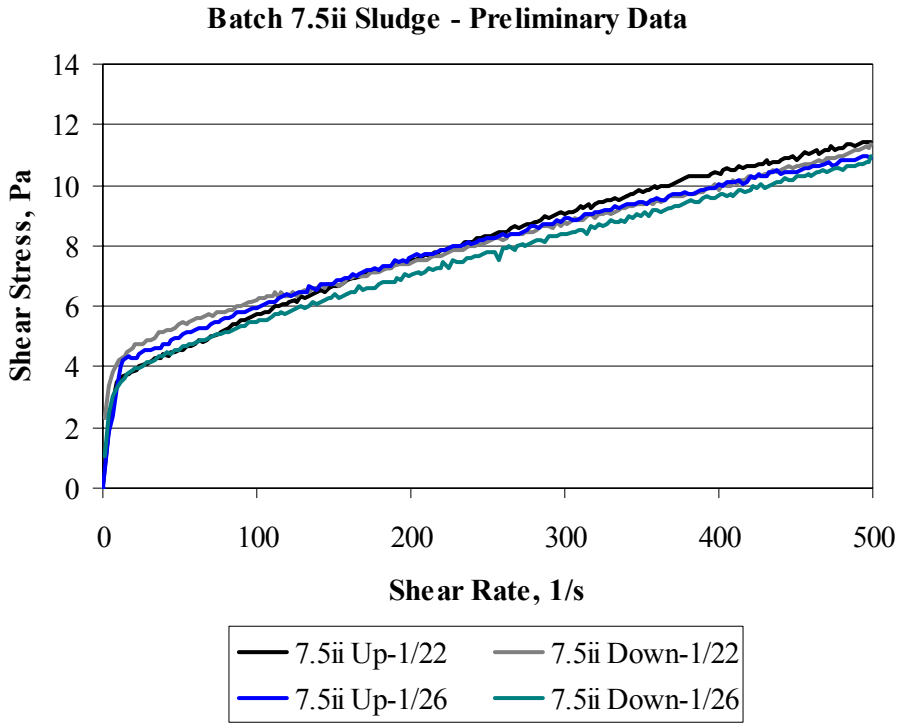

Figure D- 7. Preliminary Batch 7.5ii Sludge Rheology Data

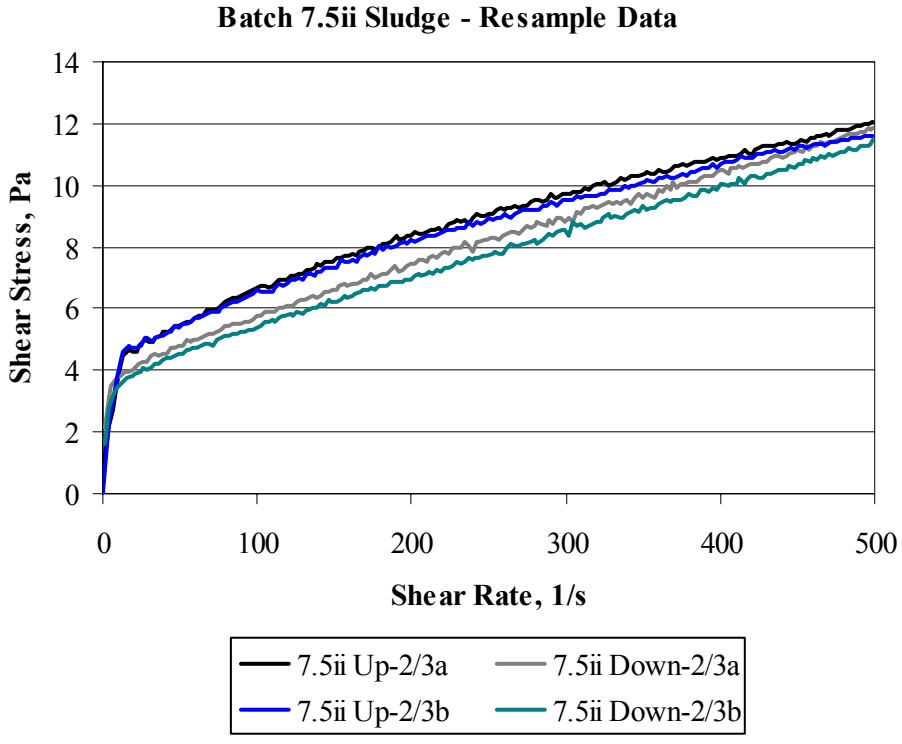

Figure D- 8. Resample Batch 7.5ii Sludge Rheology Data

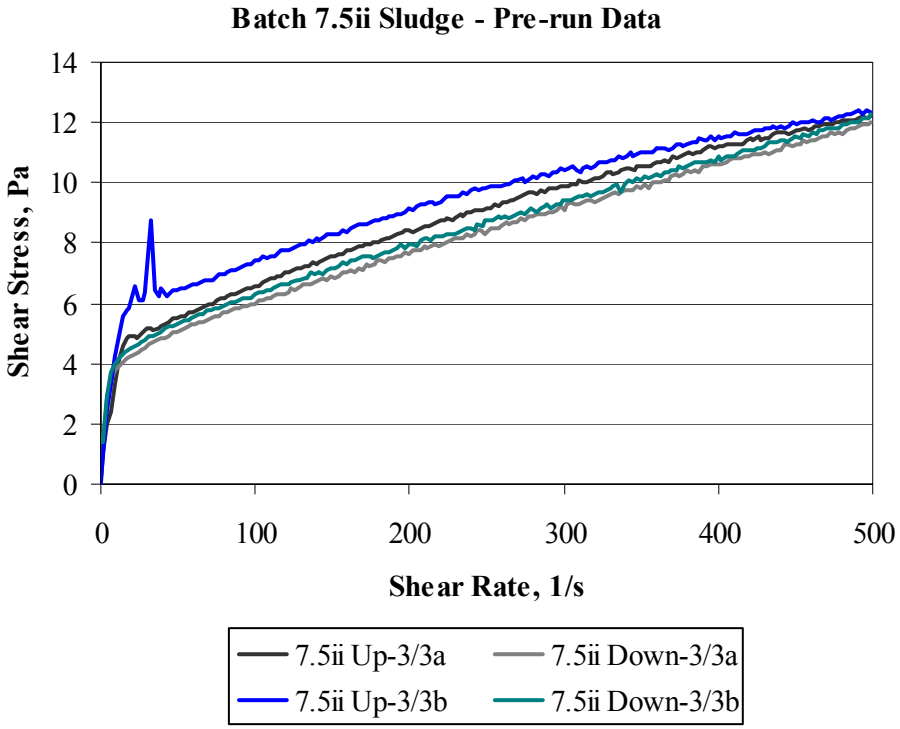

Figure D- 9. Pre-Run Batch 7.5ii Sludge Rheology Data

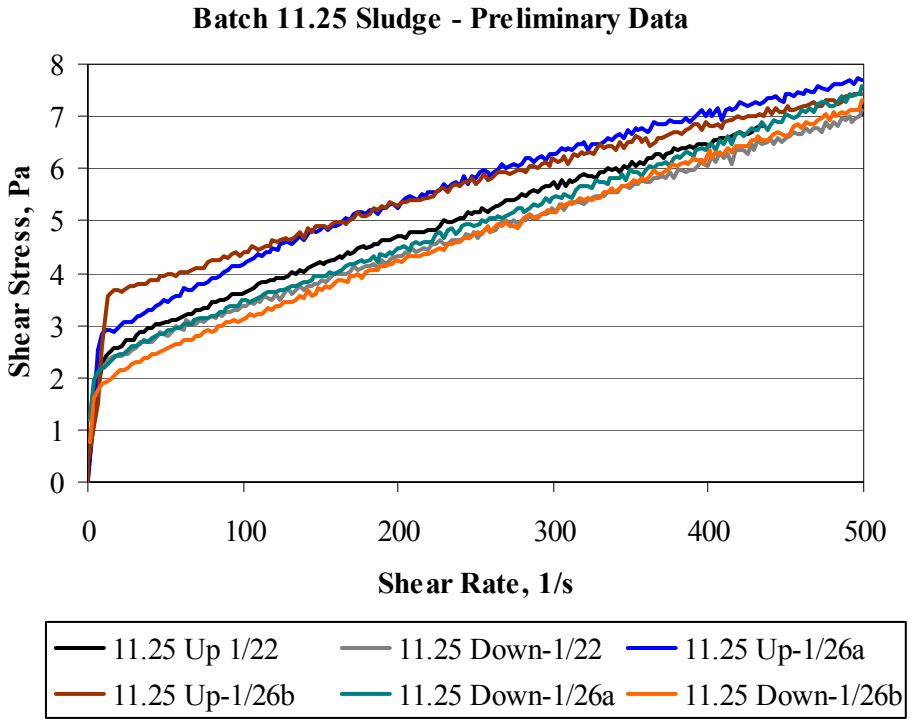

Figure D- 10. Preliminary Batch 11.25 Sludge Rheology Data

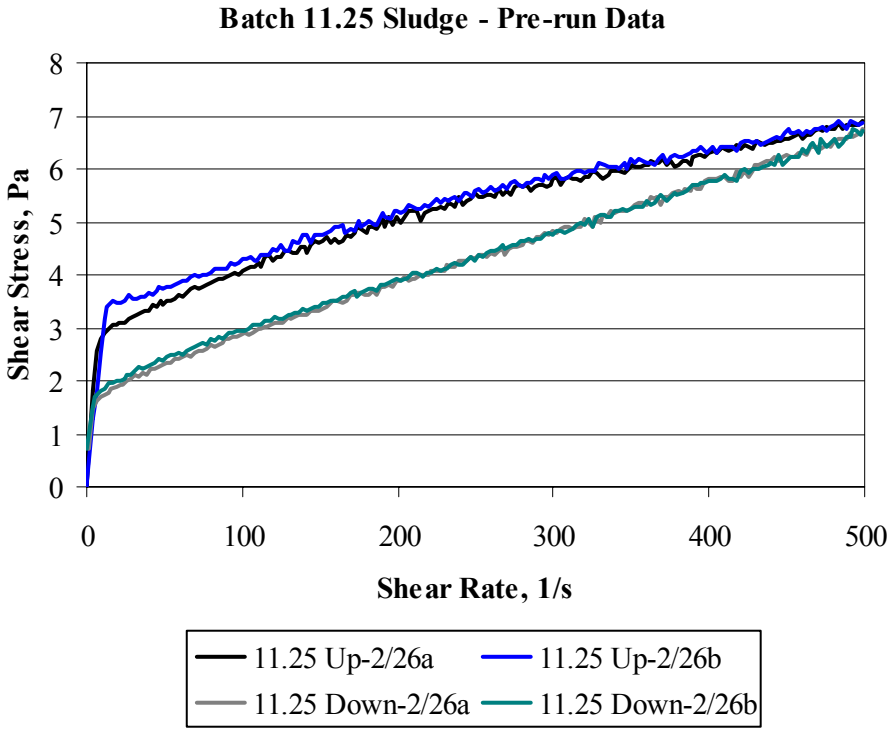

Figure D- 11. Pre-Run Batch 11.25 Sludge Rheology Data

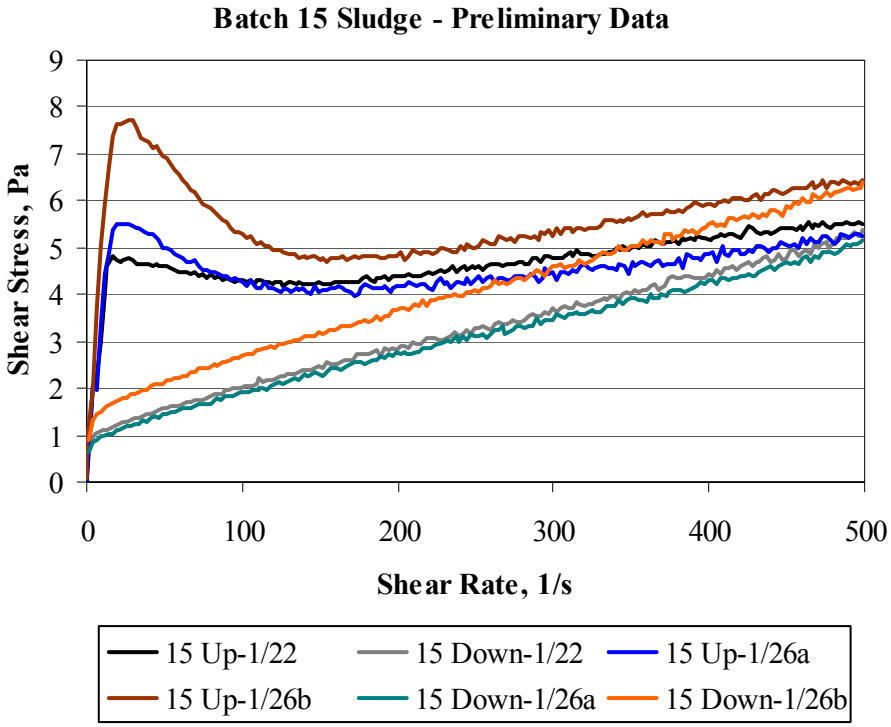

Figure D- 12. Preliminary Batch 15 Sludge Rheology Data

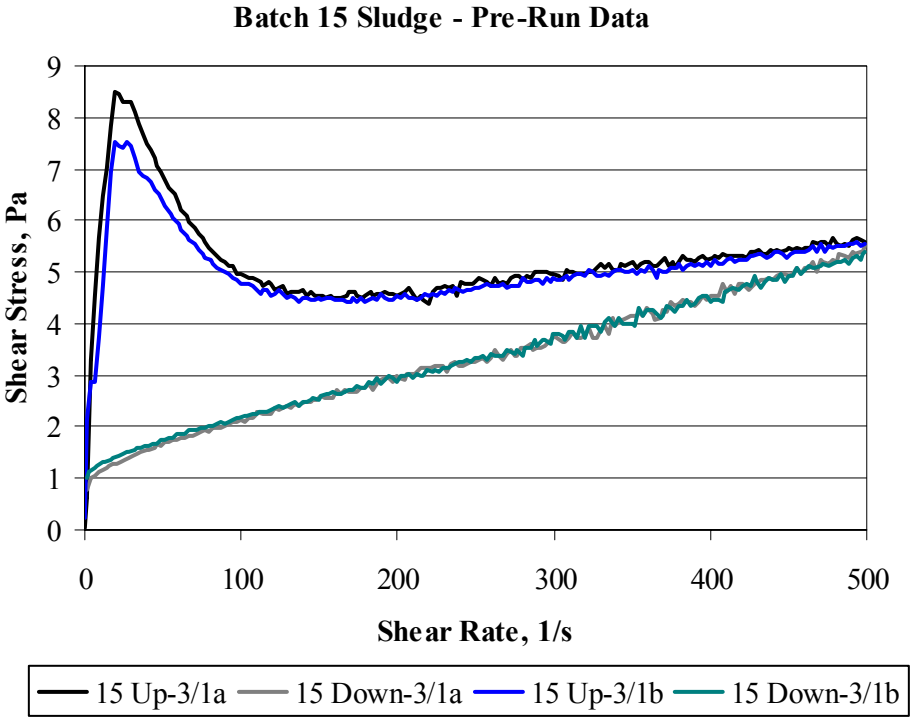

Figure D- 13. Pre-Run Batch 15 Sludge Rheology Data

APPENDIX E. SRAT FEED REGRESSION ANALYSES

Key:
Green = up curve regressions
Red = down curve regressions

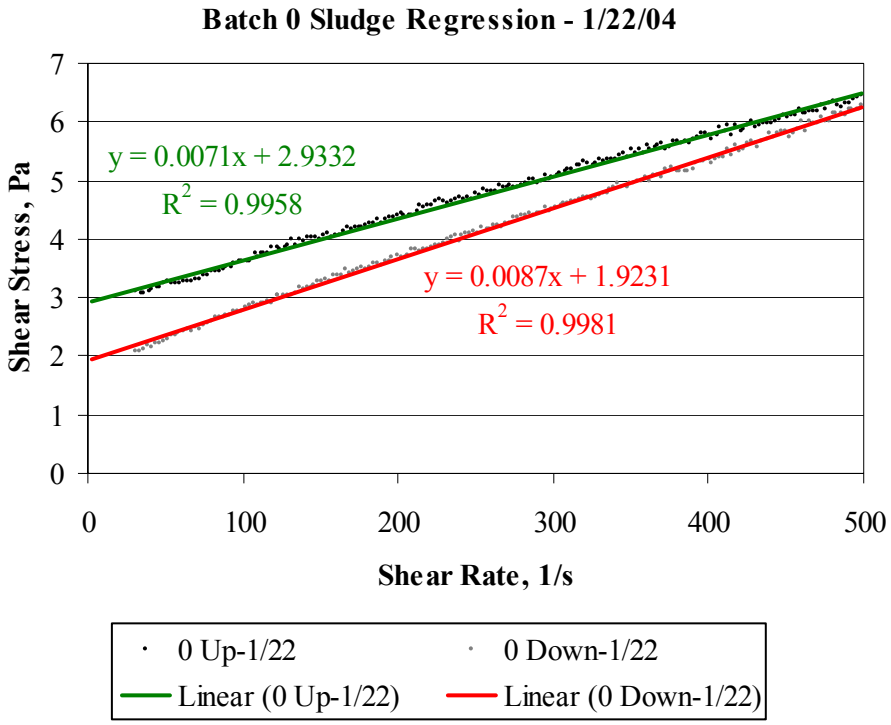

Figure E- 1. Batch 0 Sludge Regression – 1/22/04

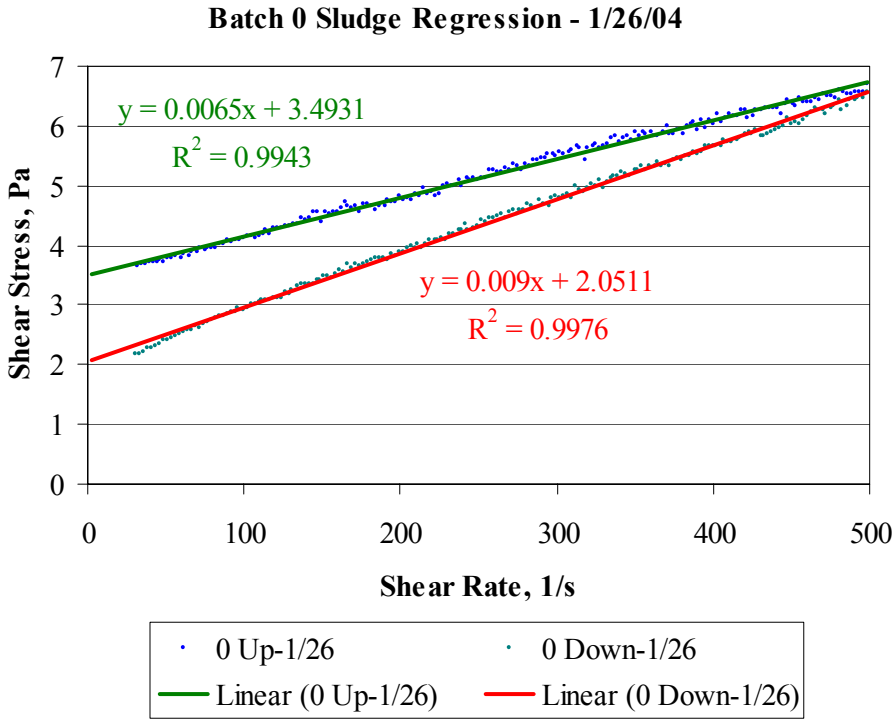

Figure E- 2. Batch 0 Sludge Regression – 1/26/04

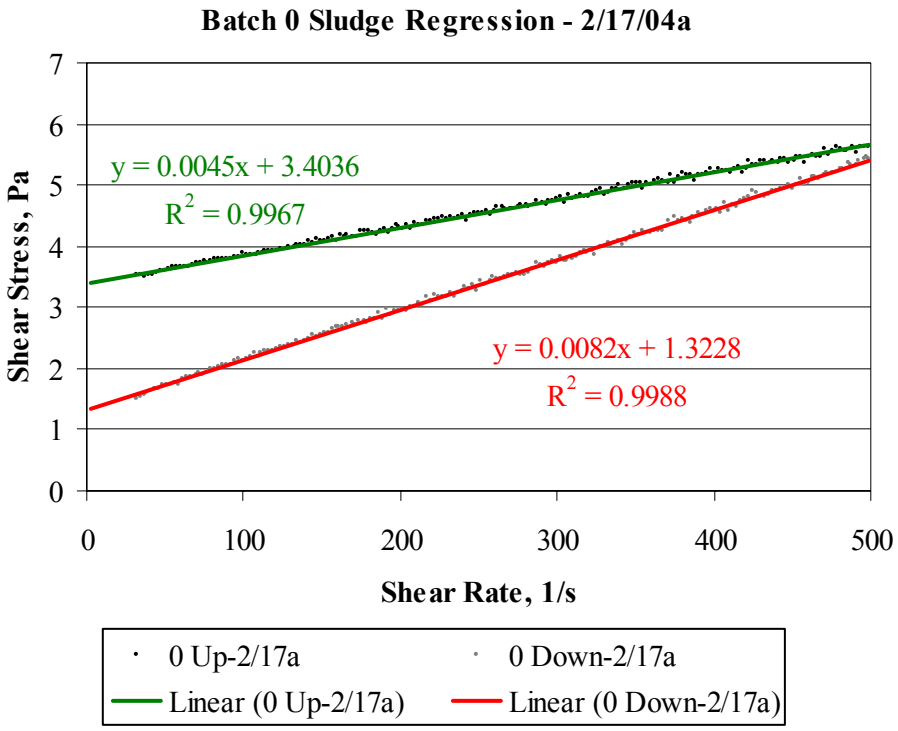

Figure E- 3. Batch 0 Sludge Regression – 2/17/04a

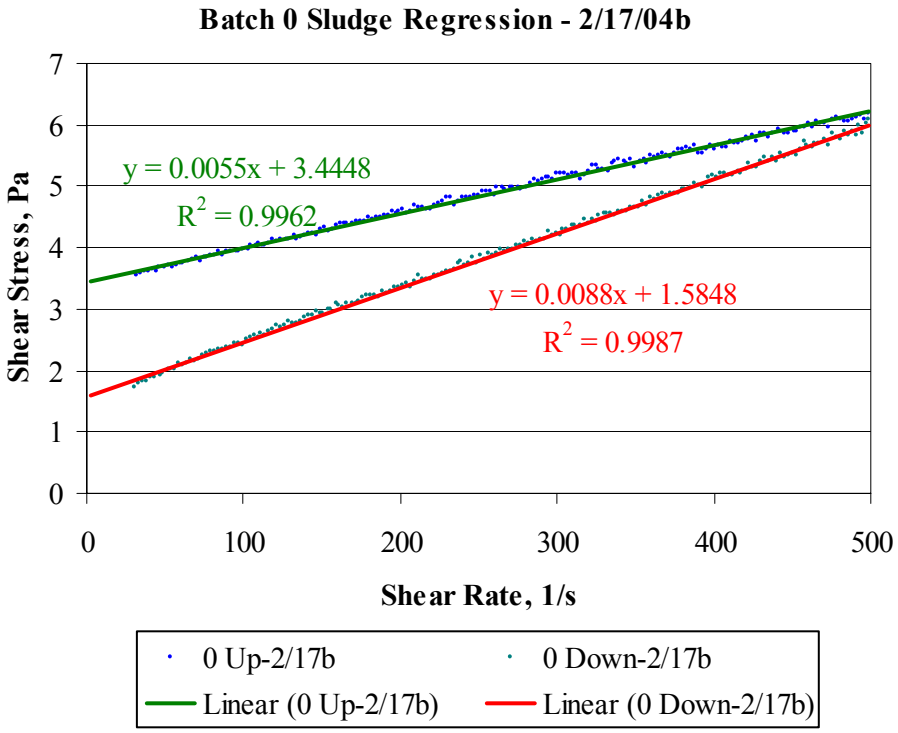

Figure E- 4. Batch 0 Sludge Regression – 2/17/04b

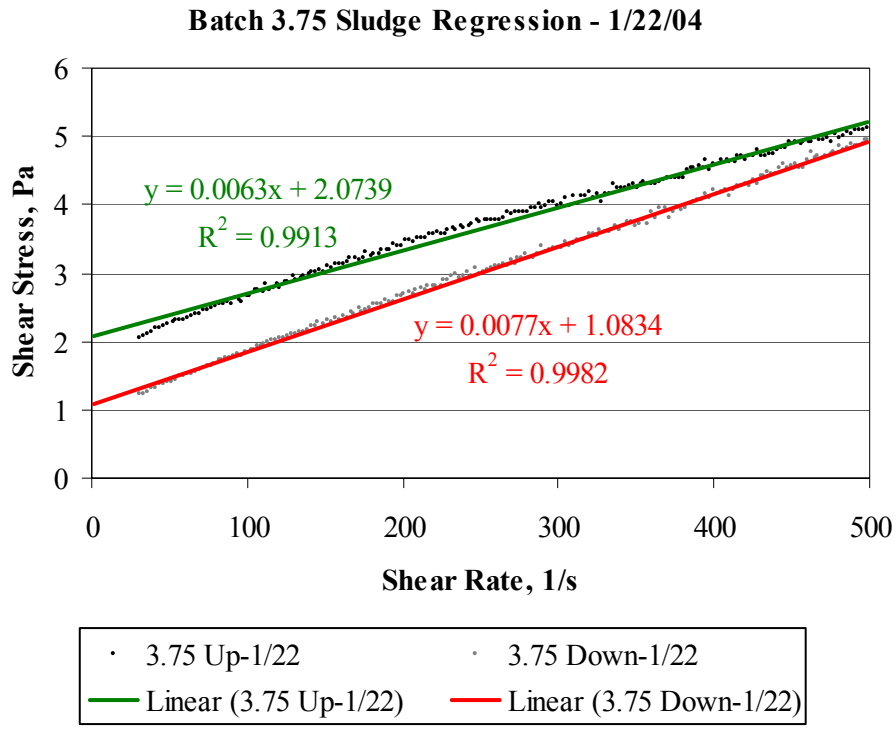

Figure E- 5. Batch 3.75 Sludge Regression – 1/22/04

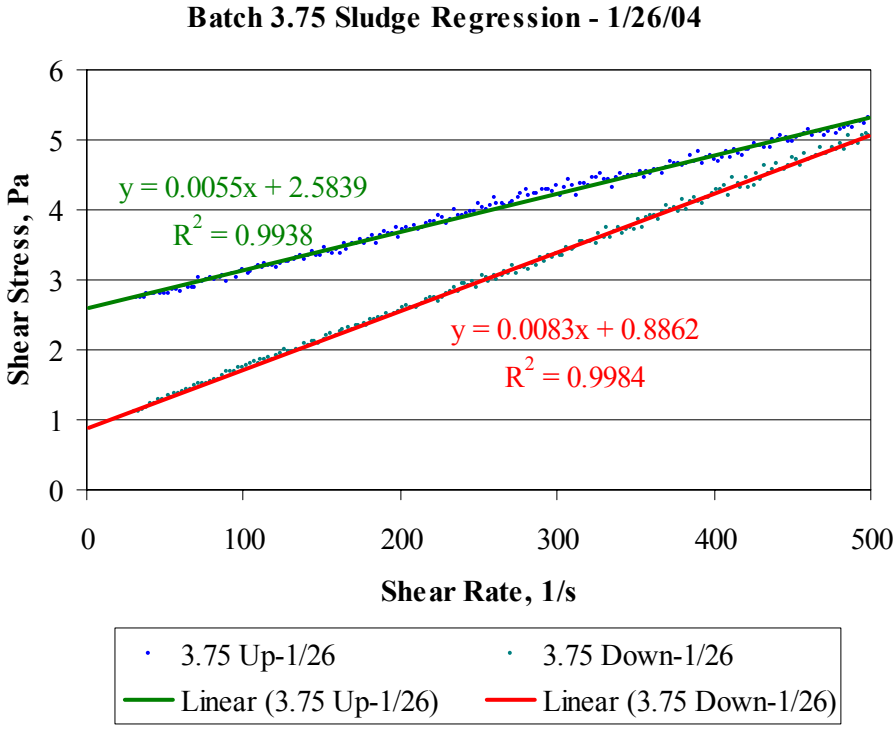

Figure E- 6. Batch 3.75 Sludge Regression – 1/26/04

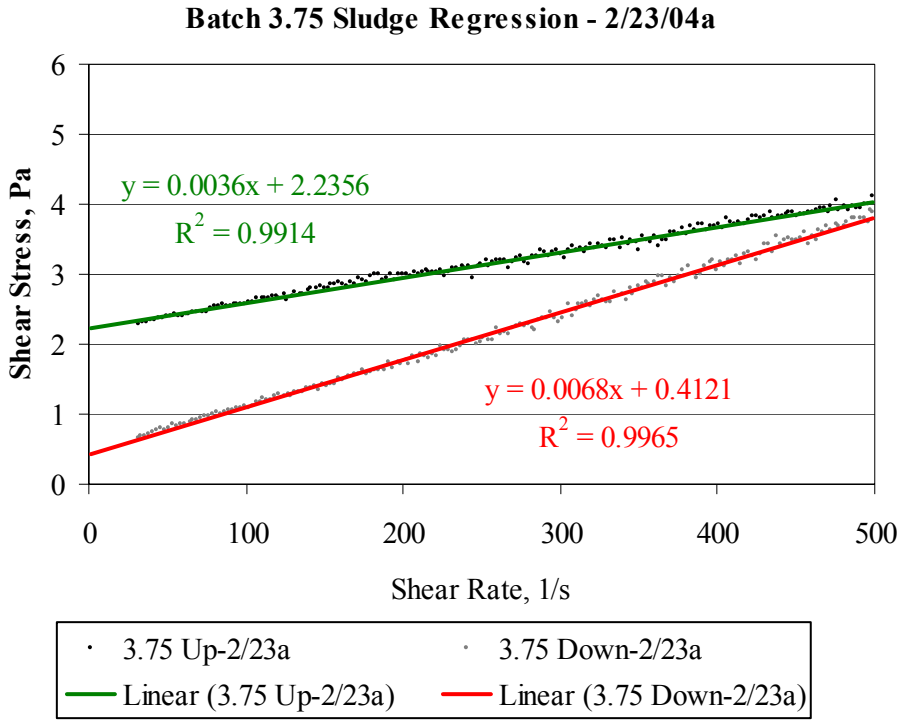

Figure E- 7. Batch 3.75 Sludge Regression – 2/23/04a

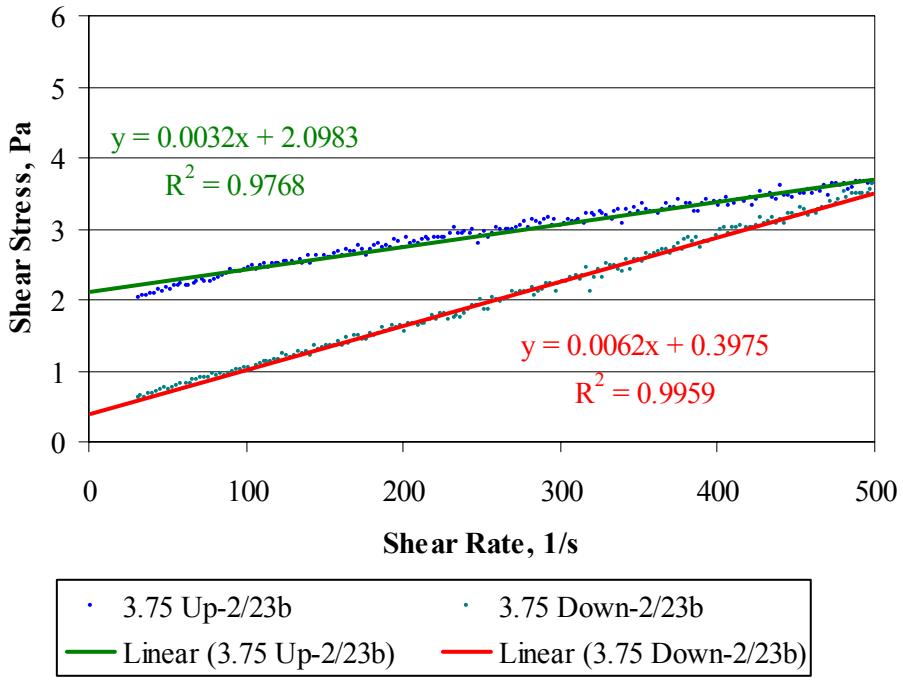

Figure E- 8. Batch 3.75 Sludge Regression – 2/23/04b

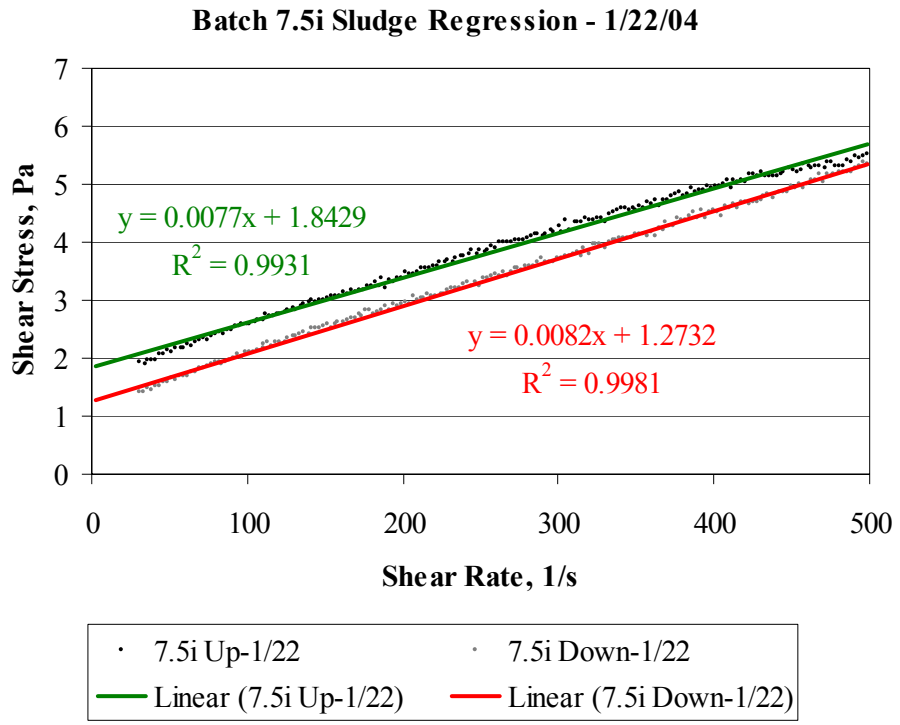

Figure E- 9. Batch 7.5i Sludge Regression – 1/22/04

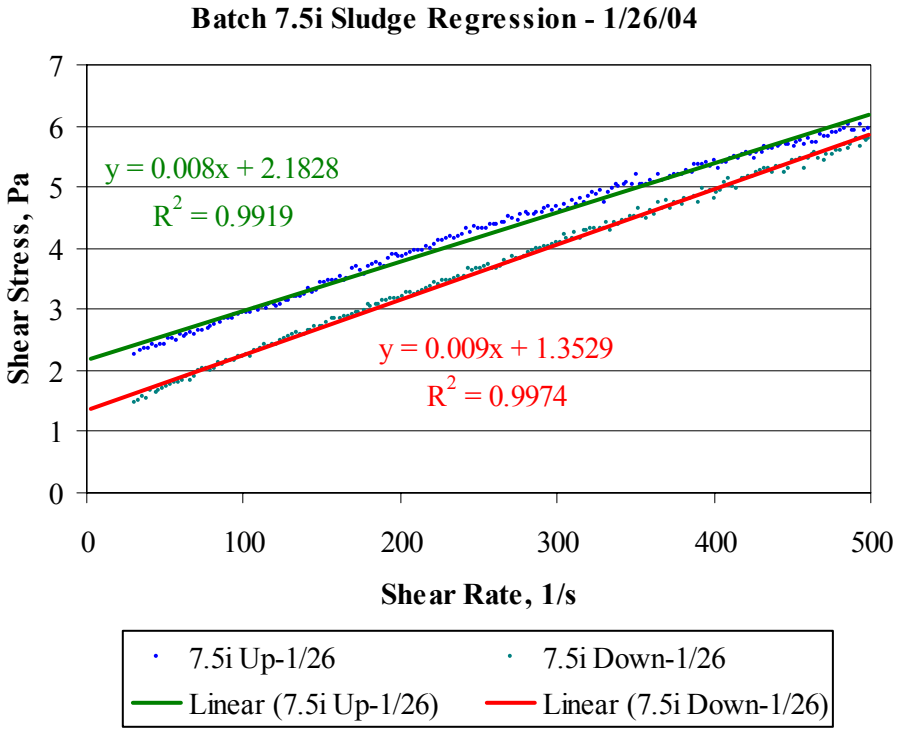

Figure E- 10. Batch 7.5i Sludge Regression – 1/26/04

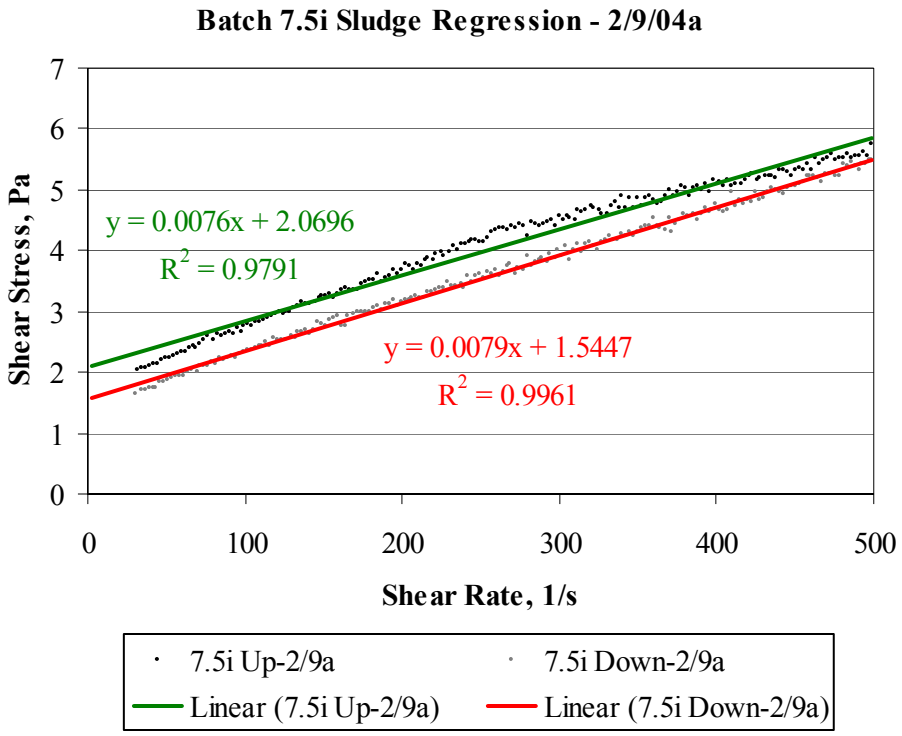

Figure E- 11. Batch 7.5i Sludge Regression – 2/9/04a

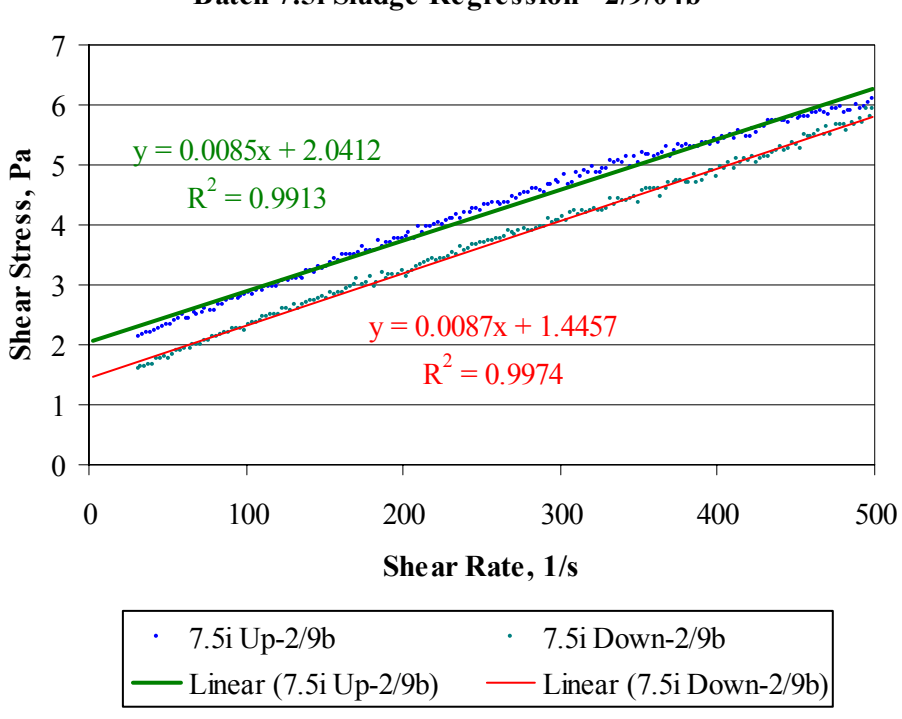

Figure E- 12. Batch 7.5i Sludge Regression – 2/9/04b

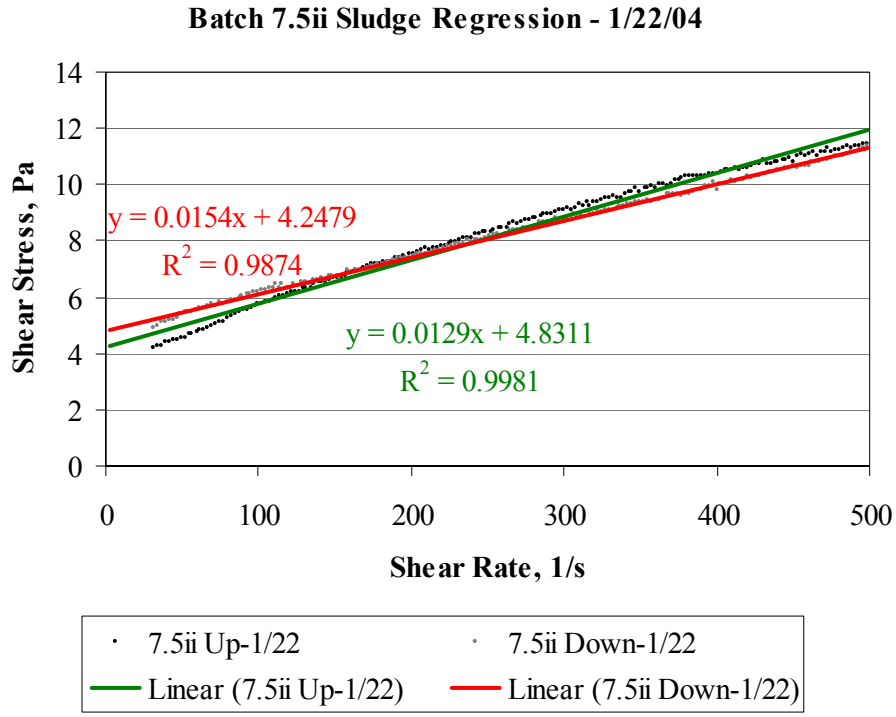

Figure E- 13. Batch 7.5ii Sludge Regression – 1/22/04

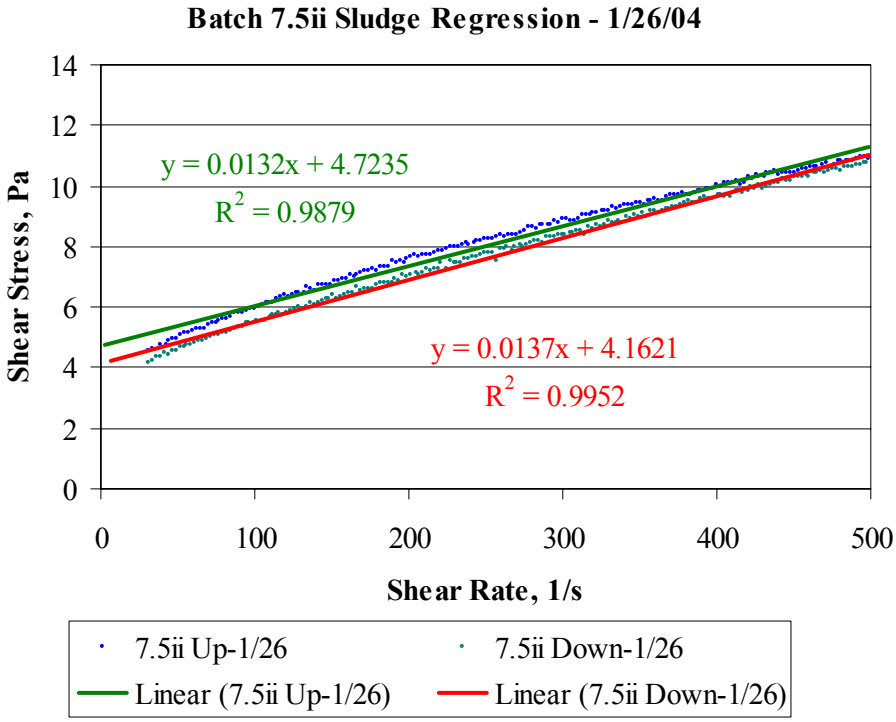

Figure E- 14. Batch 7.5ii Sludge Regression – 1/26/04

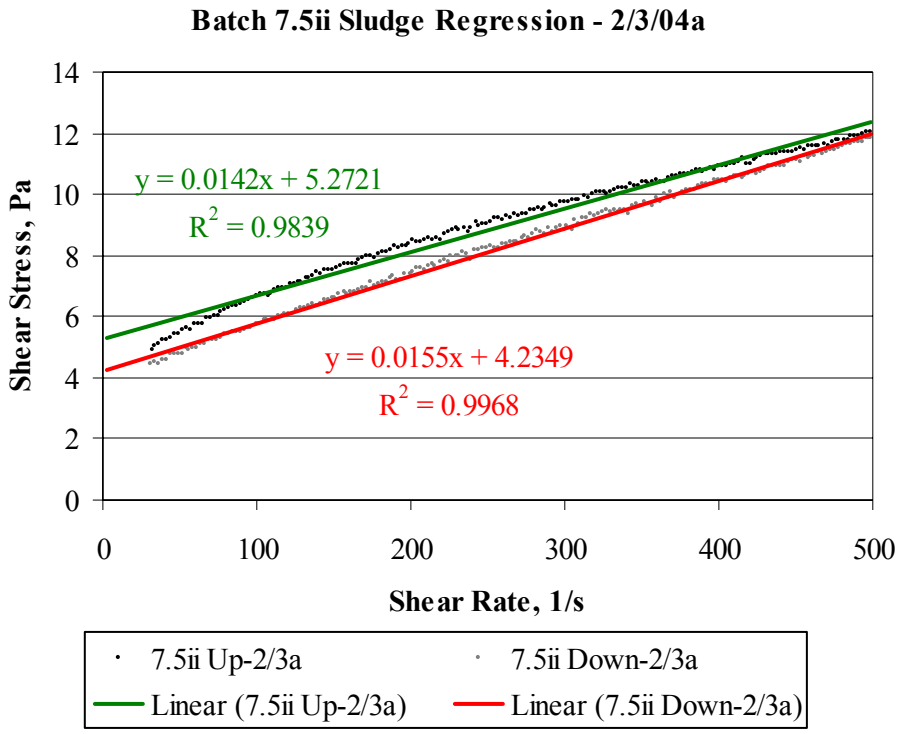

Figure E- 15. Batch 7.5ii Sludge Regression – 2/3/04a

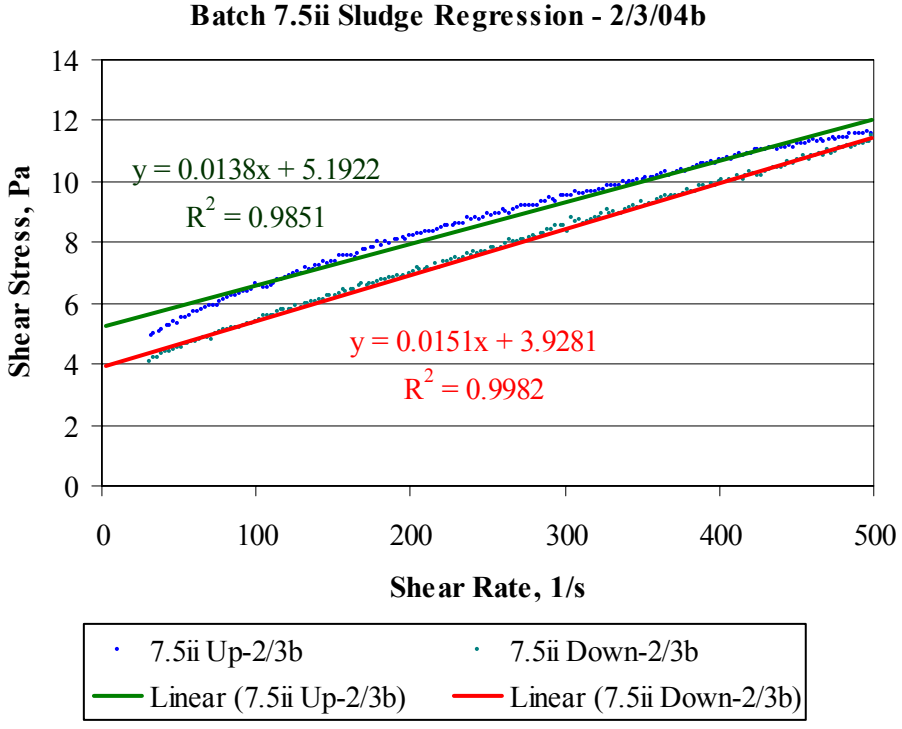

Figure E- 16. Batch 7.5ii Sludge Regression – 2/3/04b

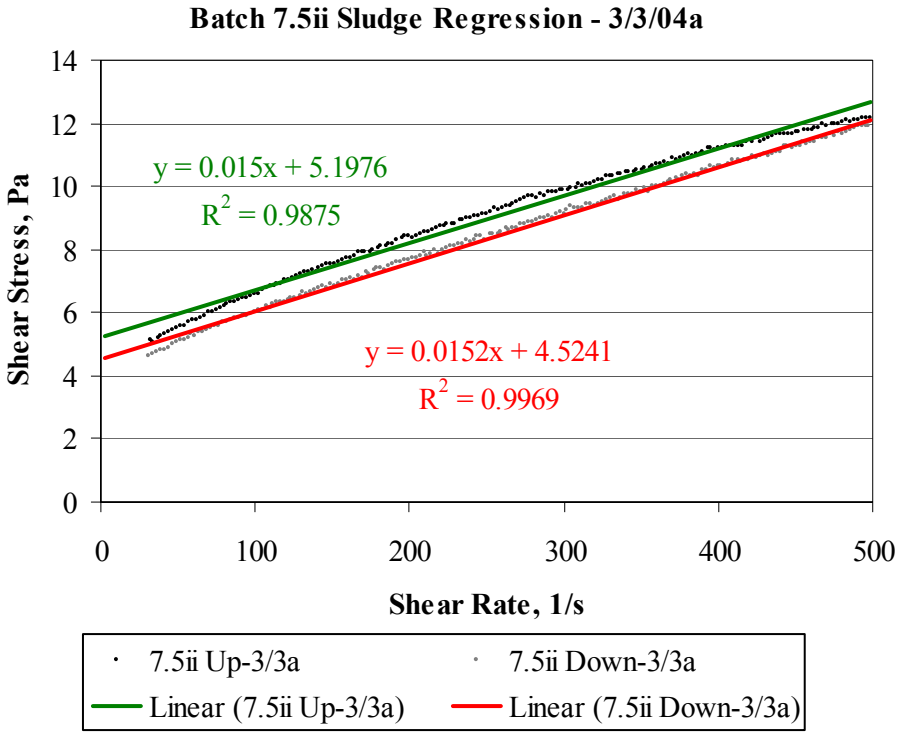

Figure E- 17. Batch 7.5ii Sludge Regression – 3/3/04a

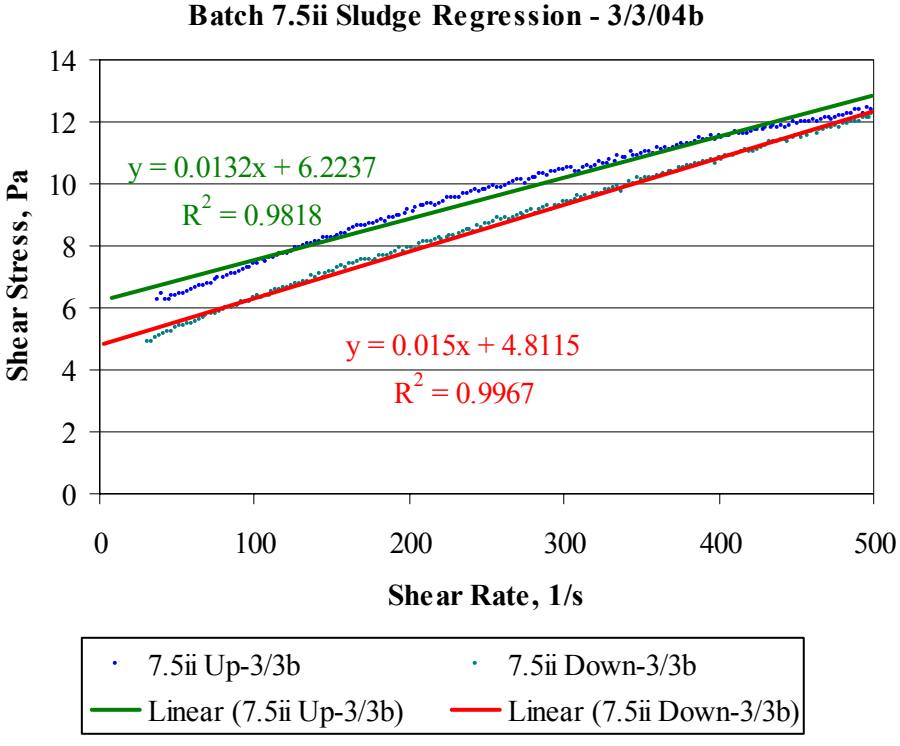

Figure E- 18. Batch 7.5ii Sludge Regression – 3/3/04b

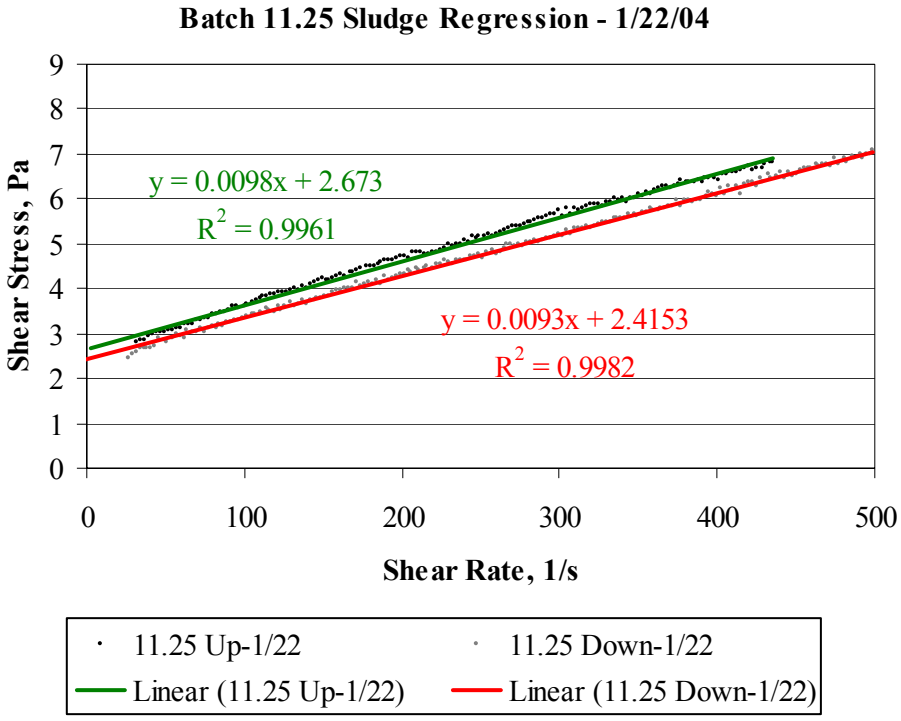

Figure E- 19. Batch 11.25 Sludge Regression – 1/22/04

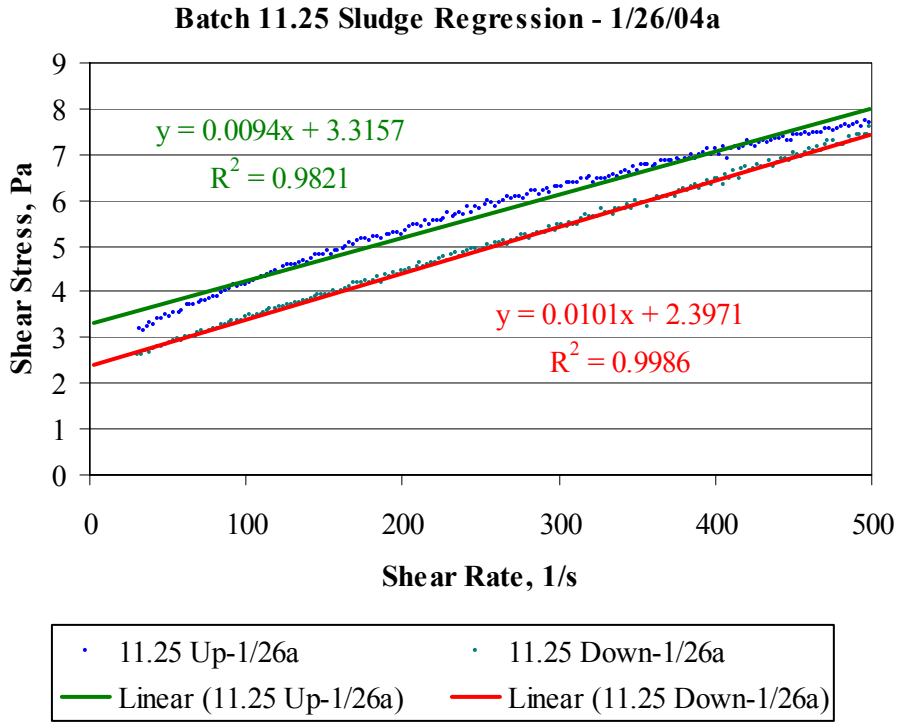

Figure E- 20. Batch 11.25 Sludge Regression – 1/26/04a

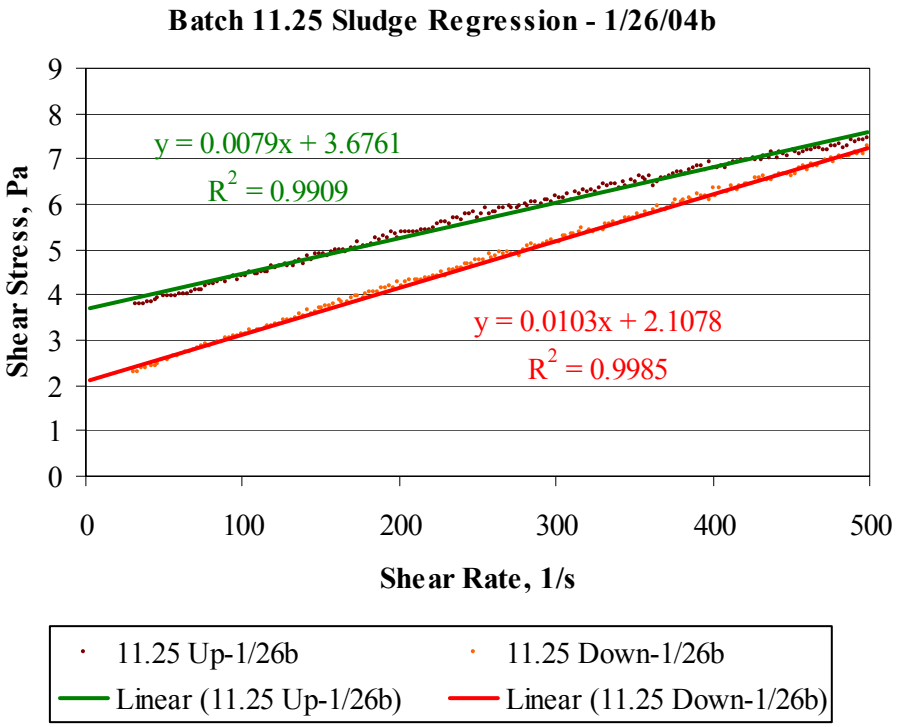

Figure E- 21. Batch 11.25 Sludge Regression – 1/26/04b

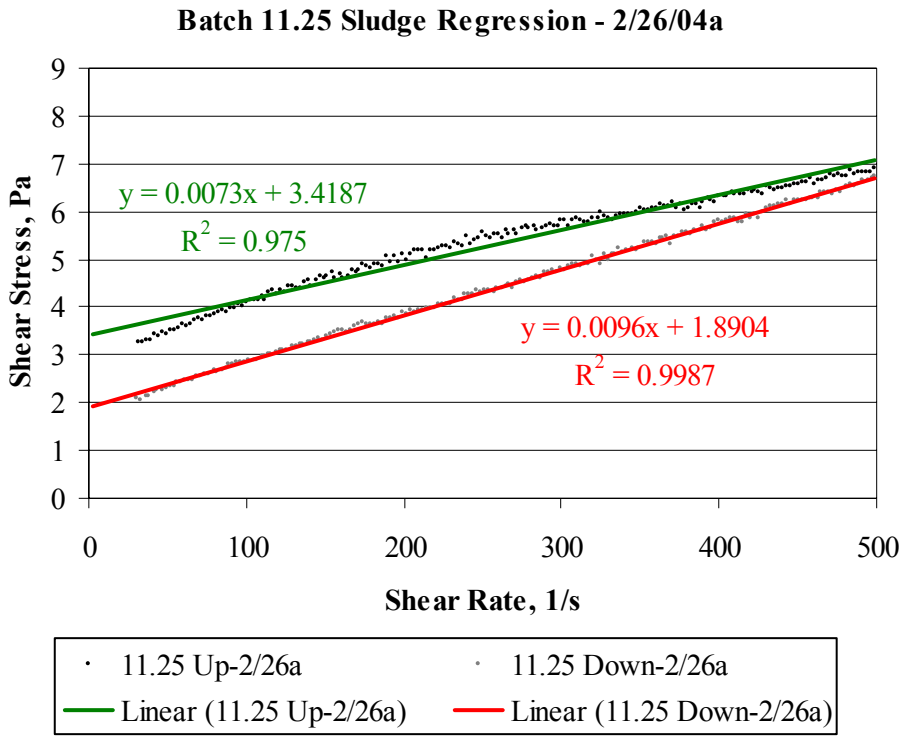

Figure E- 22. Batch 11.25 Sludge Regression – 2/26/04a

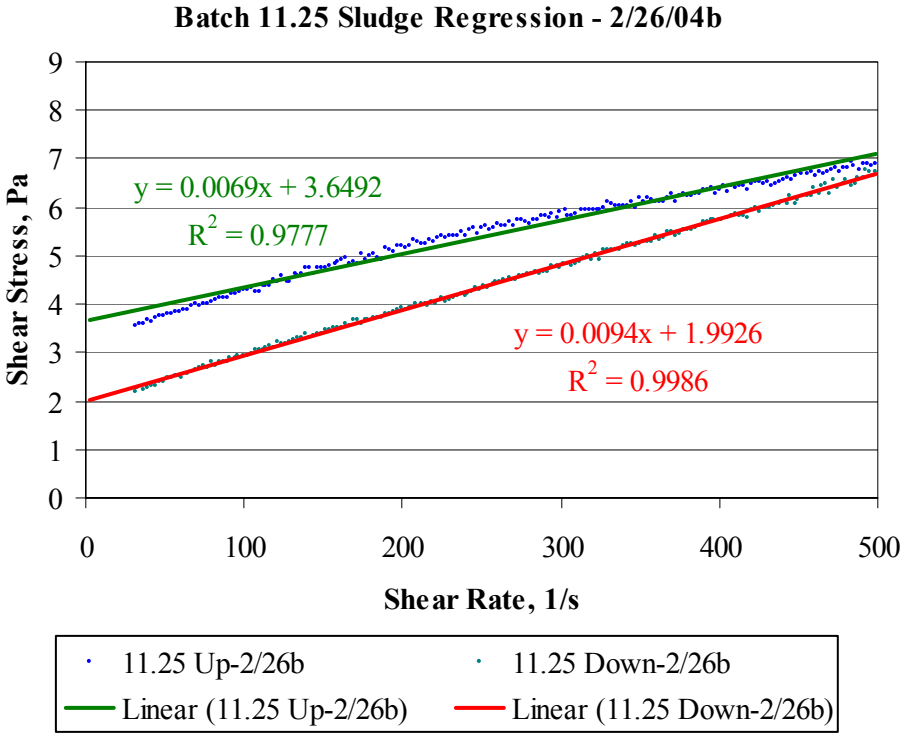

Figure E- 23. Batch 11.25 Sludge Regression – 2/26/04b

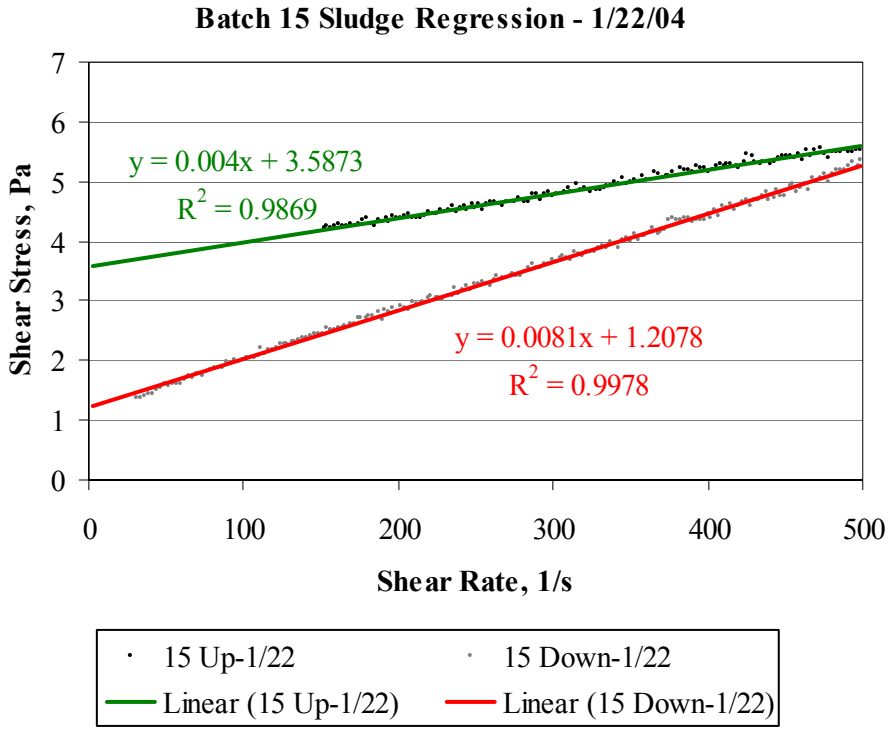

Figure E- 24. Batch 15 Sludge Regression – 1/22/04

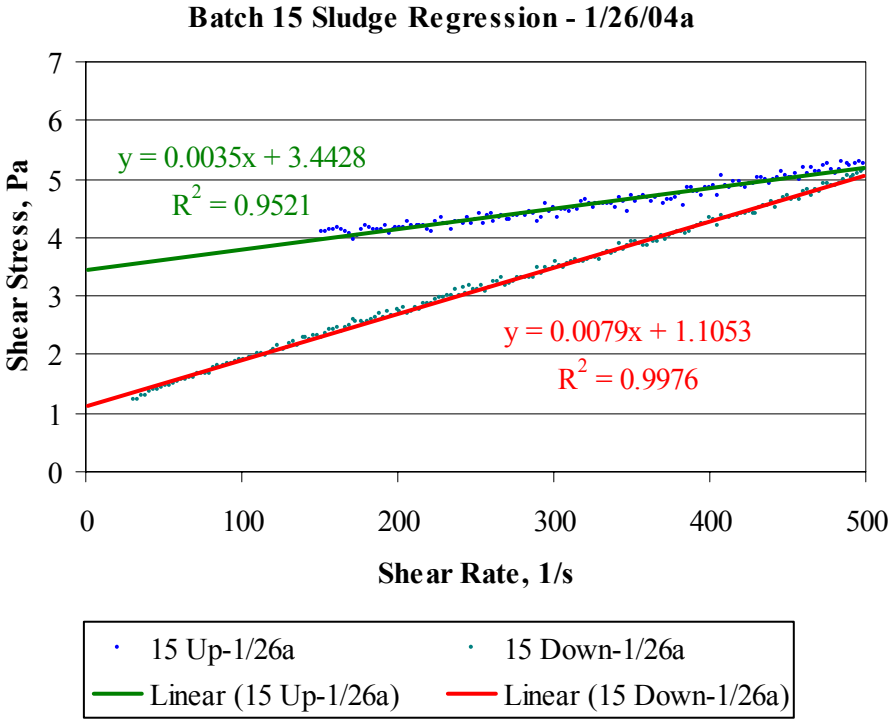

Figure E- 25. Batch 15 Sludge Regression – 1/26/04a

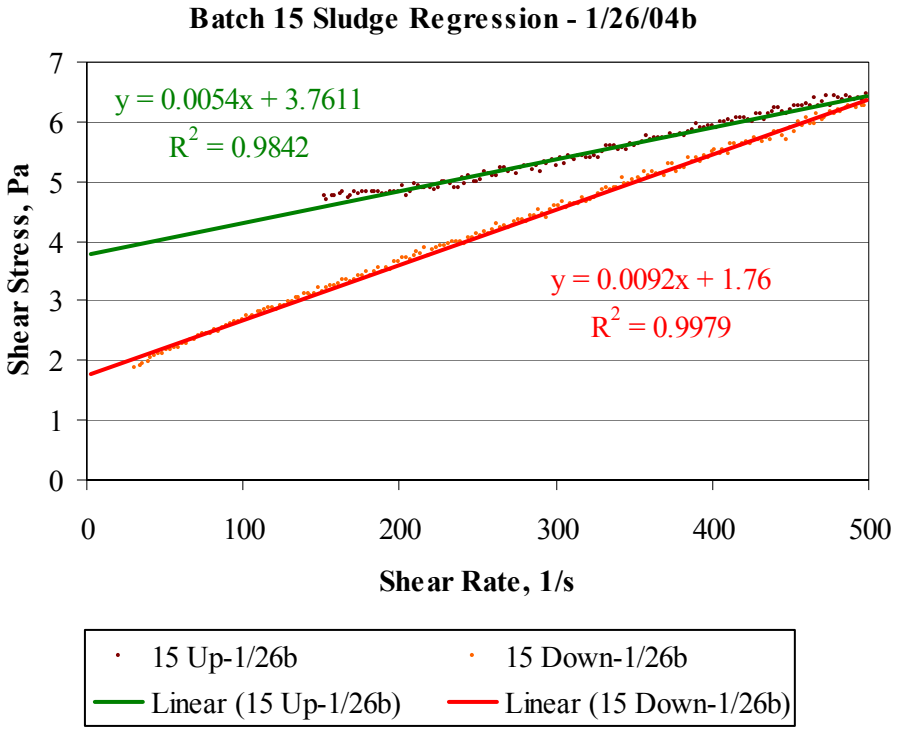

Figure E- 26. Batch 15 Sludge Regression – 1/26/04b

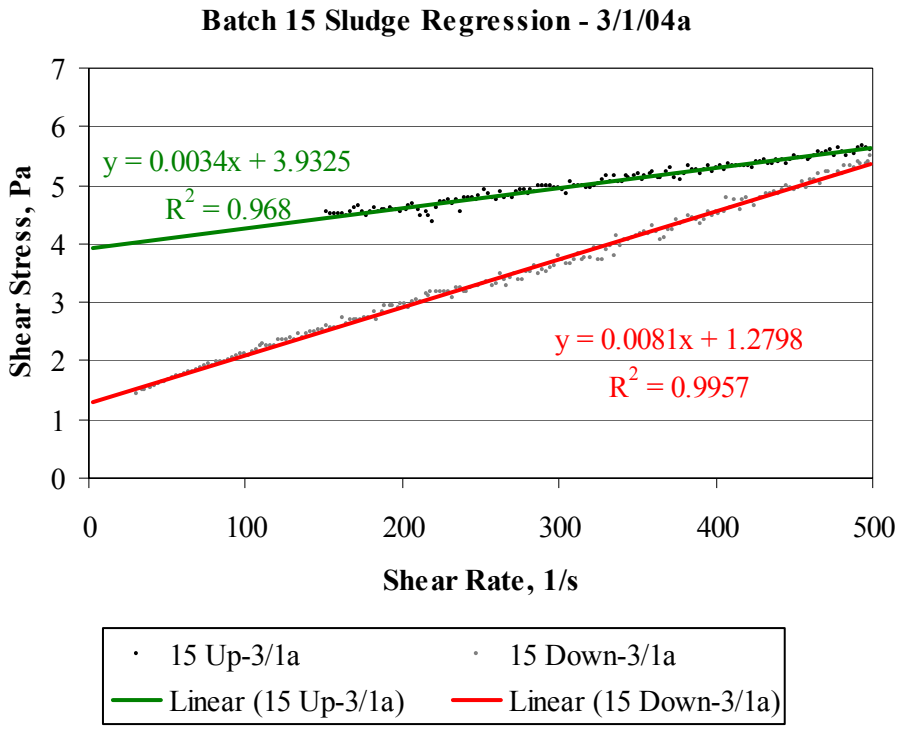

Figure E- 27. Batch 15 Sludge Regression – 3/1/04a

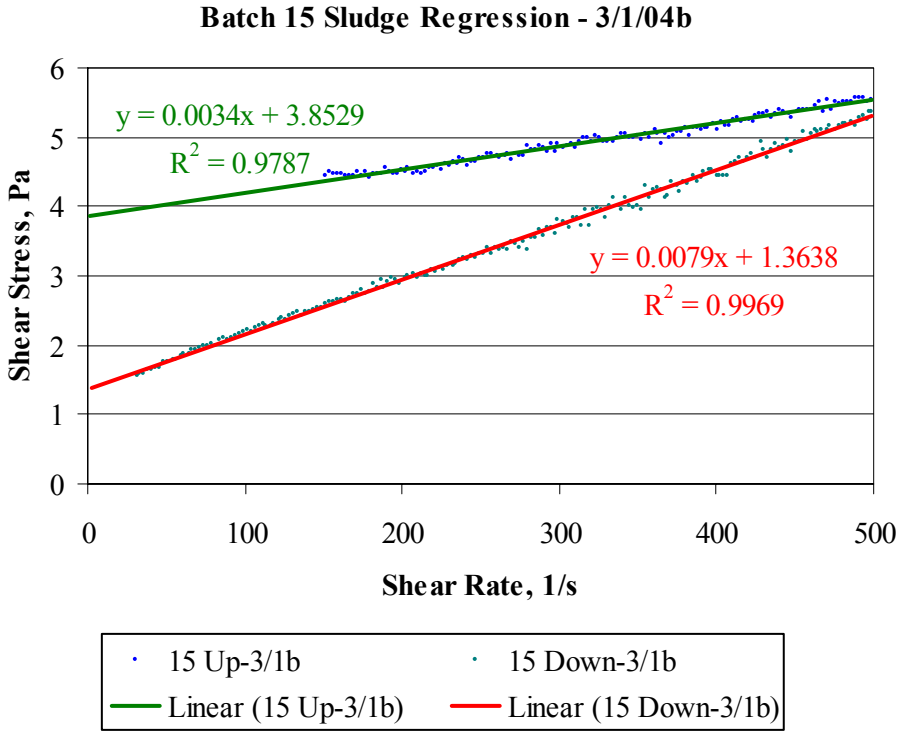

Figure E- 28. Batch 15 Sludge Regression – 3/1/04b

APPENDIX F. SRAT PRODUCT RHEOGRAMS

Key:
Black/gray = initial up/down ramp flow curves
Blue/Teal = replicate up/down ramp flow curves

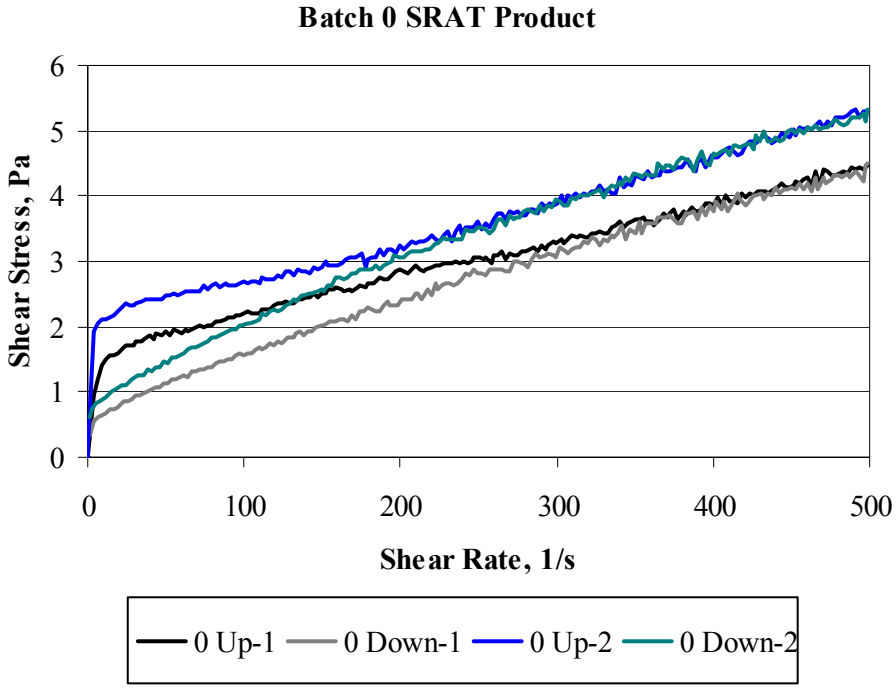

Figure F- 1. Batch 0 SRAT Product Rheology Data

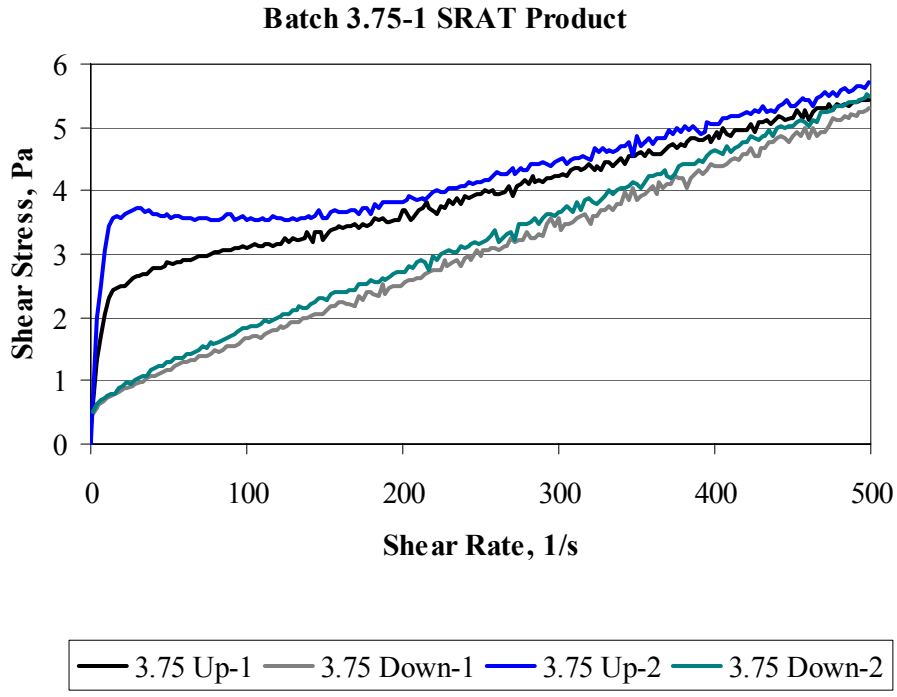

Figure F- 2. Batch 3.75-1 SRAT Product Rheology Data

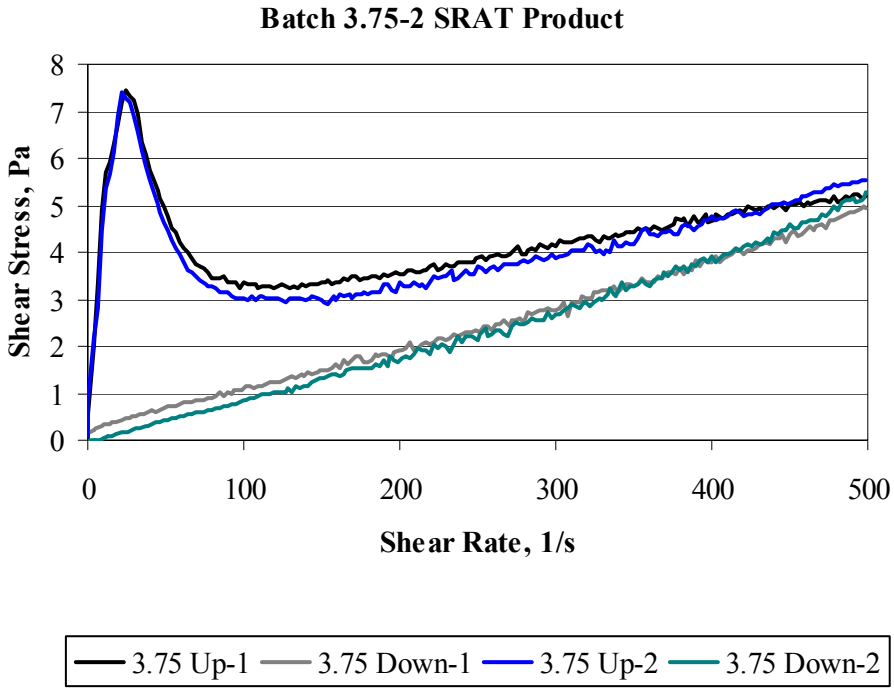

Figure F- 3. Batch 3.75-2 SRAT Product Rheology Data

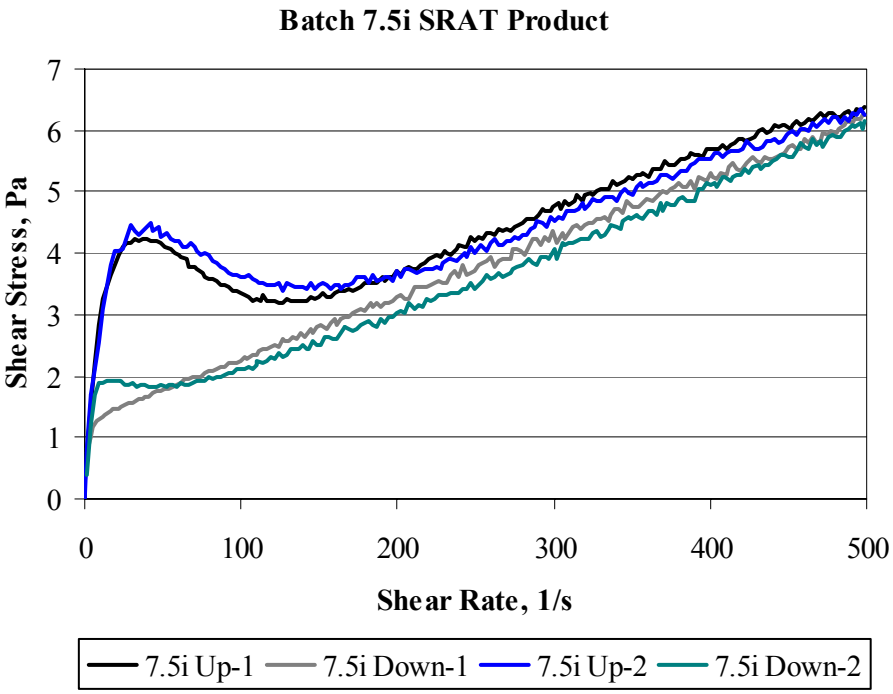

Figure F- 4. Batch 7.5i SRAT Product Rheology Data

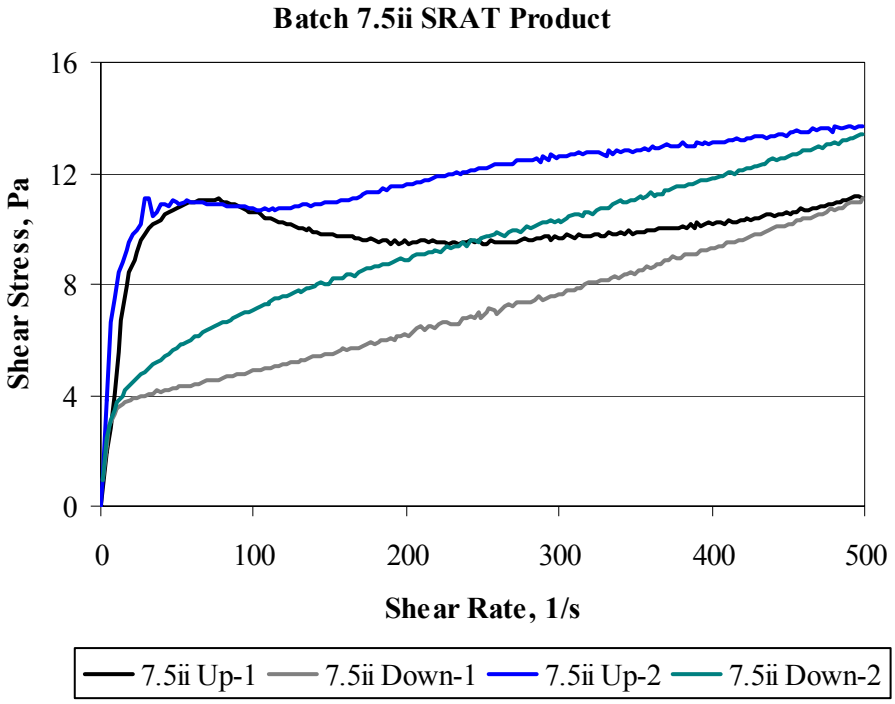

Figure F- 5. Batch 7.5ii SRAT Product Rheology Data

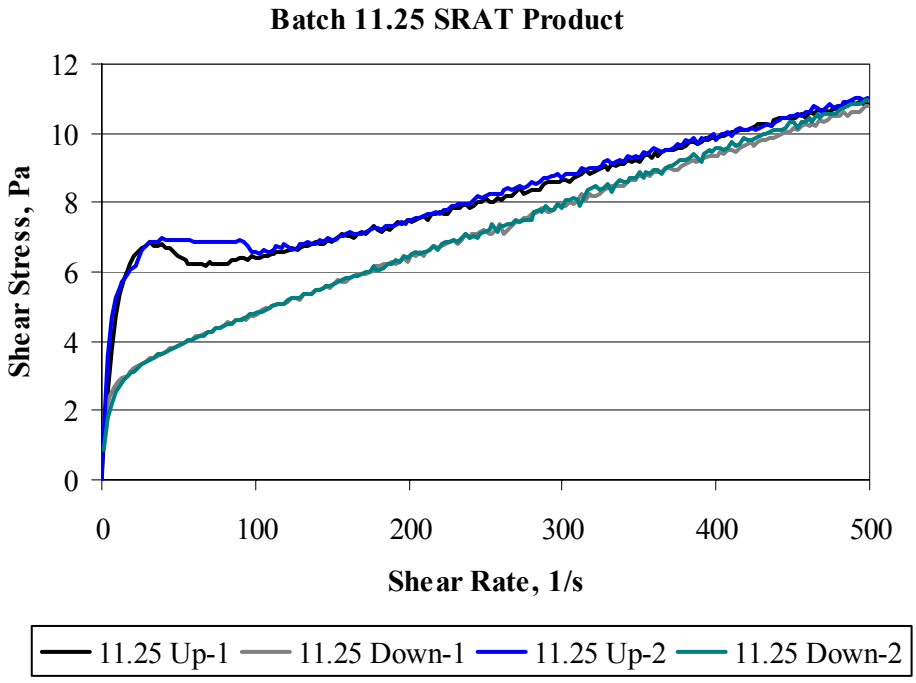

Figure F- 6. Batch 11.25 SRAT Product Rheology Data

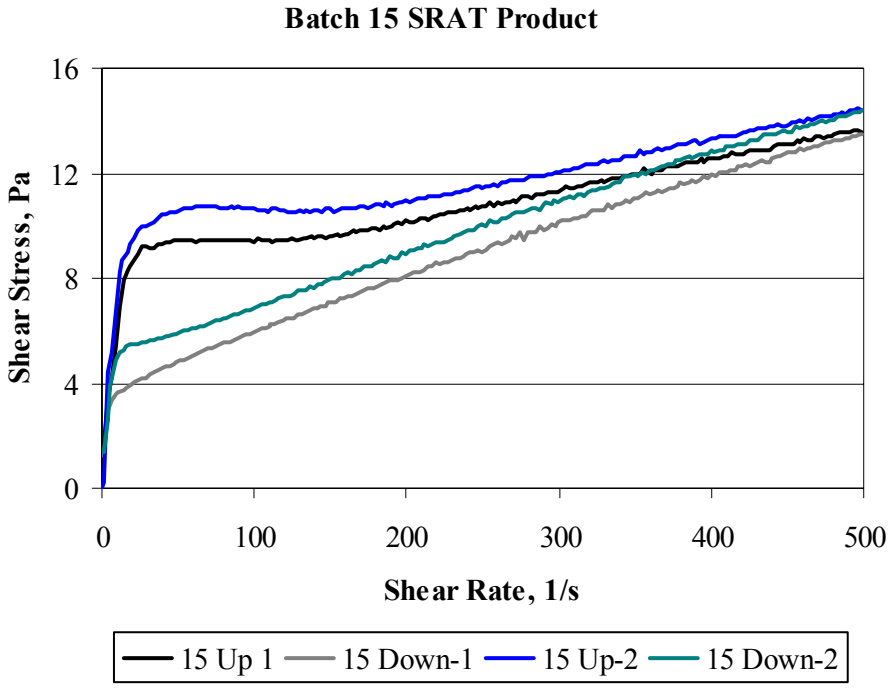

Figure F- 7. Batch 15 SRAT Product Rheology Data

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APPENDIX G. SRAT PRODUCT REGRESSION ANALYSES

Key:
Green = up curve regressions
Red = down curve regressions

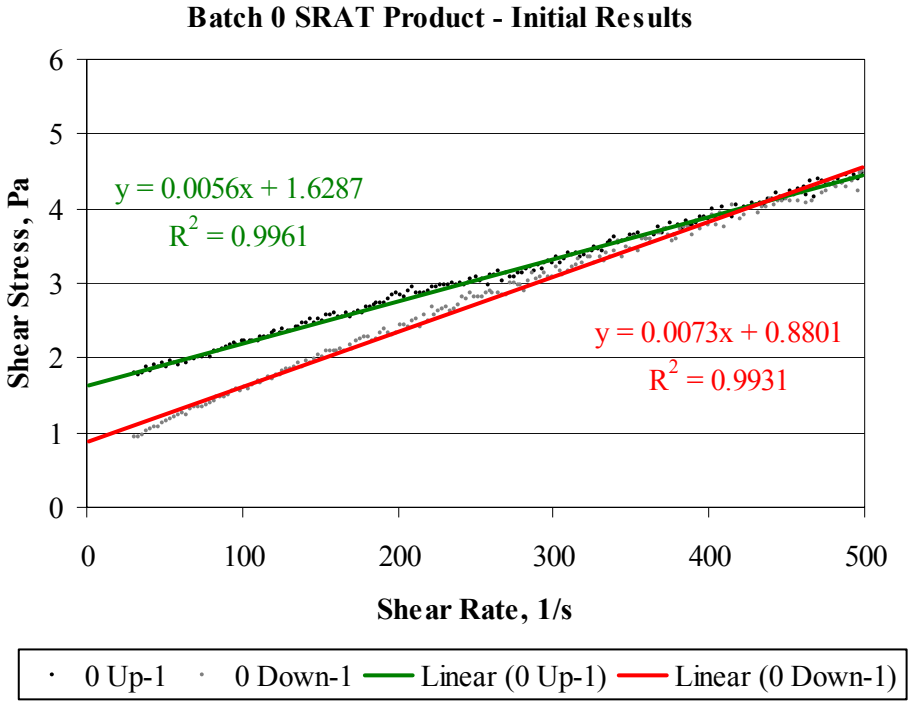

Figure G- 1. Batch 0 SRAT Product Regression – Initial

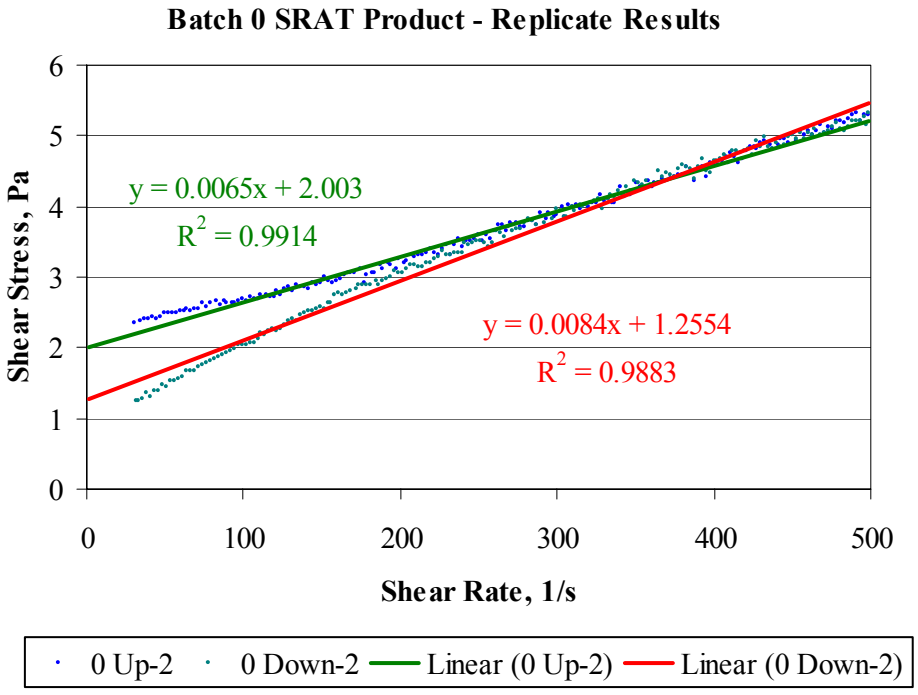

Figure G- 2. Batch 0 SRAT Product Regression – Replicate

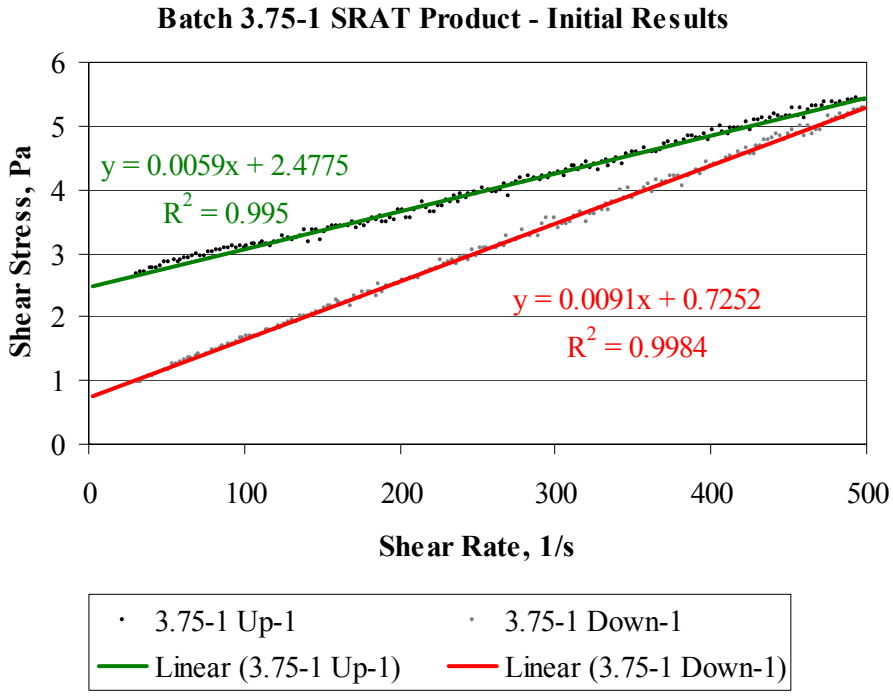

Figure G- 3. Batch 3.75 SRAT 1 Product Regression – Initial

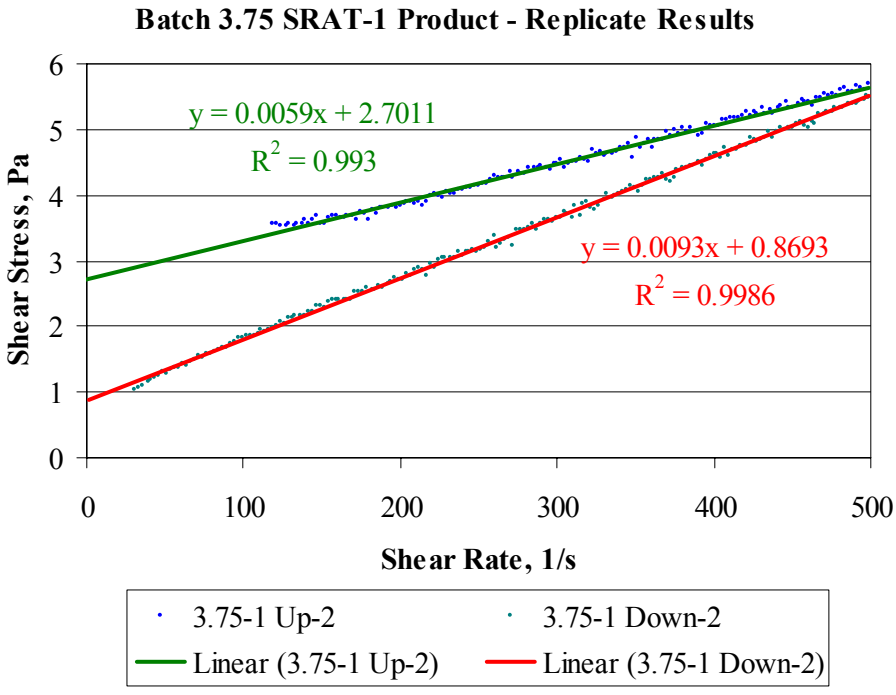

Figure G- 4. Batch 3.75 SRAT 1 Product Regression – Replicate

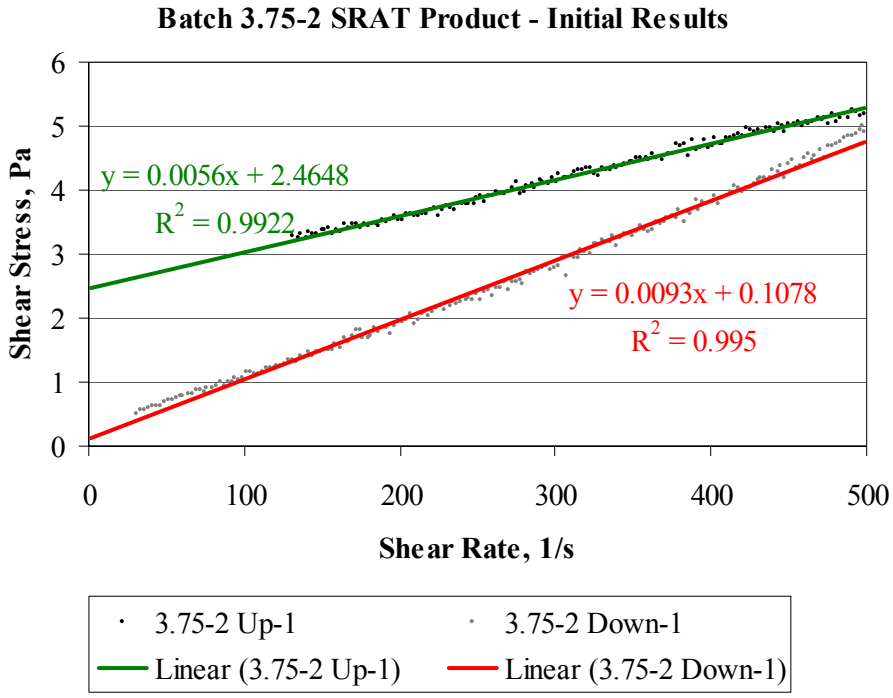

Figure G- 5. Batch 3.75 SRAT 2 Product Regression – Initial

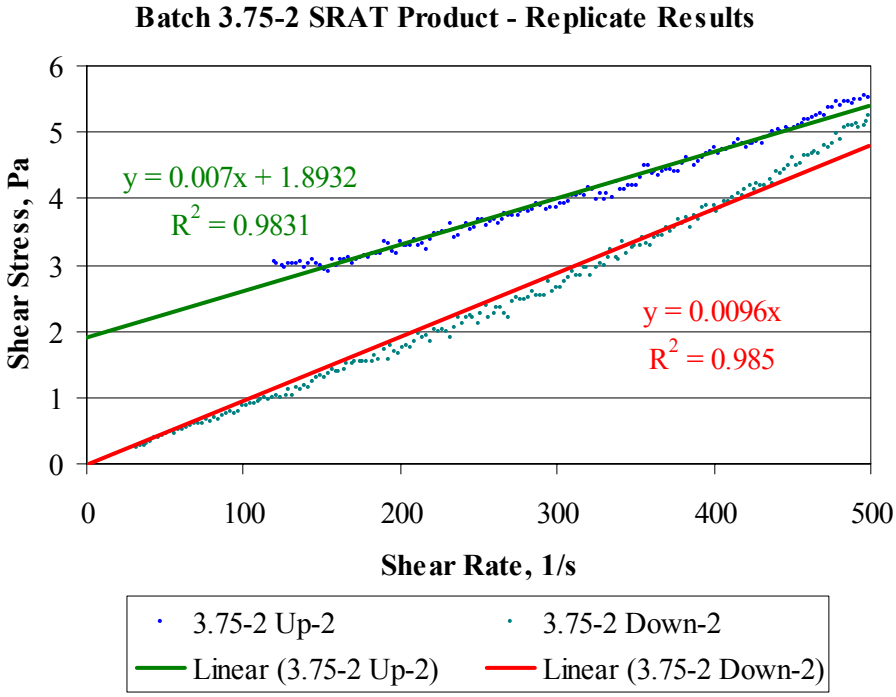

Figure G- 6. Batch 3.75 SRAT 2 Product Regression – Replicate

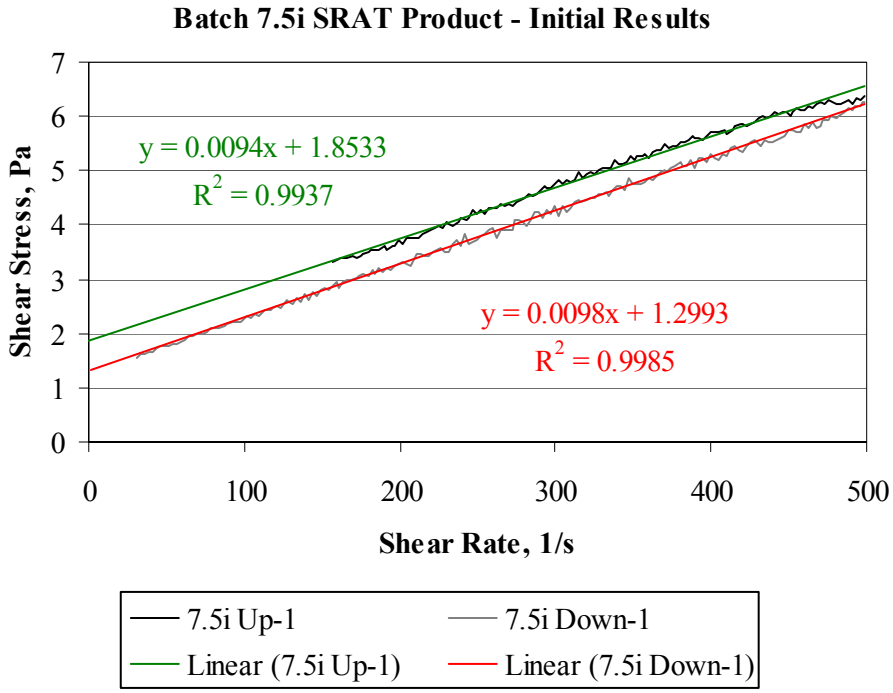

Figure G- 7. Batch 7.5i SRAT Product Regression – Initial

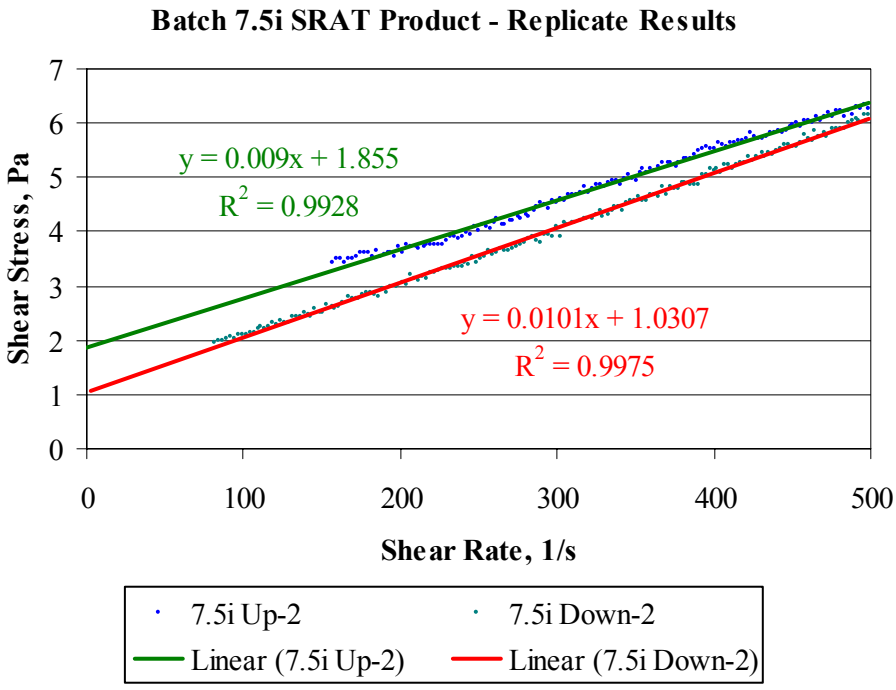

Figure G- 8. Batch 7.5i SRAT Product Regression – Replicate

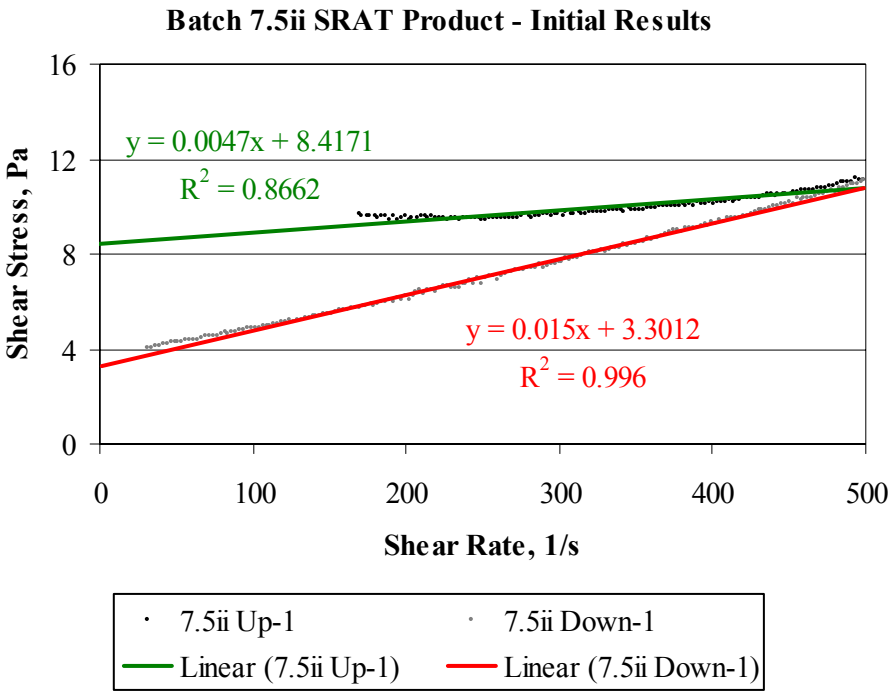

Figure G- 9. Batch 7.5ii SRAT Product Regression – Initial

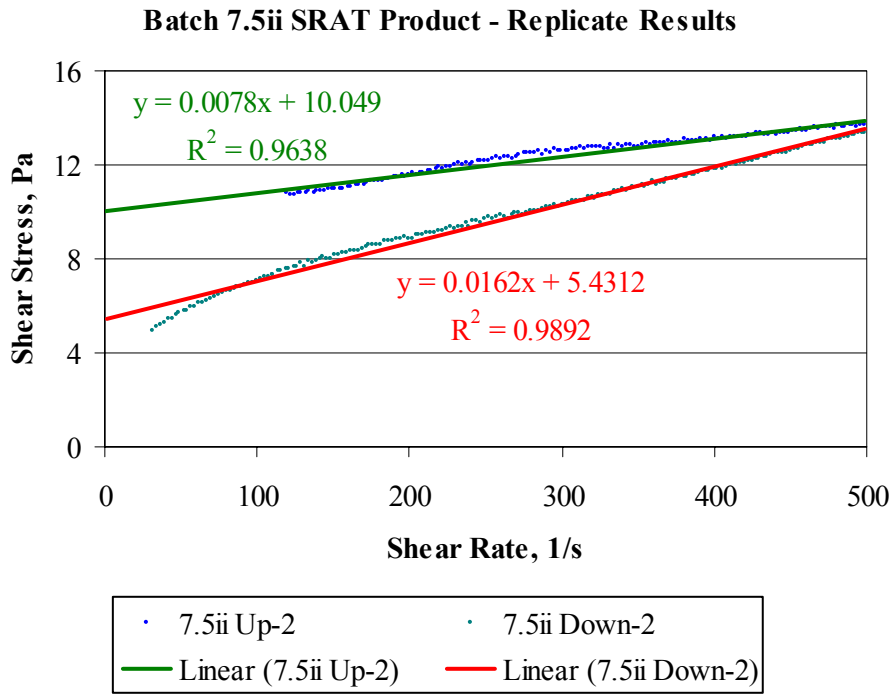

Figure G- 10. Batch 7.5ii SRAT Product Regression – Replicate

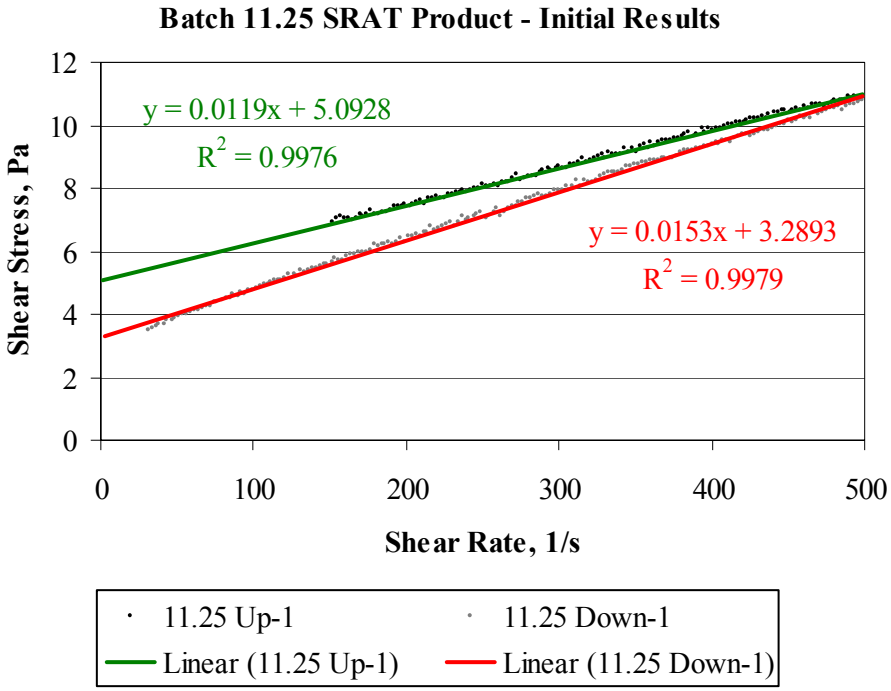

Figure G- 11. Batch 11.25 SRAT Product Regression – Initial

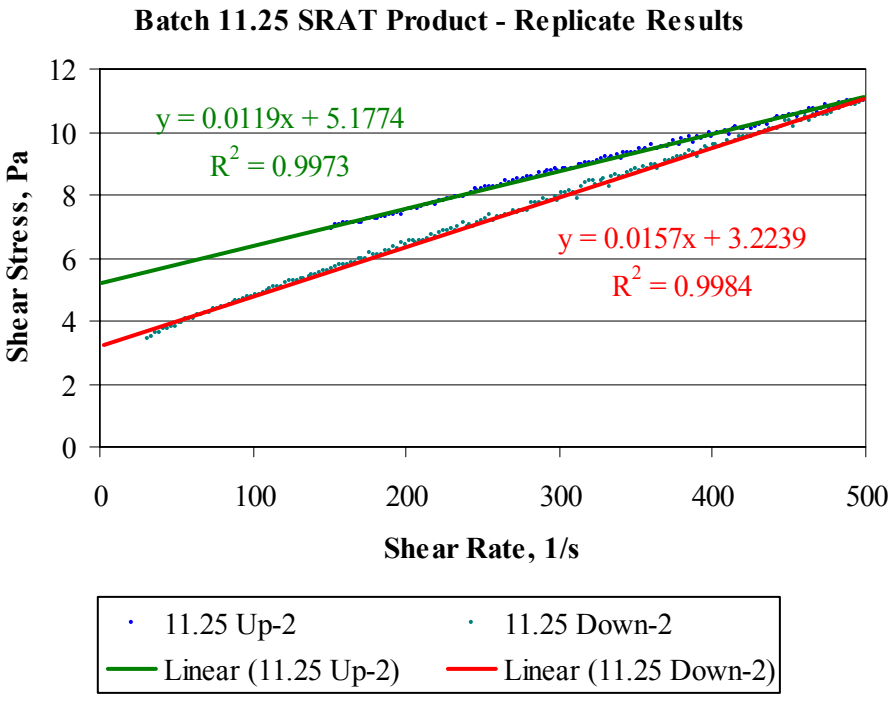

Figure G- 12. Batch 11.25 SRAT Product Regression – Replicate

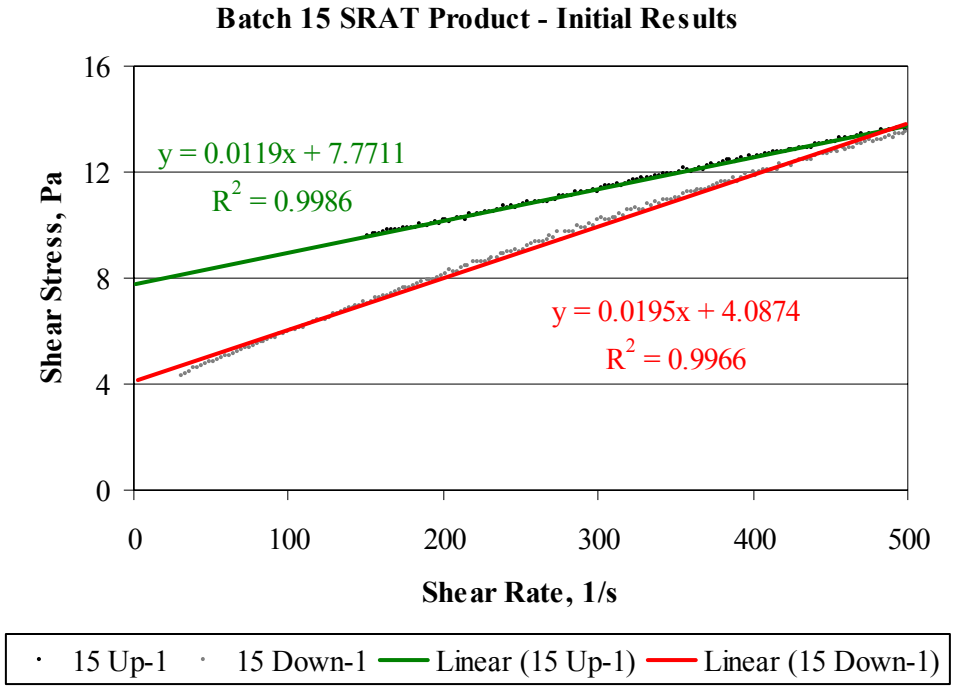

Figure G- 13. Batch 15 SRAT Product Regression – Initial

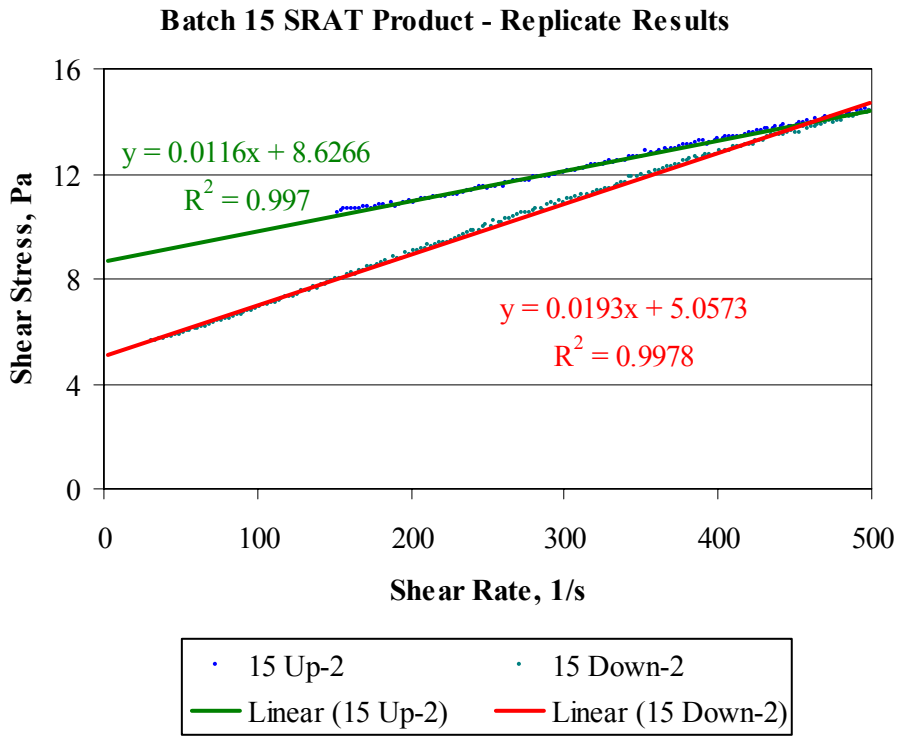

Figure G- 14. Batch 15 SRAT Product Regression – Replicate