Rheology of MonoSodium Titanate (MST) and Modified MST (mMST) Mixtures Relevant to the Salt Waste Processing Facility

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Savannah River National Laboratory™

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EXECUTIVE SUMMARY

The Savannah River National Laboratory performed measurements of the rheology of suspensions and settled layers of treated material applicable to the Savannah River Site Salt Waste Processing Facility. Suspended solids mixtures included monosodium titanate (MST) or modified MST (mMST) at various solid concentrations and soluble ion concentrations with and without the inclusion of kaolin clay or simulated sludge. Layers of settled solids were MST/sludge or mMST/sludge mixtures, either with or without sorbed strontium, over a range of initial solids concentrations, soluble ion concentrations, and settling times.

The following results were noted for the rheology of suspended solids.

- Slurries with MST, with and without sludge, exhibited a slight yield stress when undissolved solids (UDS) content was 3 wt % and above.
- Increasing UDS led to higher yield stress slurries.
- Mixtures with mMST up to 7.2 wt % UDS all fit the Newtonian viscosity model.

The following results were noted for the rheology of beds of settled solids.

- The MST/sludge layers had shear strengths of 8 to 21 Pa, with a single outlier of 49 Pa, and the mMST/sludge layers had shear strengths of 27 to 192 Pa.
- The type of MST used (MST or mMST) had the greatest correlation with settled layer shear strength.
- Using MST or mMST with sorbed strontium led to similar or slightly reduced shear strengths when compared to the analogous non-loaded material.
- The time allowed for settling the bed was statistically significant, in addition to the type of MST and the inclusion of sorbed strontium.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technical Laboratory
CSSX	Caustic-Side Solvent Extraction
DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
M&TE	Measurement and Test Equipment
mMST	Modified Monosodium Titanate
MST	Monosodium Titanate
NIST	National Institute of Standards and Technology
PSAL	Process Science Analytical Laboratory
PSD	Particle Size Distribution
PTC	Parsons Technology Center
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TT&QAP	Task Technical and Quality Assurance Plan
UDS	Undissolved Solids
WAC	Waste Acceptance Criteria

1.0 Introduction

Parsons Corporation is designing and constructing the Salt Waste Processing Facility (SWPF) to treat radioactive liquid salt solution waste at the Savannah River Site (SRS). The SWPF receives liquid radioactive salt solution waste from the SRS Tank Farm potentially containing minor quantities of entrained waste sludge solids. The process adds monosodium titanate (MST) to the waste to sorb strontium and select actinides. The strontium and actinide loaded MST and potentially entrained sludge are removed by a crossflow filter, concentrated, and washed prior to transport to the Defense Waste Processing Facility (DWPF) for vitrification. The filtrate is processed through a solvent extraction system to remove cesium. The cesium-rich strip effluent stream from solvent extraction is transferred to the DWPF for vitrification, and the decontaminated salt solution receives additional treatment with MST and crossflow filtration as needed to ensure the strontium and actinides meet the Saltstone Waste Acceptance Criteria (WAC). Following the final MST treatment, the decontaminated salt solution is transferred to the Saltstone Production Facility for disposal as grout.

SRNL has developed a modified monosodium titanate (mMST) that has faster sorption kinetics for strontium and plutonium than MST. Prior to use in the SWPF, the rheology of mMST and mMST plus sludge slurries must be understood. Parsons requested Savannah River National Laboratory (SRNL) to measure the rheology of samples containing MST, mMST, and simulated sludge.[1] The responsibilities, prerequisites, work activities, work controls and deliverables required to perform this work were established in a Task Technical and Quality Assurance Plan (TT&QAP).[2]

The objective of this task is to measure the rheology of samples containing MST, MST plus simulated sludge, mMST, and mMST plus simulated sludge. Specifically, individual tasks include the following.

- Prepare samples containing MST, mMST, MST plus simulated sludge, and mMST plus simulated sludge. A subset of testing uses MST and mMST with sorbed strontium.

- For mixtures of suspended solids containing MST, mMST, or either combined with simulated sludge, measure the yield stress, plastic viscosity, undissolved solids concentration, dissolved solids concentration, supernate density, bulk density, and soluble sodium concentration of the slurry samples prepared.

- Measure the shear strength of the solids after settling for 10, 30, and 53 days. The 30 and 53 day duration match those in concurrent[3] and prior[4] Parsons suspension testing for slurries using Air Pulse Agitators.

The term shear strength is sometimes referred to as a vane yield stress, settled solids yield stress, or vane shear strength. The term yield stress is sometimes referred to as a flow curve yield stress. The term plastic viscosity is sometimes referred to as consistency, flow curve consistency, or infinite viscosity.

2.0 Experimental Procedure

2.1 Testing Overview

There were two main types of testing. The first addressed the rheology of suspended mixtures of MST or mMST with and without simulated sludge. The second addressed the rheology of settled beds of solids containing simulated sludge and MST or mMST. For the rheology of suspended mixtures, materials were prepared as described in Section 2.2, and the rheological measurements were made in a coaxial cylinder rheometer as described in Section 2.4. For the rheology of beds of settled solids, mixtures were prepared as described in Section 2.2, beds of settled solids were formed as described in Section 2.3, and rheological vane measurements of the beds were performed in a vane rheometer as described in Section 2.4

2.2 Preparation of Mixtures

The following materials were obtained from Parsons Technology Center in Aiken, SC.

- MST [from Blue Grass Chemical Specialties]
- mMST [from Harrell Industry, Lot 060211]
- Sludge simulant [from Harrell Industries]
- Caustic Side Solvent Extraction (CSSX) simulant (salt supernate, nominally 5.6 M Na^+) [from Optima Chemical], prepared per Parson's specification: SPC-ME-6204-0007. Simulant in material used in the Parson's CSSX test program and is reconstituted to bring up to specification values.
- Kaolin [Barden Clay, from Kentucky-Tennessee Clay Company]

Kaolin was included in testing due to use in prior Parsons Air Pulse Agitator tests as a surrogate for sludge.[4] The materials were brought to the SRNL facilities at the Aiken County Technology Laboratory (ACTL) for use in this testing. Materials were split into containers that were more easily handled in the laboratory, and the solids and salt contents of the various materials were determined.

In preparation of test mixtures, all mixtures of MST to sludge or kaolin are at a ratio of 1:1.5 on a solids basis. This is based on the planned addition of 0.4 g/L of MST to a batch of salt feed that may contain up to 0.6 g/L of sludge solids. All mixtures of mMST to sludge or kaolin are at a ratio of 1:3 on a solids basis. This is based on the planned addition of 0.2 g/L of mMST to a batch of salt feed that may contain up to 0.6 g/L of sludge solids. The two systems are considered to be equivalent in terms of sorption capacity.

Table 1 contains the matrix for the target mixtures prepared for the suspended solids rheology testing. The suspended solids rheology tests span a range of undissolved solids (UDS) concentrations and supernatant liquid sodium concentrations that exceed those expected in operations for SWPF. The UDS includes both the MST or mMST solids and the sludge or kaolin solids (if included in the test). UDS does not include soluble solids in the MST, mMST, or sludge feeds. Mixtures were prepared that represent the 14 apparent conditions in Table 1 using MST solids or mMST solids, resulting in 28 different test mixtures. Test samples were prepared in duplicate, resulting in a total of 56 test samples.

Table 1: Test matrix for suspended solids rheology of mixtures containing MST or mMST

Non-MST Solids Type	UDS	Supernatant Liquid
kaolin	7 wt %	5.6 M Na^+
sludge	7 wt %	0.5 and 5.6 M Na^+
	5 wt %	0.5, 3.3 and 5.6 M Na^+
	2 wt %	0.5 and 5.6 M Na^+
	0.08 wt %	5.6 M Na^+
none	3 wt %	0.5 and 5.6 M Na^+
	1 wt %	0.5 and 5.6 M Na^+
	0.04 wt %	5.6 M Na^+

Table 2 contains the matrix of target mixtures for creating layers of solids for shear strength testing. The conditions were selected through discussions between Parsons, DOE, DNFSB Staff members, and SRNL to provide a balance in augmenting prior testing (i.e., provide continuity with prior tests) and adequately covering the range of operations for SWPF. The variables in testing included the type of MST used (MST or mMST), the use of MST material with or without sorbed strontium, the settling time used for formation of settled layers, the original mixture UDS content, and the liquid phase sodium content. The matrix included a total of 38 test conditions. Eight test conditions were performed in duplicate (i.e., the 30 day settling time tests with 7 wt % UDS and with 0.5 or 5.6 M Na^+), for a total of 46 tests. Test mixture volumes were designed to provide the desired level of settled solids for the vane rheology measurement per the details described in Section 2.3. Per the TT&QAP, all of the samples contained simulated sludge in addition to MST or mMST solids. Examination of the original request from Parsons reveals that the tests using lower solids content to form settled layers (i.e., 3 wt %) should have contained no simulated sludge. However, all settled solids samples contained simulated sludge. Several additional tests were performed slightly outside of the test matrix of Table 2, and the details are provided in the results section.

Table 2: Test matrix for settled solids rheology of layers containing sludge and MST or mMST

Sr Content	MST Type	Settling Time	UDS	Supernatant Liquid
with and without sorbed Sr	MST and mMST	10 and 30 days	7 and 3 wt %	0.5 and 5.6 M Na^+
	MST	10, 30 and 53 days	7 wt %	3.3 M Na^+

A portion of the settling column tests used MST or mMST materials that sorbed strontium. The Sr was sorbed onto the MST and mMST to their theoretical maximum uptake for the pH at which the loading was performed. Some of the sorbents were contacted with strontium nitrate solution containing strontium calculated to equal 14 grams of strontium per 100 grams of MST or mMST. The 14 wt % sorption was selected to match the maximum strontium sorption measured during SRNL testing with MST or mMST.[5,6] This high level of sorbed strontium used a level greater than the level of sorbed strontium and actinides achieved in actual processing in an effort to make up for not having actinides.

The strontium solution was added to the MST or mMST in 2 L bottles and the contents diluted with water to aid in stirring. The system was allowed to contact for 7 days, after which solution analysis by Inductively Coupled Plasma—Emission Spectroscopy (ICP-ES) showed that 12 wt % and 10 wt % Sr sorption were obtained on the MST and mMST, respectively. Additional strontium was added to all containers and allowed to stir for another 7 days. Table 3 indicates the final strontium content achieved on MST and mMST, based on solution analysis by ICP-ES.

Table 3: Strontium content of MST and mMST material (nominally 2% or less relative standard deviation (RSD))

	MST	mMST
Sr (wt %)	13.18 to 13.22	13.52

The test mixtures for both the undissolved suspended solids and the settled layer rheology measurements were to use only the four materials provided by Parsons, plus water if necessary. This introduced difficulty in attaining the target high salt condition of [Na^+] = 5.6 M. The CSSX supernatant had a salt concentration of approximately 5.6 M. However, the three slurries each had significant liquid interstitial to the solid particles, and those liquids had salt concentrations considerably less than 5.6 M. Therefore, to approach the high salt condition, a portion of the MST, mMST, and sludge simulant were adjusted prior to use. Each slurry material was contacted multiple times with CSSX supernatant simulant, the solids were settled, and the excess liquid was decanted. This process essentially “washed” concentrated salt solution into the interstitial volume of the solids. At the end of this process, the slurries used for the high salt mixtures each had soluble sodium concentrations around 3 to 4 M. The high salt mixtures slurries made from these adjusted materials typically had sodium concentrations of 5 M and above. After this adjustment with CSSX simulant, the mMST began to release gas slowly – as anticipated from prior literature for mMST[7] – and the MST and sludge appeared stable.

2.3 Settling Equipment

The vane rheology tests outlined in Table 2 were performed on settled layers of solids. To accommodate vane measurement, the settled layer needed to have an appropriate geometry for the vane to be used. For the FM22 vane described in Section 2.4, the layer of settled solids needed to be a minimum of 2 inches tall in a cylindrical cup of at least 1.75-inch diameter (a 2.44 inch internal diameter cup was used here).

To form layers of settled solids that were nominally 2.5 inches tall, settling columns needed to be significantly taller than 2.5 inches to accommodate the dilute mixtures outlined in Table 2.

Cylindrical columns were chosen over other cross-sections to minimize sample volume. Thus, columns were used that were approximately 20 inches tall. In the rheometer, however, the shaft of the vane is only a few inches long. Thus, columns were developed that were tall to allow for formation of adequate layers and also separable to allow the upper section to be removed and expose the settled bed for the vane measurement.

Figure 1 is a photograph of a few of the settling columns in a rack on the laboratory bench. The complete columns are nominally 20 inches tall and 2.44 inches in diameter. The bottom three inch "cup" portions of the settling columns were separable from the upper 17 inch "column" portions. There was an O-ring to prevent leakage of the column at the separation point and a piece of tape to insure that the column did not separate prematurely when lifted out of the rack. Glued on caps at the very bottom of the columns provided a water-tight seal. Removable caps were placed on the top of the columns to minimize evaporative losses of supernate during the lengthy settling periods.

Figure 1: Settling column assemblies loaded with test mixtures

Columns were loaded with material so that the target level of settled solids ultimately formed would be 2 to 2.5 inches in depth (an approximately 150 to 200 mL layer of settled solids). Tighter control of the settled volume was not possible, since the packing behavior of the solids during settling as a function of time was not well characterized. The overall sample volume was further limited by the maximum volume of material that could fit in the complete column. The maximum volume was approximately 1.5 L. The approximate column loading to produce a 2 to

2.5 inch settled layer was determined experimentally. In general, for a feed of 7 wt % UDS, 410 mL was used for mixtures containing 1:1.5 MST:sludge, and 765 mL was used for mixtures containing 1:3 mMST:sludge. Empirically, mMST/sludge mixtures settled more compactly than MST/sludge mixtures.

Settling was performed at room temperature on the laboratory bench. At the end of the required settling time, the supernatant liquid was carefully pumped or decanted from the upper portion of the column to below the 3-inch column separation point. A small amount of supernatant was left on the top of the layer of settled solids to prevent drying. The samples were carefully transported to the rheometer in the adjacent laboratory for vane measurements. Figure 2 contains photographs of typical settled layers in the cup portions of the settling columns. Note that rulers attached to the cup sections have 0.1 inch gradations.

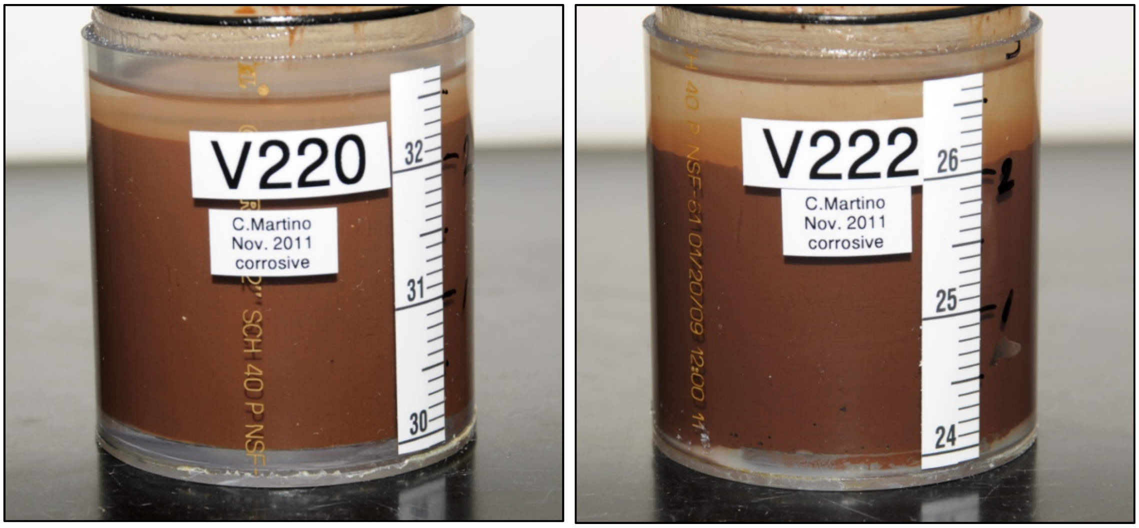

Figure 2: Typical sample cups for settled layers of MST/Sludge (left) and mMST/Sludge (right)

2.4 Rheology Measurements

Rheological measurements of shear strengths and flow curves were performed using a Haake RheoStress 600 rheometer at ACTL.

The flow curve measurements provide rheological properties of mixed slurries and are applicable to the transport of slurries between facilities. Flow curve measurements were made using previously documented methods and the standard DWPF slurry sample protocols.[2] The Z41 sensor (small gap) was used, since particle sizes were small enough that bridging of the annular gap was not an issue. Functional performance of the RS600 was checked daily using National Institute of Standards and Technology (NIST) traceable viscosity standards. Flow curve measurement temperature of 25 ± 0.5 ºC was controlled using an integrated water jacket surrounding the RS600 measurement cup that was supplied by an external constant temperature bath. External bath temperature was controlled by the RS600 software from a thermocouple inside the water jacket.

Shear strength was measured with the FL22 vane sensor, shown in Figure 3. The four vane section has an effective diameter in rotation of 22 mm; the vane was lowered to a nominal vane position where the top of the vane was 15.5 mm into the settled solids and the bottom of the vane was 31 mm into the settled solids. In most samples, the bottom of the vane sensor measured >20 mm above the bottom of the settled solid layer (bottom of the sample cup).

Figure 3: FL22 vane sensor

The shear stress, τ, is calculated from the torque by τ = torque/K, where

$$K = \left[\frac{\pi D^3}{2}\right]\left[{}^{H}\!/_{D} + 1/3\right] \quad , \qquad [1]$$

and where D is the vane diameter and H is the vane height. The torque has units of N·m, K has units of m^3, and tau has units of $N{\cdot}m^2$, which are Pascals.

The positioned vane was rotated at 0.30 revolutions per minute for exactly 90 seconds, or 45% of a full single revolution. Solids in the spaces between the four vanes are forced to move relative to the solids above, below, and further out from the tips of the vanes. The friction between the moving and stationary particles creates torque, which is recorded by the rheometer. The maximum torque is typically observed in the first 15 seconds. This value is combined with the effective shearing area of the vanes to calculate the shear strength of the settled solids in Pascals (force/unit area). The conversion from torque to stress for the FL22 is accomplished by multiplying the torque by an A-factor of 56,370 Pa/Nm. For example, a torque of 1,000 µNm gives a stress of 56.37 Pa. Vane measurements were taken at ambient lab temperatures, nominally 22 to 24 °C.

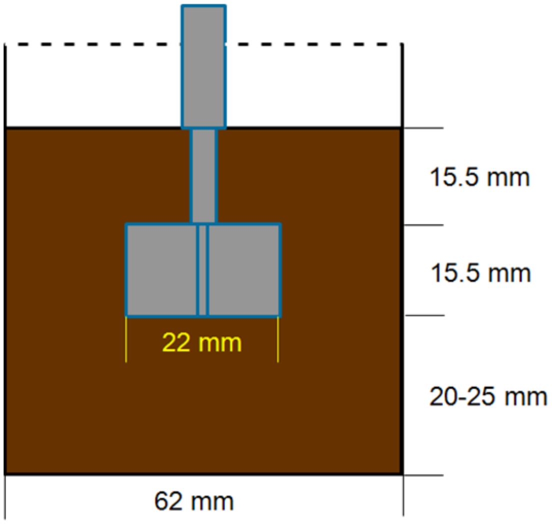

Figure 4: Illustration of FL22 vane measurement sample geometry

A vane measurement disturbs the settled solids near the vane. The measurement protocol included lowering the vane 15-20 mm further into the sample cup and obtaining a second shear strength measurement after completing the nominal measurement. In the shallow 50-55 mm settled layers formed, however, the deeper measurement was likely influenced by either the initial measurement region or the bottom wall of the cup. The deeper measurement was primarily qualitative, and it was intended to detect the presence of unusually compacted or lumpy material below the zone of the nominal vane measurement. A subset of the matrix samples was prepared in duplicate so that quantitative values of the shear strength could be obtained at two different depths without the presence of previously disturbed solids or proximity to the bottom wall being issues.

The settled solid layer and cup were photographed prior to the vane measurement during the early tests. Unusual appearance was noted and documented in the lab notebook for subsequent comparison to other samples. Typically only 4-7 vane measurements were made per day, so a photo record was necessary to cover the entire test program. The vane sensor was photographed after removal from the sample in most cases. Visual observations were also noted in the laboratory notebook. The photographs created a visual log of the quantity of sample adhering to the vanes. Photographic evidence generally supported unusual vane measurement data, suggesting that a sample had been corrupted by leakage of the interstitial liquid phase or excessive evaporation.

Because the vane had performed nearly half a rotation, the blades came up through the same disturbed region created by the blades on the opposite side when the vane was first immersed into the settled bed. This partially mitigated any tendency of the undisturbed settled solids to scrape off solids sticking onto the vane blades.

2.5 Supporting Analytical Measurements

Several analytical methods were used for physical and chemical characterization of materials to support the rheological measurements. The majority of these methods were made by the Process Science Analytical Laboratory (PSAL) at ACTL. Measurements included total solids and dissolved solids by halogen lamp drying. These measurements permitted the determination of the soluble solids and insoluble solids contents of the slurry by calculation. The slurry density and liquid phase density were measured by a Anton-Parr DMA 4J70 instrument at 25 ºC. Filtrate sodium concentration was measured by inductively coupled plasma –emission spectroscopy (ICP-ES). Additionally, for confirmation of strontium loading onto MST and mMST, the SRNL Analytical Development measured filtrate strontium concentration by ICP-ES. All preparations requiring filtration were performed using 0.45-micron pore size filters.

To validate that the materials were within specifications, the Analytical Laboratory at the Parson's Technology Center (PTC) performed particle size measurements of the MST and mMST batches used for this testing using a Microtrac S3500 Particle Size Analyzer. The particle size measurement results are contained in Appendix A.2. The MST required sonication to disperse conglomerated materials and obtain an accurate particle size determination, while the mMST did not require sonication. The test data also suggests sonication is needed for mixtures that include sludge, presumably due to inter-particle affinity or clumping in the presence of sludge.

3.0 Results and Discussion

3.1 Mixture Rheology

Table 4 contains the rheology results for the sludge slurry mixtures listed in Table 1. The table includes the target values (from Table 1) and analytically measured values for wt % UDS and liquid phase sodium concentration. The rheology results include regressions to the two parameter Bingham plastic model and the Newtonian fluid model. If a Bingham Yield Stress of 0.1 Pa or above was noted, only the Bingham model parameters (yield stress and plastic viscosity) are reported. Where Bingham Yield Stress of below 0.1 Pa was noted, the Bingham model parameters are listed in grey and the Newtonian viscosity is assessed to be the appropriate rheological parameter for use.

For each of the 28 conditions listed in Table 1, duplicate samples were prepared for rheology measurement. Two flow curves were obtained for each of the prepared samples. Thus, the averages and standard deviations reported for the rheology model fits were each based on four measurements.

All slurries with kaolin at 7 wt % UDS exhibited yield stresses. Slurries with MST, both with and without sludge, exhibited slight yield stresses when the total UDS content was 3 wt % and above. All MST and MST/sludge mixtures were near the Newtonian regime, with the Bingham yield stress values being 0.57 Pa and lower. Slurries with mMST all fit the Newtonian model up to 7 wt% UDS. Figure 5, Figure 6, and Figure 7 show example flow curves for various MST and mMST mixtures at the nominal $[Na^+] \approx 5.6$ M condition. As evident from Figure 6, the addition of sludge to MST slurries resulted in lower viscosities than the MST slurries without sludge at the same MST solids content.

Note that kaolin may react with solution components in highly alkaline mixtures such as those used in our rheology tests, potentially leading to dissolution and precipitation of solids. Such interactions were not investigated in this study. These reactions are not expected for MST and mMST.

Table 4: Rheology of suspended solids applicable to SWPF

Insoluble Solids (wt%)			Sodium (M)			Bingham Plastic Equation Fits				Newtonian Fit		
						Yield Stress (Pa)		Viscosity (cP)		Viscosity (cP)		Assesment
target	average	st.dev.	target	average	st.dev.	average	st.dev.	average	st.dev.	average	st.dev.	Newtonian?
1:1.5 MST:Kaolin												
7.0	6.63	0.54	**5.6**	5.18	0.10	**1.20**	0.06	**7.29**	0.14	--	--	no
1:1.5 MST:Sludge												
7.0	6.62	0.07	**0.5**	0.537	0.003	**0.28**	0.03	**2.37**	0.16	--	--	no
7.0	6.51	0.21	**5.6**	4.71	0.02	**0.40**	0.02	**5.01**	0.12	--	--	no
5.0	4.74	0.05	**0.5**	0.524	0.004	**0.13**	0.01	**1.75**	0.14	--	--	no
5.0	4.70	0.10	**3.3**	3.27	0.05	**0.10**	0.01	**3.13**	0.11	--	--	no
5.0	4.63	0.24	**5.6**	5.13	0.05	**0.16**	0.01	**4.58**	0.09	--	--	no
2.0	1.89	0.06	**0.5**	0.509	0.010	*0.00*	*0.01*	*1.33*	*0.11*	**1.36**		yes
2.0	2.18	0.24	**5.6**	5.60	0.07	*-0.03*	*0.01*	*4.06*	*0.06*	**3.98**	0.07	yes
0.08	<0.1	--	**5.6**	6.14	0.07	*-0.08*	*0.01*	*3.78*	*0.07*	**3.53**	0.07	yes
MST												
3.0	2.89	0.09	**0.5**	0.504	0.008	**0.14**	0.01	**1.98**	0.10	--	--	no
3.0	*2.38*	0.09	**5.6**	5.03	0.04	**0.57**	0.02	**5.21**	0.12	--	--	no
1.0	0.92	0.05	**0.5**	0.503	0.004	*0.00*	*0.00*	*1.34*	*0.03*	**1.39**	0.03	yes
1.0	*1.55*	0.16	**5.6**	5.62	0.02	*0.03*	*0.01*	*4.31*	*0.03*	**4.42**	0.06	yes
0.04	<0.1	--	**5.6**	5.88	0.04	*-0.08*	*0.00*	*3.82*	*0.08*	**3.57**	0.09	yes
1:3 mMST:Kaolin												
7.0	*4.91*	0.24	**5.6**	6.02	0.06	**0.37**	0.06	**6.76**	0.06	--	--	no
1:3 mMST:Sludge												
7.0	7.22	0.20	**0.5**	0.508	0.009	*0.03*	*0.03*	*1.63*	*0.25*	**1.83**	0.12	yes
7.0	6.20	0.28	**5.6**	5.53	0.07	*0.01*	*0.00*	*4.60*	*0.11*	**4.63**	0.09	yes
5.0	5.08	0.11	**0.5**	0.497	0.004	*0.00*	*0.02*	*1.40*	*0.21*	**1.45**	0.10	yes
5.0	4.87	0.07	**3.3**	3.26	0.04	*0.01*	*0.02*	*2.51*	*0.14*	**2.60**	0.07	yes
5.0	4.69	0.09	**5.6**	5.63	0.06	*-0.04*	*0.00*	*4.30*	*0.04*	**4.19**	0.04	yes
2.0	2.03	0.20	**0.5**	0.504	0.004	*0.00*	*0.00*	*1.13*	*0.01*	**1.12**	0.01	yes
2.0	1.81	0.14	**5.6**	5.78	0.05	*-0.06*	*0.00*	*3.94*	*0.10*	**3.74**	0.09	yes
0.08	0.158	0.089	**5.6**	5.98	0.06	*-0.08*	*0.00*	*3.83*	*0.07*	**3.56**	0.07	yes
mMST												
3.0	3.34	0.04	**0.5**	0.432	0.003	*-0.01*	*0.00*	*1.17*	*0.02*	**1.12**	0.02	yes
3.0	2.27	0.20	**5.6**	5.90	0.04	*-0.01*	*0.01*	*4.03*	*0.18*	**4.02**	0.16	yes
1.0	1.10	0.09	**0.5**	0.479	0.004	*-0.01*	*0.00*	*1.17*	*0.01*	**1.10**	0.01	yes
1.0	0.90	0.11	**5.6**	6.05	0.07	*-0.05*	*0.00*	*3.87*	*0.02*	**3.73**	0.02	yes
0.04	0.237	0.131	**5.6**	6.21	0.12	*-0.08*	*0.00*	*3.81*	*0.08*	**3.55**	0.08	yes

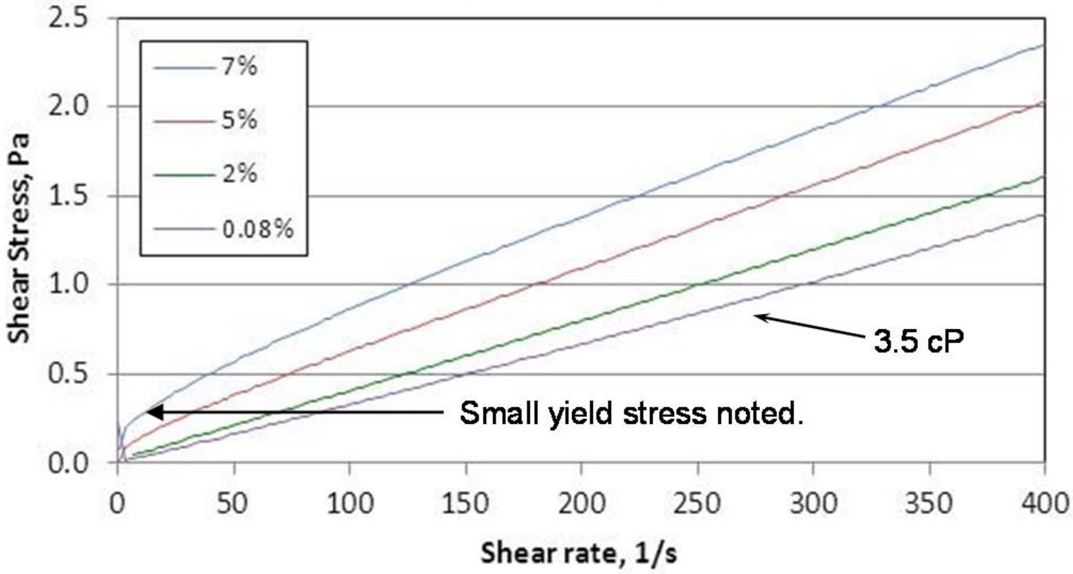

Figure 5: Flow curves for MST/sludge mixtures, at the high sodium condition

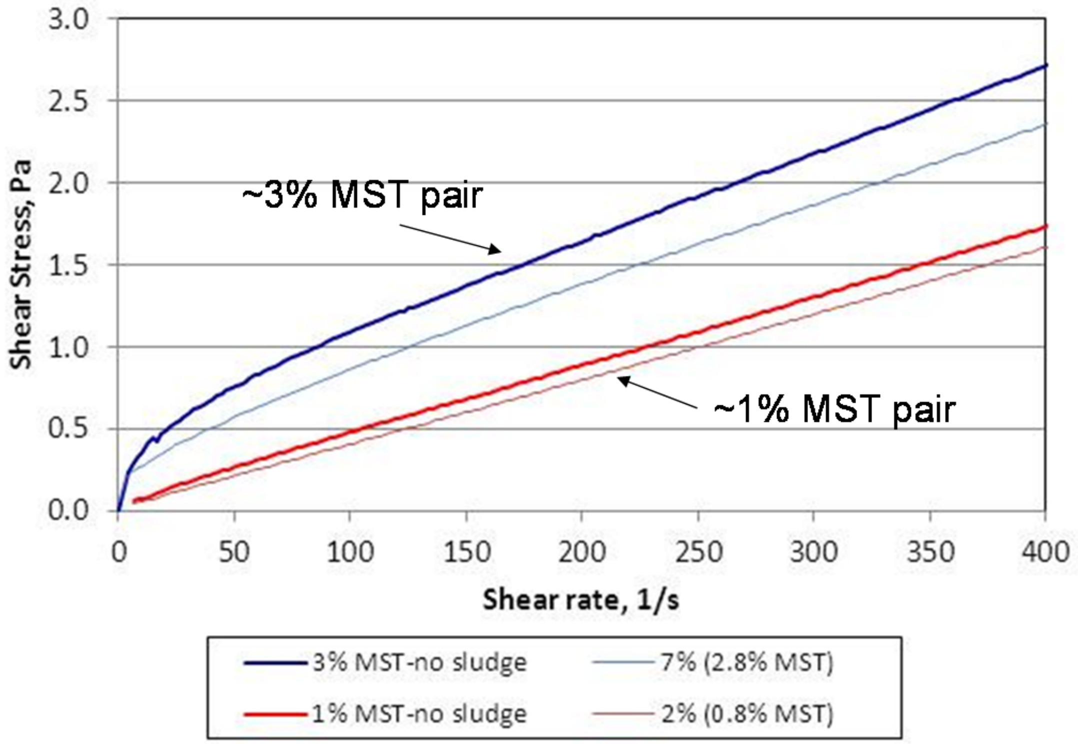

Figure 6: Comparison of MST flow curves with the analogous MST/sludge flow curves, at the high sodium condition

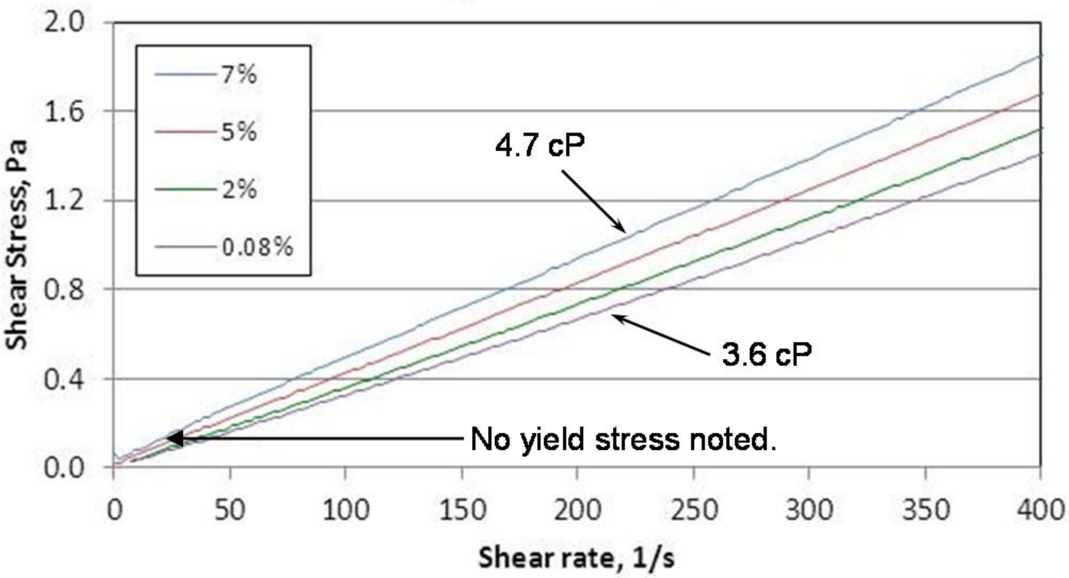

Figure 7: Flow curves for mMST/sludge mixtures, at the high sodium condition

Equation 2 is a fit of the viscosity (in cP) for mixtures of mMST (with and without added sludge simulant) over the range of variables explored during testing, where UDS is in wt % and [Na] is in mol/L. The statistical model did not require a term for whether the UDS were mMST only or included 75% sludge solids because that term was rejected at the 99% level. The R^2 of this fit was 0.97.

$$\mu = 0.688 + 0.492 * [Na] + 0.112 * UDS \qquad [2]$$

Modeling indicated there was still some potentially significant non-linearity in the data linked to the sodium molarity term (either singly or in combination with UDS), which is not unexpected for a range of over 5M. The UDS range for Equation 2 was 0 to 7 wt%. A linear dependence of viscosity on the volume fraction of solid material is also the expected relationship in the limit of fairly small solids contents. (Volume fraction is directly related to solids mass fraction which is directly related to wt % UDS for a given set of particles.)

3.2 Settled Solids Rheology

Table 5 contains the results for the shear strength measurements of the settled solids layers that fell within the planned test matrix. The test matrix contained five dimensions (starting wt % UDS, settling time, type of MST, sorbed Sr, and sodium concentration). Table 5 includes the results for the two vane rheometer measurements were performed for each settled layer as described in Section 2.4. Also included in Table 5 are the estimated sodium concentration based on a mass balance of the starting materials, the measured volumes of the initial slurry (total volume) and the settled bed of solids (bed volume), and an indication of whether a leak of liquid from the bottom of the column was noted that might bias the shear strength measurement.

Table 5: Test samples for shear strength measurements

UDS (wt %)	settling (days)	MST type	sorbed strontium	Na^+ (M)		volume (mL)		column leak (mL)	shear strength (Pa)	
				target	estimate	total	bed		first	second
7	10	MST	yes	*0.5*	0.50	430	180	none	11	17
7	10	mMST	yes	*0.5*	0.50	850	190	none	71	77
7	10	MST	yes	*3.3*	3.30	420	190	none	10	16
7	10	MST	yes	*5.6*	4.46	440	180	none	11	21
7	10	mMST	yes	*5.6*	4.71	830	200	none	37	42
7	30	MST	yes	*0.5*	0.50	440	200	none	10	10
7	30	MST	yes	*0.5*	0.50	440	180	none	9	15
7	30	mMST	yes	*0.5*	0.50	820	210	none	76	55
7	30	mMST	yes	*0.5*	0.50	830	180	none	83	88
7	30	MST	yes	*3.3*	3.30	420	190	none	9	9
7	30	MST	yes	*5.6*	4.46	440	180	none	16	
7	30	MST	yes	*5.6*	4.46	440	170	none	16	27
7	30	mMST	yes	*5.6*	4.71	820	200	none	147	128
7	30	mMST	yes	*5.6*	4.71	830	180	none	158	155
7	10	MST	no	*0.5*	0.50	430	160	none	11	15
7	10	mMST	no	*0.5*	0.50	800	160	none	125	133
7	10	MST	no	*3.3*	3.30	370	190	none	10	16
7	10	MST	no	*5.6*	4.64	440	200	< 10	14	20
7	10	mMST	no	*5.6*	5.08	820	200	none	63	41
7	30	MST	no	*0.5*	0.50	440	170	none	11	17
7	30	MST	no	*0.5*	0.50	440	170	none	13	15
7	30	mMST	no	*0.5*	0.50	700	150	> 100	192	161
7	30	mMST	no	*0.5*	0.50	800	150	none	110	96
7	30	MST	no	*3.3*	3.30	430	190	none	14	16
7	30	MST	no	*5.6*	4.64	440	200	none	18	33
7	30	MST	no	*5.6*	4.64	440	210	none	21	39
7	30	mMST	no	*5.6*	5.08	820	180	none	167	108
7	30	mMST	no	*5.6*	5.08	830	200	none	125	70
3	10	MST	yes	*0.5*	0.50	980	180	< 10	11	20
3.2	10	mMST	yes	*0.5*	0.50	1490	190	none	72	27
3	10	MST	yes	*5.6*	5.42	990	180	none	9	18
3.2	10	mMST	yes	*5.6*	5.52	1500	180	none	27	32
3	30	MST	yes	*0.5*	0.50	980	180	none	9	9
3.2	30	mMST	yes	*0.5*	0.50	1470	190	none	55	52
3	30	MST	yes	*5.6*	5.10	990	180	> 100	13	23
3.2	30	mMST	yes	*5.6*	5.18	1480	170	none	115	119
3	10	MST	no	*0.5*	0.50	990	170	none	9	15
3	10	mMST	no	*0.5*	0.50	1450	130	none	88	72
3	10	MST	no	*5.6*	5.40	990	200	< 10	8	11
3.16	10	mMST	no	*5.6*	5.57	1450	200	none	55	38
3	30	MST	no	*0.5*	0.50	990	170	none	11	18
3	30	mMST	no	*0.5*	0.50	970	110	> 100	137	
3	30	MST	no	*5.6*	5.40	990	210	none	16	29
3.16	30	mMST	no	*5.6*	5.57	1480	190	none	115	90
7	53	MST	yes	*3.3*	3.30	370	190	none	11	19
7	30	MST	no	*3.3*	3.30	410	190	> 100	42	54
7	53	MST	no	*3.3*	3.30	430	180	none	17	

Table 6 is a more concise summary table of shear strength measurements, where only the first, or nominal, result is reported. The second, or less quantitative, result was very subjective and depended strongly on settled bed depth and measurement position. For conditions where replicate settled samples were prepared and measured, both results are reported in Table 6 (for example, see 7 wt % UDS, 30 day settling time.) Replicate samples were used to evaluate statistical error due to preparation and measurement protocols rather than due to variation in material properties related to time, solids type, solids loading, and supernate concentration.

Table 6: Summary of the shear strength (Pa) of settled MST/sludge layers

	Settling Time				
	10 days		30 days		53 days
Nominal Sodium Concentration	3 wt % UDS	7 wt % UDS	3 wt % UDS	7 wt % UDS	7 wt % UDS
5.6 M	MST: **8 Pa** MST+Sr: **9 Pa** mMST: **55 Pa** mMST+Sr: **27 Pa**	MST: **14 Pa** MST+Sr: **11 Pa** mMST: **63 Pa** mMST+Sr: **37 Pa**	MST: **16 Pa** MST+Sr: **13 Pa** mMST: **115 Pa** mMST+Sr: **115 Pa**	MST: **18, 21 Pa** MST+Sr: **16, 16 Pa** mMST: **125, 167 Pa** mMST+Sr: **147, 158 Pa**	
3.3 M		MST: **10 Pa** MST+Sr: **10 Pa**		MST: **14, 49 Pa** MST+Sr: **9 Pa**	MST: **17 Pa** MST+Sr: **11 Pa**
0.5 M	MST: **9 Pa** MST+Sr: **11 Pa** mMST: **88 Pa** mMST+Sr: **72 Pa**	MST: **11 Pa** MST+Sr: **11 Pa** mMST: **125 Pa** mMST+Sr: **71 Pa**	MST: **11 Pa** MST+Sr: **9 Pa** mMST: **137 Pa** mMST+Sr: **55 Pa**	MST: **11, 13 Pa** MST+Sr: **9, 10 Pa** mMST: **110, 192 Pa** mMST+Sr: **76, 83 Pa**	

A typical graph of vane measurement data is shown in Figure 8. The y-axis has the applied shear strength derived from the torque. The shear strength of the settled solid layer sample is taken at the maximum value on the curve. A small angular movement of the vane sensor is usually sufficient to disrupt the layered bed structure and establish angular rotation of an essentially cylindrical plug of solids contained between the four vanes. Frictional forces above, below and radially outside this plug must be overcome giving rise to the shear strength. At 50 s into the measurement, the vane sensor has made one-quarter revolution, and the vane blades begin passing through a region that has already been swept by the vane ahead of them. In this study, the one-quarter rotation point was primarily marked by little more than a transition to reduced slope in the declining torque versus time data.

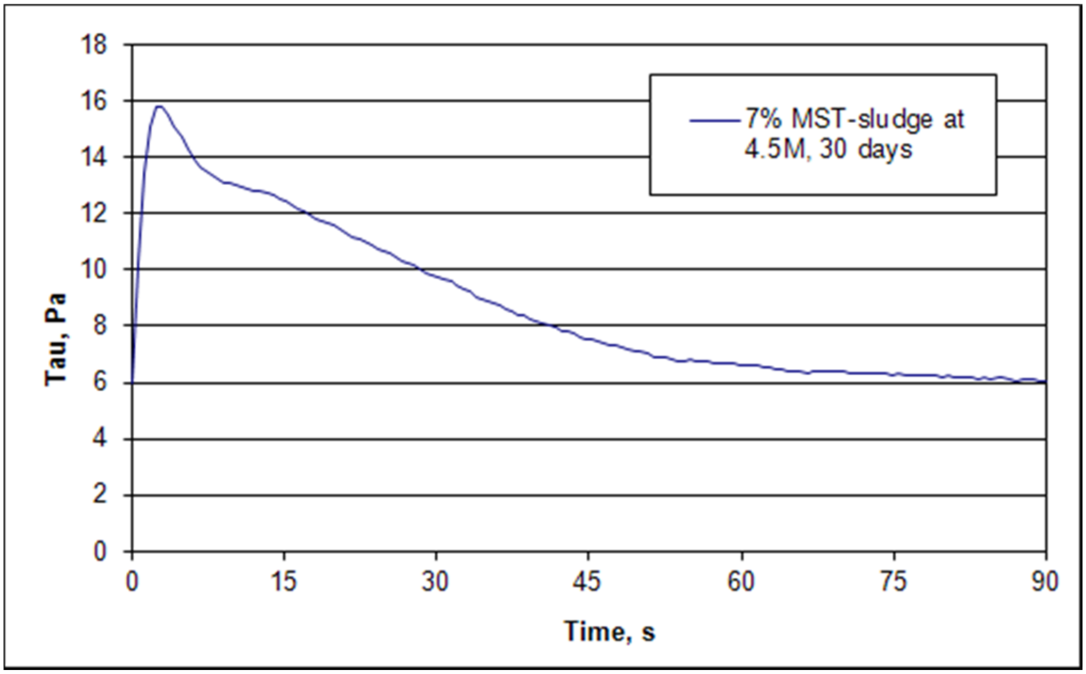

Figure 8. Typical MST vane data in the nominal measurement position

Figure 9 shows the typical outcome for the settled layers with mMST instead of MST. This figure also contains a replicate pair test from two identically batched settling columns. These two settling columns started with mMST with sorbed Sr plus sludge at 7 wt % UDS in high molarity supernate. The two columns were undisturbed for 30 days while the solids settled and packed into the layers that were subjected to the two vane measurements.

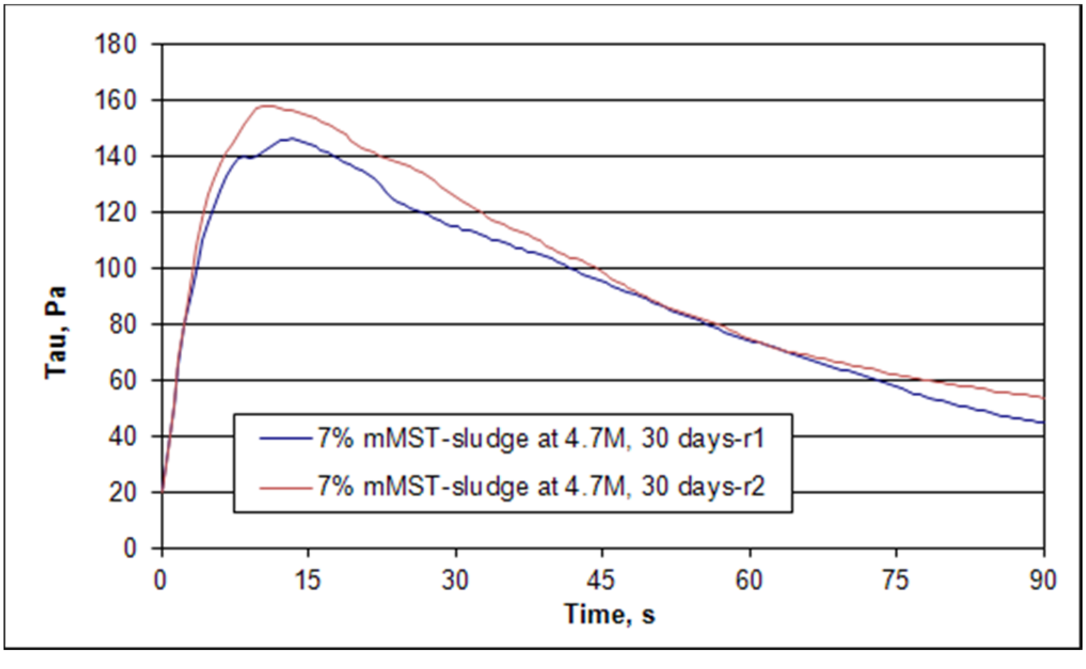

Figure 9. Replicate measurements for a pair of Sr-loaded mMST layers

The two settled layers behaved nearly identically for the first 2.5 seconds of the vane rotation (at about 90 Pa). This was sufficient time (vane rotation) to break down the MST structure in Figure 8, but structure still remained to be disrupted in the settled mMST-sludge bed. This longer-range structure may have extended somewhat beyond the boundary defining the cylinder of rotation of the four metal vanes. Consequently, more time was required to build up and propagate the necessary magnitude shear forces outwards into the sample matrix and produce the yielding seen at about 147-158 Pa (after 10 seconds).

As evident from Table 6, shear strength measurements ranged from near 10 Pa for many of the MST/sludge layers to above 100 Pa for many mMST/sludge layers. More precisely, the MST/sludge layers had shear strengths of 8 to 21 Pa, with a single outlier of 49 Pa, and the mMST/sludge layers had shear strengths of 27 to 192 Pa. A statistical analysis was performed on the data and is presented later in this section, but a few trends were evident without rigorous analysis.

The shear strength of settled mMST/sludge layers is consistently greater than that for settled MST/sludge layers over almost the entire range of measurements. This is the most obvious trend noted throughout the data set. There are several observations that corroborate, and may help to explain, the differences between shear strengths of MST/sludge and mMST/sludge settled layers.

One factor, as previously discussed, is that 1.9 times as much mMST/sludge was required to make the same height of settled solids when compared with MST/sludge with the same mixture UDS content. Thus, the settled layer of mMST/sludge consisted of more tightly packed particles than the analogous MST/sludge layer. One spot check of the total solids content within the settled layers revealed that a MST/sludge layer was 18.3 wt % UDS while a mMST/sludge layer was 32.5 wt % UDS. This approximately 1.8 times increase in the settled layer UDS for mMST/sludge over MST/sludge is consistent with the settling column loading and observed settling behavior and settled bed depth versus time.

Another factor that may influence the relatively high shear strength of mMST/sludge mixtures is potential interactions between sludge or mMST particles with mMST leading to formation of a weak gel within the settled solid layer. Figure 10 contains photographs of the vane after being removed from samples. For the MST/sludge layers, a thin film of material was evident on the vane indicating only a weak attractive force between the solids and vane. For the mMST/sludge layers, however, larger clumps of mMST/sludge material adhered to the vertical vane faces. The presence of clumps showed an attractive potential between the vane surface and the settled solids as well as the existence of significant attractive forces between the particles that were able to maintain the clump shapes against the pull of gravity (the absence of which would have permitted the solids to mostly drop off the vanes as the sensor was lifted out of the settled solids layer). The different physical nature of the settled layers was observed repeatedly with the two different sludge sample matrices (MST or mMST); that is, Figure 10 was not an isolated observation.

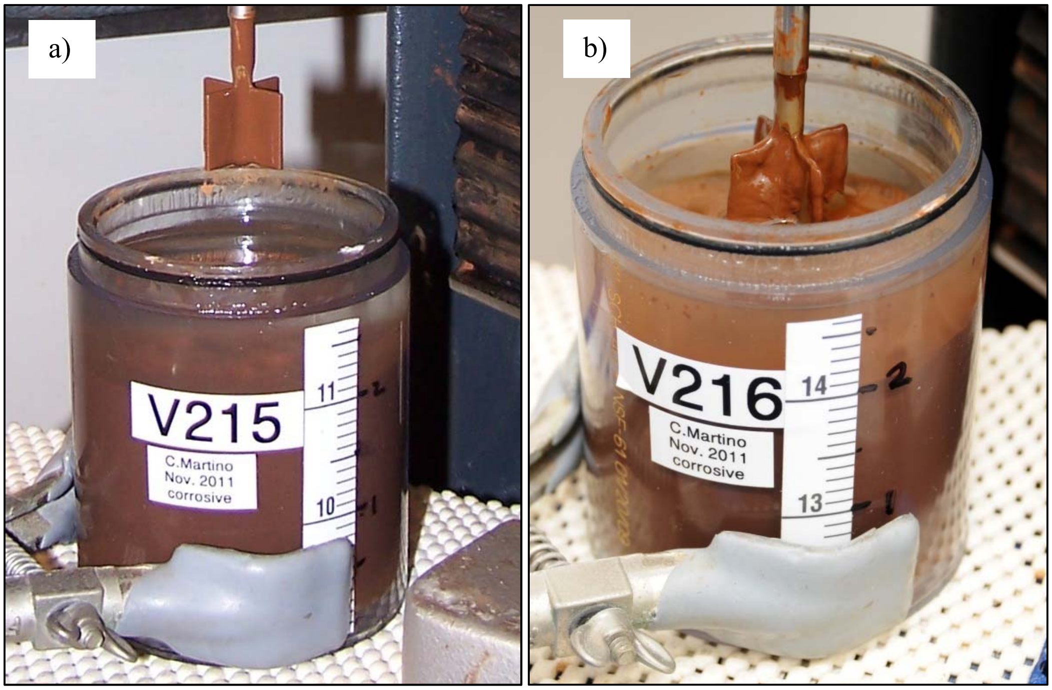

Figure 10: typical appearance of settled samples upon vane removal: a) MST/sludge, and b) mMST/sludge

Strontium sorption appears to have little effect on the shear strength of MST/sludge layers, and the effect might be a slight reduction in the shear strength of the layers when the MST is loaded with strontium. Similarly, for layers of settled mMST and sludge, the shear strength for strontium-sorbed mMST layers appears lower than that for most analogous cases without strontium sorption. A prior hypothesis was that the increased density of strontium loaded MST and mMST would cause a significant increase in the shear strength of the settled layers due to an increase in the solid density. This result was counter to that hypothesis, and substantiates the case for using MST and mMST without sorbed Sr in pilot scale mixing testing.

As expected, increased settling time appears to contribute to slight increases in shear strength in many of the cases. Between the 10 day and 30 day settled samples, the shear strength measurements typically increased by a factor of two or less. Sodium concentration of the salt and initial column loading UDS concentration did not have a readily apparent effect. The lack of significant impact from the initial UDS concentration indicates that any differential settling by particles of different sizes and/or densities had a minimal impact on the shear strengths of the settled beds.

As mentioned previously, two shear strength measurements were performed in series on each settled layer of solids, and the first is reported as the shear strength result. In practice, the vane was lowered to the required depth and the first shear strength measurement was taken, the vane was then lowered further into the bed of solids and the second shear strength measurement was taken. The first measurement is reported as the valid measurement because the second measurement is thought to be influenced by disturbing the solids during the first measurement or by getting too close to the vessel bottom. A review of the results shows that for MST/sludge layers, the second measurement tends to be slightly higher than the first measurement, while for mMST/sludge layers, the second measurement tends to be lower than the first measurement. A small increase in shear strength is expected for a measurement underneath a taller column of settled solids with weak interparticle forces simply due to the increased weight pushing down on the particles rotating with the vanes creating more friction.

For mMST the observation of reduced shear strength at slightly lower depth presumably indicates that the settled layer gel structure was disrupted by the initial vane measurement beyond the boundaries of the cylinder of material that was rotated with the vane (indicative of the presence of a larger-scale structure within the settled layer). Consequently, the region of material rotated by the second, lower measurement had already been disrupted by the first measurement. Therefore, less torque was needed than in the first measurement because structure had already been partially broken down within the cylindrical region of the second measurement. Figure 4 above showed that there was not much room to reposition the vane between the nominal position and vessel bottom.

Replicate sample pairs did not always produce equivalent settled solids volumes, even though they contained nearly identical masses of the matrix components. Small differences in the degree of dispersion of the starting particles are a potential cause of differences in settling rate and ultimate packing behavior. The majority of sample pairs with different settled volumes had higher shear strength on the more compacted bed of solids. Such a result is intuitively expected based on the general understanding of forces within beds of settled solids.

A statistical factor screening using JMP® statistical software of the entire vane data set indicated that the type of MST material had the largest influence on the vane shear strength. Other terms that could be brought into the statistical regression model of all vane data primarily served to explain variations within the mMST data, since the MST data were all grouped tightly together at the low shear strength end of the range. The result of general data fitting is shown in Figure 11. The figure compares a statistical model to the actual vane data. Points closest to the 45º line are well modeled, while points far from this line are poorly modeled.

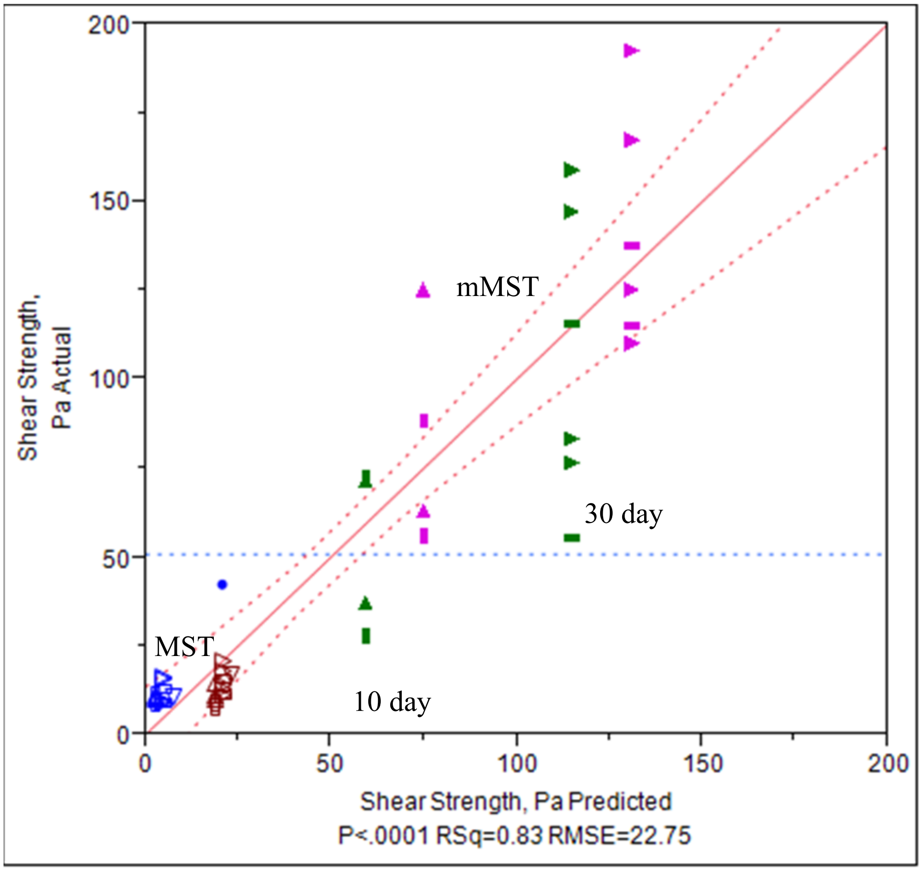

Figure 11. Four factor model of vane shear strength

In Figure 11, hollow triangles and rectangles are MST data. Solid triangles and rectangles are mMST data. Triangles represent settled measurements from 7 wt % UDS slurries while rectangles represent settled measurements from 3 wt % UDS slurries for both MST and mMST data. Blue symbols represent measurements with sorbed Sr and brown symbols represent measurements without Sr sorption for MST. Green symbols represent measurements for sorbed Sr and purple symbols represent measurements without Sr sorption for mMST. A suspicious MST result is shown by a solid blue circle. Triangles pointing up and vertical rectangles settled for 10 days, triangles pointing to the right and horizontal rectangles settled for 30 days, triangles pointing down (2 with MST) settled for 53 days.

Figure 11 shows clearly that the two sorbents represent separate populations of shear strength data. The final prediction model generated by step-wise regression analysis included sorbent type (MST/mMST), days settled, Sr sorption (yes/no), and a cross term between days settled and resin type. These terms were statistically significant at the 95% confidence level in explaining variations in the data set. With 46 data points, there were still 41 degrees of freedom for error with the five term model. Settling time and the settling time cross product with titanate type were somewhat more significant in explaining variation than was the Sr sorption variable. Sample molarity was not a significant factor in the presence of these other factors (presumably because ionic strength would be considered high in the inter-particle region of the settled beds for all cases studied).

The vane data was partitioned into essentially six sub-groups by the model. These show up as six more or less vertical columns of data points in Figure 11. All blue points (i.e., MST slurries with sorbed Sr) were to the left, or lower shear strength, of the brown points (i.e., MST absent Sr sorption) due to Sr sorption for MST. Upward pointing green triangles and tall green rectangles (i.e., mMST slurries with sorbed Sr after 10 days contact) were to the left of corresponding purple ones (i.e., mMST slurries absent Sr sorption), and right pointing green triangles and flat rectangles (i.e., mMST slurries absent sorbed Sr after 30 days contact) were to the left of corresponding purples ones also due to Sr sorption for mMST. Hence, longer settling time increased shear strength.

Splitting the mMST data from the MST and applying the same approach led to a revised statistical model for mMST only systems, Figure 12.

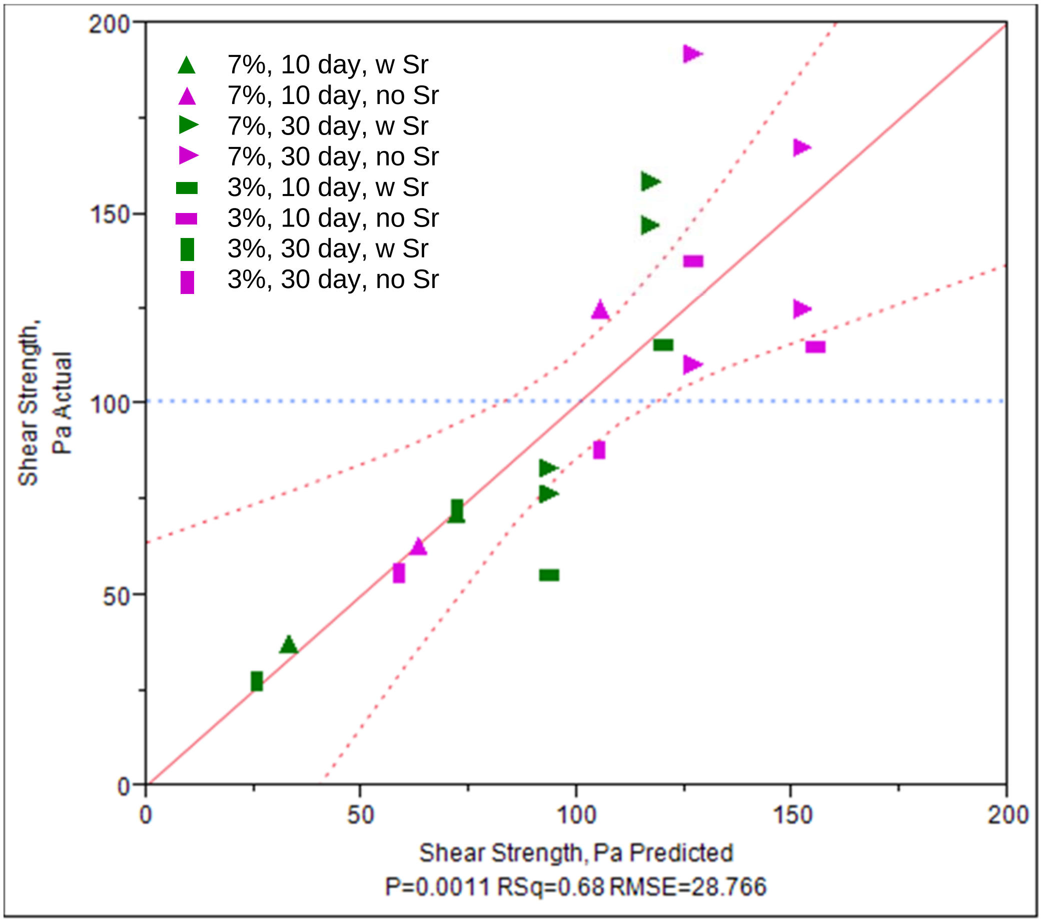

Figure 12. Four factor vane model for mMST only

The model included effects from settling time, Sr sorption, and sodium molarity, plus a cross term between settling time and sodium molarity. An interesting feature of this model is that it predicted many of the lower shear strength results (<80 Pa) fairly well. The model struggled somewhat on the high end which included two replicate pairs, shown by purple right pointing triangles, that had fairly wide scatter (at predicted shear strengths of 125 and 150 Pa). The mid to high end also included two replicate pairs, shown by green right pointing triangles, that had fairly good reproducibility. One pair was above the model curve, and one pair was below the model curve. The model did not capture the difference between these two pairs well. The implication from the four pairs, however, is that modeling has gone far enough in trying to explain residual error. The model indicated that shear strength decreased with Sr sorption (green points) and decreased with increasing sodium molarity. The linear dependence of settling time in the direct term and cross term nearly cancelled out, but the cross of settling time with molarity indicated shear strength increased with increasing settling time as expected for the more compacted settled layers that form given longer time.

Of the settling column samples listed in Table 5, three had a minor leak (possibly a few mL) and five developed major leaks (>100 mL). The leaks were from the bottoms that were glued on and usually were not evident until several days into settling. The leaks were liquid only, as solids did not pass through the leak site. This unintentionally introduced a downflow through the bed of settled solids and may have contributed to beds becoming more consolidated. Such a downflow would not be expected to be analogous to a condition within the SWPF process vessels. This downward flow may have ultimately led to higher shear strengths in those beds.

All of the samples with minor leaks and four of the five samples with major leaks survived to undergo shear strength measurement and the results are included in Table 5 and Table 6. The sample that was planned as the 53 day settling test for the unloaded MST/sludge condition developed a major leak. Thus, the shear strength was measured after 30 days and the settling of a replacement 53 day sample was initiated. For this reason, the 30 day condition (3.3M Na, 7 wt % UDS, MST) had a duplicate. The shear strength of the non-leaking replicate measured 14 Pa while the leaking replicate measured 49 Pa. This discrepancy appears anomalous when looking at the overall repeatability of the shear strength results, so it was possibly influenced by the leaking. There was one other major-leak/non-leak replicate pair. For mMST without sorbed Sr with 30 days settling 0.5 M Na^+ and 7 wt % UDS, the leaking sample measured 192 Pa and the non-leaking sample measured 110 Pa. However, the other two samples with a major leak and the three slowly leaking samples had results that were internally consistent with the rest of the data set. For those cases, there was no obvious effect of the leaking on the shear strength results.

Figure 13: Typical settled layer of MST/sludge for vane rheology testing, formed from the low initial solids loading condition (3 wt % UDS).

Figure 13 shows the side view of a cup containing an approximately 2.2 inch tall settled layer of MST/sludge. This is the bottom portion of a settling column after removal of the supernate and separation from the top portion of the column. Although difficult to discern in this photo, there are more white specks visible against the inner wall of the column in the bottom several tenths of an inch than there are visible against the inner wall throughout the remainder of the settled layer. This observation was consistent with most other MST/sludge layers that were initiated from the low initial solids loading condition (3 wt % UDS). Such a bottom layer was not visually evident in the MST/sludge samples with the high initial solids loading (7 wt % UDS). Such a layer was also not noted in mMST/sludge samples.

Figure 14: Top view of settled solid samples prior to vane rheology measurement

The mMST mixtures evolved small amounts of gas after being mixed with the caustic salt solution. In some cases, this gas evolution occurred during the adjustment stage where the 5.6 M Na^+ CSSX simulant was mixed with mMST. This gas likely has an influence on the overall shear strength measured on the settled beds of mMST and sludge. Gas released during the settling period caused channels to form in the beds of solids, as noted in the top view of samples shown in Figure 14. This photograph was taken just prior to shear strength measurement and shows that the two samples of this set that contained mMST (V216 and V238) had noticeable channels in the surface of the settled layer. Gas that is not released prior to shear strength measurement can cause pockets of low shear strength. Liquid-filled channels formed by gas evolution and release are also likely to cause regions of low shear strength reducing the average resistance seen by the rotating vane. In some mMST/sludge settled layers, the gas is released from the sludge just after the supernate is decanted from the surface of the layer, as seen in Figure 15.

Figure 16 reveals an unexpected observation made for a sample of settled mMST/sludge that was accidentally created using the incorrect sludge to mMST ratio. This test mixture had twice the normal amount of mMST, which included sorbed strontium. The soluble sodium concentration was 0.5 M and the initial UDS concentration was approximately 3 wt %. Not long after the supernatant liquid was removed from the settled layer of solids and the column was separated, a large amount of small gas bubbles were released from the settled layer in a manner that caused significant disturbance/mixing of the settled layer. This indicates that this sample was no longer representative of solids that had been sitting undisturbed for many days, and its results could not be compared to the larger data set.

Figure 15: Typical gas release after supernatant decant from a nominal 1:3 mMST:sludge settled layer

Figure 16: Greater than typical gas release after supernate removed from a (mistakenly created) 1:1.5 mMST:sludge settled layer

4.0 Conclusions

SRNL performed measurements of the rheology of suspensions and settled layers applicable to the Savannah River Site Salt Waste Processing Facility. Suspended solids mixtures included MST or mMST at various solid concentrations and soluble ion concentrations with and without the inclusion of kaolin clay or simulated sludge. Layers of settled solids were MST/sludge or mMST/sludge mixtures, either with or without sorbed strontium, over a range of initial solids concentrations, soluble ion concentrations, and settling times.

The following results were noted for the rheology of suspended solids.

- Slurries with MST, with and without sludge, exhibited a slight yield stress when undissolved solids (UDS) content was 3 wt % and above.
- Increasing UDS led to higher yield stress slurries.
- Mixtures with mMST up to 7.2 wt % UDS all fit the Newtonian viscosity model.

The following results were noted for the rheology of beds of settled solids.

- The MST/sludge layers had shear strengths of 8 to 21 Pa, with a single outlier of 49 Pa, and the mMST/sludge layers had shear strengths of 27 to 192 Pa.
- The type of MST used (MST or mMST) had the greatest correlation with settled layer shear strength.
- Using MST or mMST with sorbed strontium led to similar or slightly reduced shear strengths when compared to the analogous non-loaded material.
- The time allowed for settling the bed was statistically significant, in addition to the type of MST and the inclusion of sorbed strontium.

5.0 Quality Assurance

The data from these experiments are contained in Laboratory Notebooks SRNL-NB-2011-00134 and SRNL-NB-2011-00139.

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

6.0 Acknowledgements

Material handling and creation of test mixtures and settled beds was accomplished by H. L. Bolton. The assistance of V. J. Williams and B. G. Wall with the measurement of weight percent solids and rheological properties was an essential component of the successful completion of this task and their help is greatly appreciated. E. K. Hansen contributed to this work by developing protocols for making vane measurements on settled solids layers and obtaining the necessary equipment to perform the rheological measurements. T. G. Forehand and the SRNL Machine Shop were instrumental in producing the transparent two-part settling columns.

7.0 References

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[4] S. Shicks, “Salt Waste Processing Facility Project Test Report: Air Pulse Agitator Scale-Up Validation,” P-RPT-J-00008, April 28, 2008.

[5] T. B. Peters, D. T. Hobbs, and S. D. Fink, “Determination of Fissile Loadings onto Monosodium Titanate (MST) under Conditions Relevant to the Actinide Removal Process Facility,” WSRC-TR-2005-00514, Rev. 1, August 12, 2006.

[6] T. B. Peters, D. T. Hobbs, and S. D. Fink, “Results of Supplemental MST Studies,” WSRC-STI-2006-00012, Rev. 0, July 24, 2006.

[7] K. M. L. Taylor-Pashow and D. T. Hobbs, “Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Modified Monosodium Titanate Phase III Final Report,” SRNL-STI-2010-00383, Rev. 0, September 2010.

Appendix

A.1 Additional rheological data.

Figure 17 and Figure 18 show the influence of sodium molarity on the fully suspended rheological properties of MST and mMST at ~5 wt.% UDS.

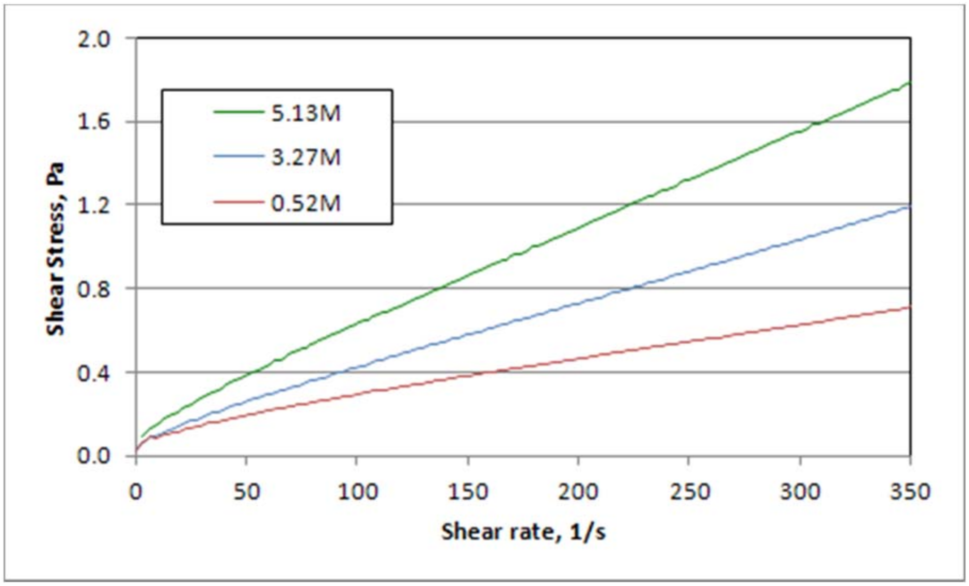


Figure 17: MST-sludge systems

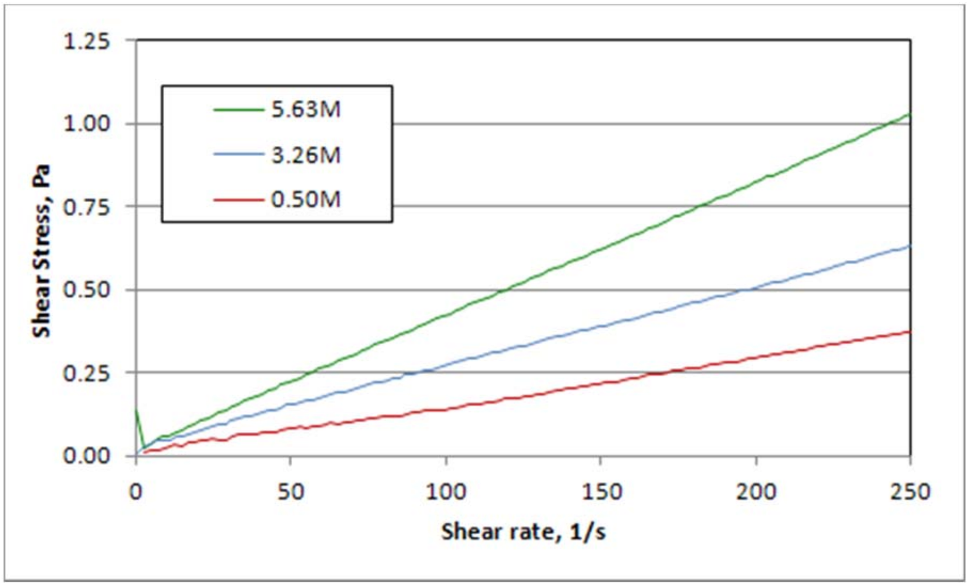


Figure 18: mMST-sludge systems

It can be seen that there are signs of a small yield stress (0.1-0.2 Pa off the origin at zero shear rate) for the MST-sludge slurries, but essentially no sign of a yield stress for the mMST-sludge slurries.

Figure 19 and Figure 20 show the influence of changing wt % UDS for MST-sludge systems on the rheological properties at approximately constant supernate sodium molarity (two cases).

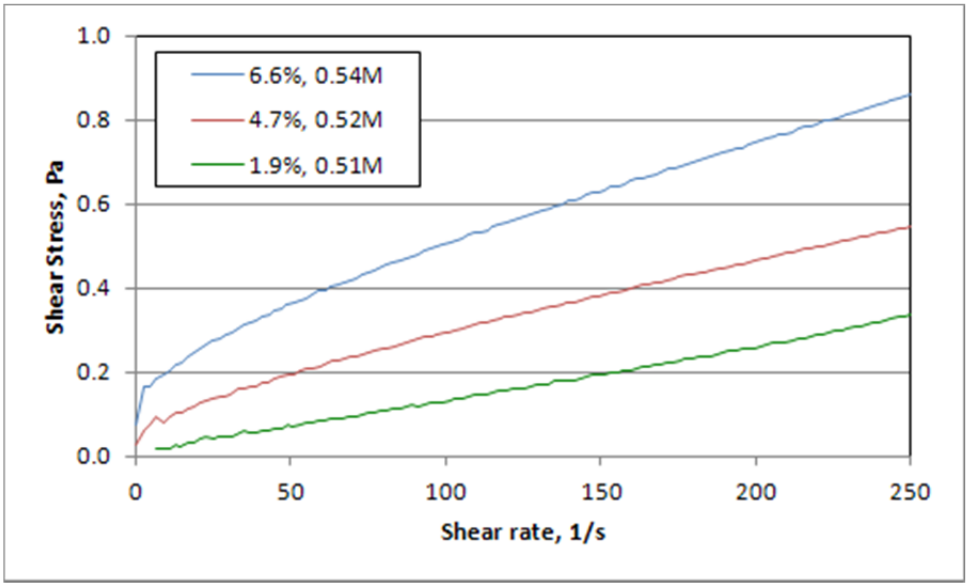


Figure 19: MST-sludge at ~0.5M as wt% UDS changes

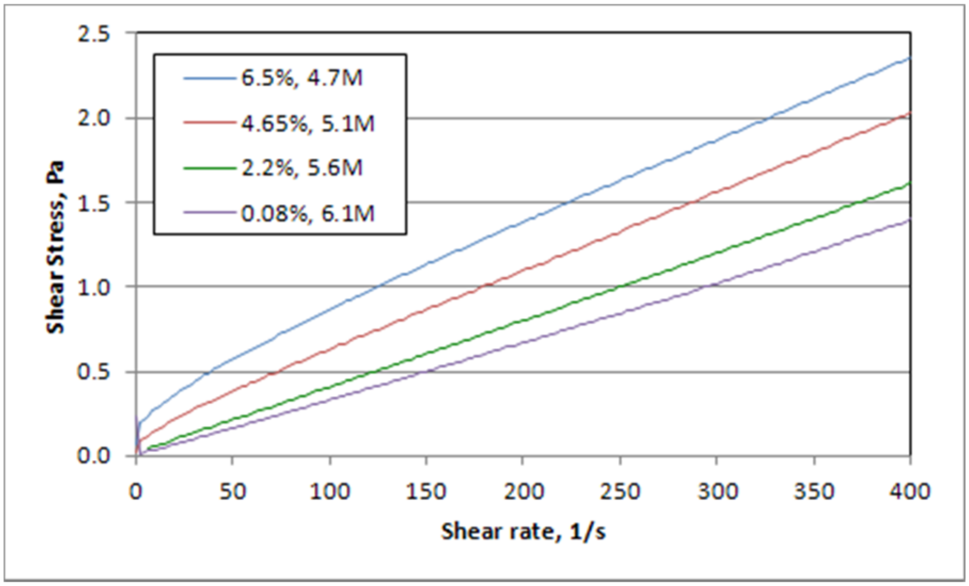


Figure 20: MST-sludge at ~5.6M as wt% UDS changes

A small yield stress was apparent at wt % UDS above 3 wt %, but at lower UDS the slurries behaved as essentially Newtonian liquids.

Figure 21 and Figure 22 show the influence of changing w t% UDS for mMST-sludge systems on the rheological properties at approximately constant supernate sodium molarity (two cases).

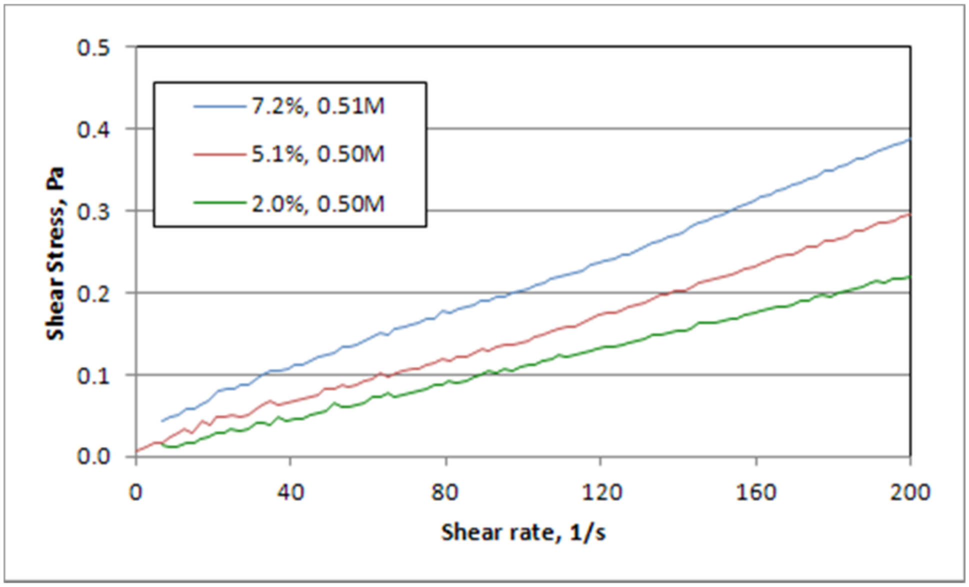


Figure 21: mMST-sludge at ~0.5M as wt % UDS changes

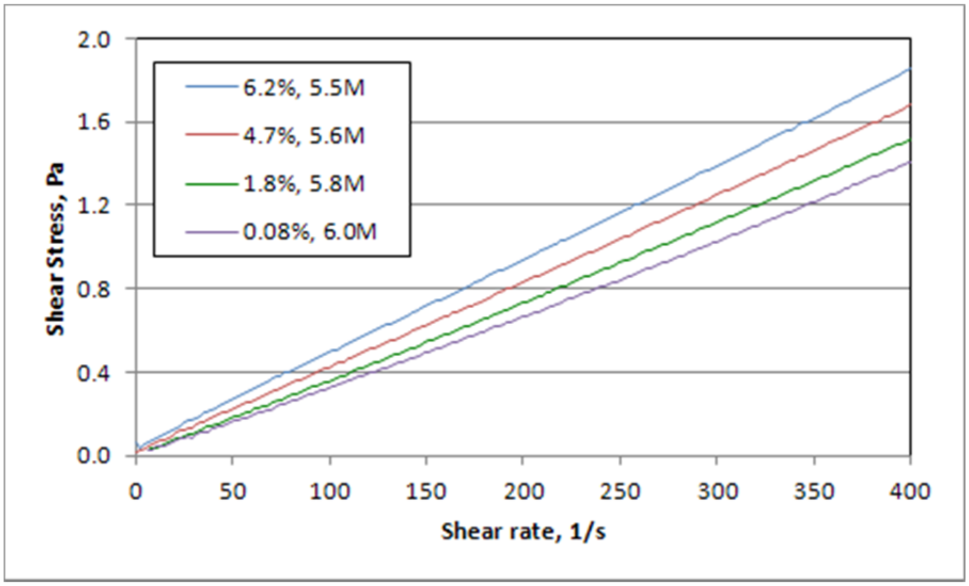


Figure 22: mMST-sludge at ~5.6M as wt % UDS changes

No significant yield stress was apparent at any wt % UDS for the mMST-sludge slurries in contrast to the behavior seen in the MST-sludge slurries.

Figure 23 and Figure 24 compare the rheological behavior of MST slurries to mMST slurries in high sodium molarity liquids in the absence of entrained sludge solids.

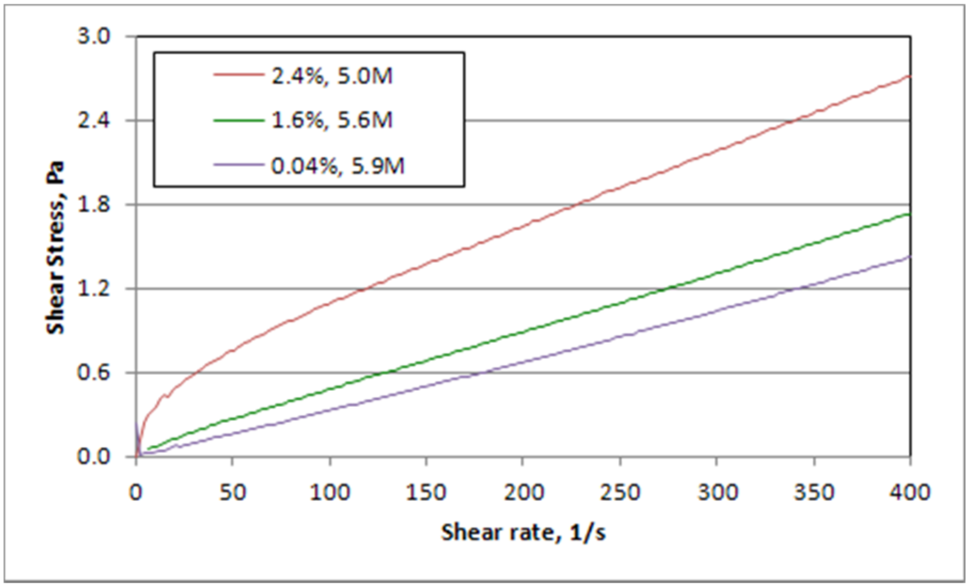


Figure 23: MST at three UDS levels in high sodium molarity liquid

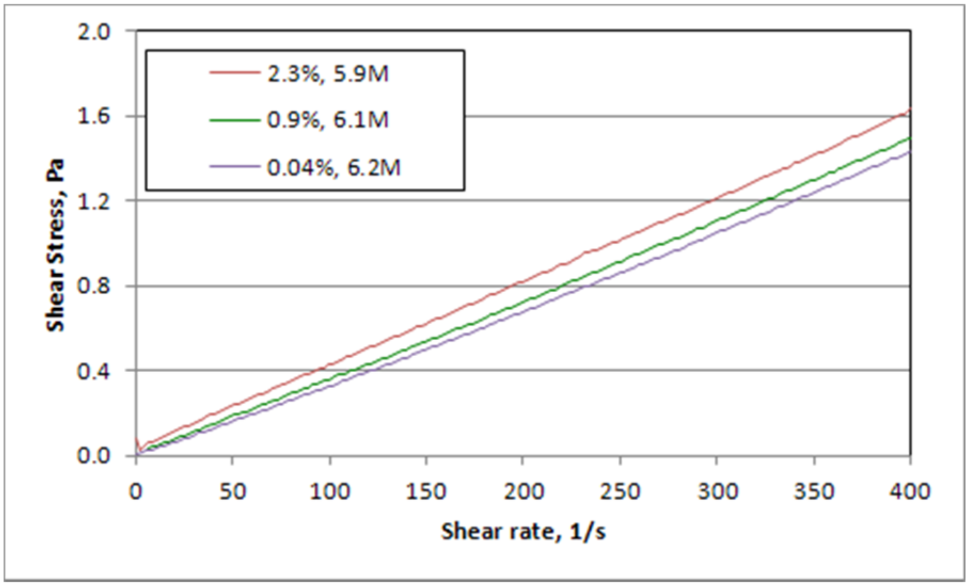


Figure 24: mMST at three UDS levels in high sodium molarity liquid.

Rheological behavior of these sorbent-only slurries was dominated by the viscosity of the liquid phase (3.5-4.5 cP) with the exception of the 2.4 wt % UDS MST slurry that showed the presence of a small yield stress (0.6 Pa). Similar behavior was seen in the limited sludge-free data at low sodium molarities.

The origin of the yield stress behavior seemed to lie with the MST particles based on the previous figures. To confirm this, flow curves were obtained for the sludge simulant and are displayed in Figure 25.

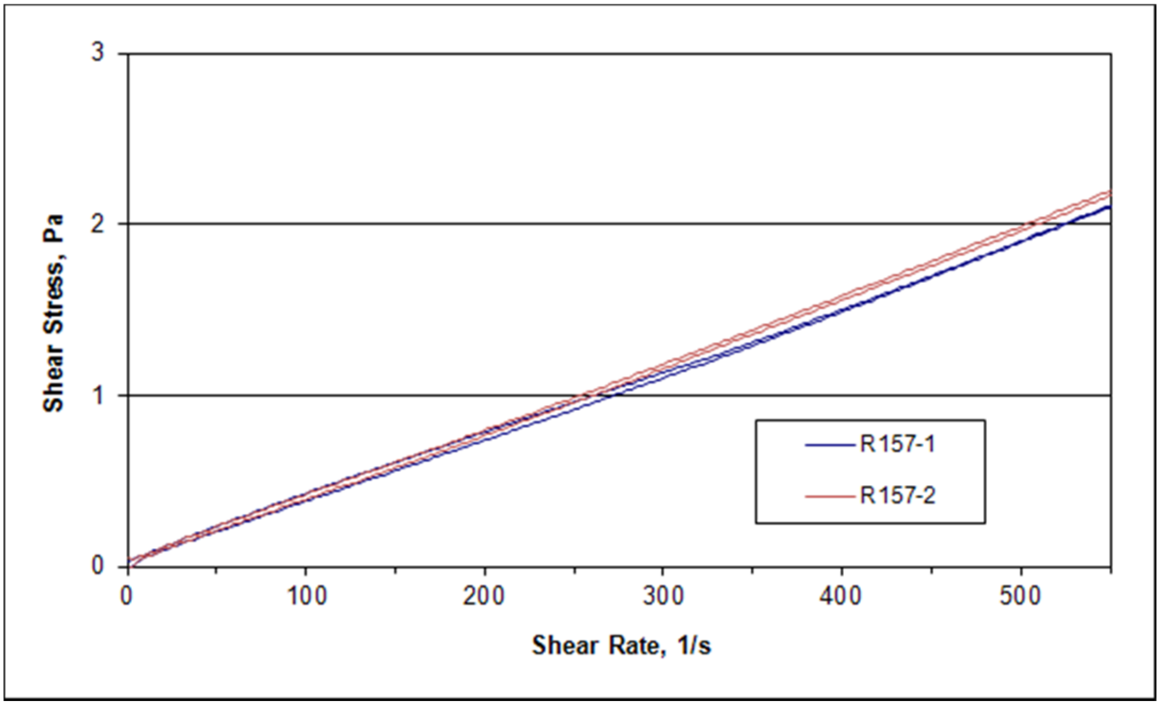
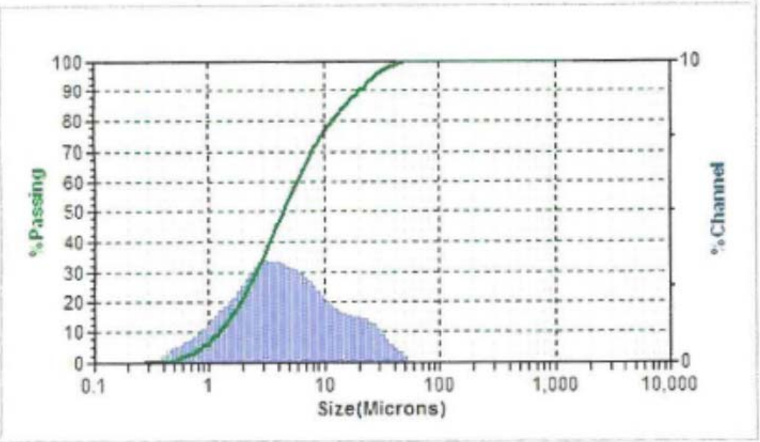


Figure 25: Replicate flow curves for sludge simulant diluted to 5.5 wt % UDS

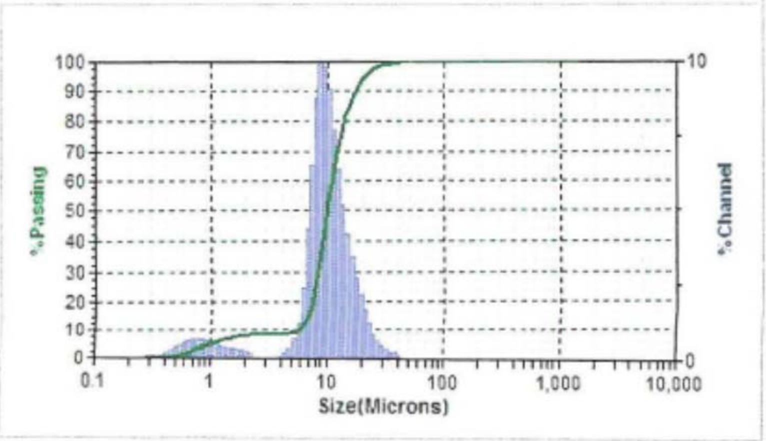
The sludge-only rheological data show no yield stress at sludge UDS greater than were found in any of the sludge-MST or sludge-mMST slurries. The conclusion is that sludge-MST and MST-MST particle interactions are responsible for the yield stress behavior of the higher UDS MST systems in this study.

A.2 Particle size distribution (PSD) data provided by Parsons



Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
1408	0.00	100.00	74.00	0.00	100.00	3.89	3.29	45.49			
1291	0.00	100.00	67.86	0.00	100.00	3.57	3.31	42.20			
1184	0.00	100.00	62.23	0.00	100.00	3.27	3.37	38.89			
1086	0.00	100.00	57.06	0.00	100.00	2.999	3.31	35.52			
995.6	0.00	100.00	52.33	0.18	100.00	2.750	3.17	32.21			
913.0	0.00	100.00	47.98	0.32	99.82	2.522	2.98	29.04			
837.2	0.00	100.00	44.00	0.43	99.50	2.312	2.76	26.06			
767.7	0.00	100.00	40.35	0.58	99.07	2.121	2.53	23.30			
704.0	0.00	100.00	37.00	0.76	98.49	1.946	2.32	20.77			
645.6	0.00	100.00	33.93	0.94	97.73	1.783	2.14	18.45			
592.0	0.00	100.00	31.11	1.11	96.79	1.635	1.98	16.31			
542.9	0.00	100.00	28.53	1.24	95.68	1.499	1.84	14.33			
497.8	0.00	100.00	26.16	1.34	94.44	1.375	1.71	12.49			
456.5	0.00	100.00	23.99	1.42	93.10	1.261	1.56	10.78			
418.6	0.00	100.00	22.00	1.45	91.68	1.156	1.42	9.22			
383.9	0.00	100.00	20.17	1.49	90.23	1.060	1.26	7.80			
352.0	0.00	100.00	18.50	1.51	88.74	0.972	1.10	6.54			
322.8	0.00	100.00	16.96	1.54	87.23	0.892	0.97	5.44			
296.0	0.00	100.00	15.56	1.59	85.69	0.818	0.85	4.47			
271.4	0.00	100.00	14.27	1.66	84.10	0.750	0.75	3.62			
248.9	0.00	100.00	13.08	1.76	82.44	0.688	0.68	2.87			
228.2	0.00	100.00	12.00	1.87	80.68	0.630	0.60	2.19			
209.3	0.00	100.00	11.00	2.02	78.81	0.578	0.53	1.59			
191.9	0.00	100.00	10.09	2.18	76.79	0.530	0.45	1.06			
176.0	0.00	100.00	9.25	2.36	74.61	0.486	0.38	0.61			
161.4	0.00	100.00	8.48	2.52	72.25	0.446	0.23	0.23			
148.0	0.00	100.00	7.78	2.68	69.73	0.409	0.00	0.00			
135.7	0.00	100.00	7.13	2.82	67.05	0.375	0.00	0.00			
124.5	0.00	100.00	6.54	2.92	64.23	0.344	0.00	0.00			
114.1	0.00	100.00	6.00	3.02	61.31	0.315	0.00	0.00			
104.7	0.00	100.00	5.50	3.09	58.29	0.2890	0.00	0.00			
95.96	0.00	100.00	5.04	3.17	56.20	0.2650	0.00	0.00			
88.00	0.00	100.00	4.62	3.25	52.03						
80.70	0.00	100.00	4.24	3.29	48.78						

Figure 26: PSD of MST used in current testing, with sonication treatment



Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
1408	0.00	100.00	74.00	0.00	100.00	3.89	0.00	8.68			
1291	0.00	100.00	67.86	0.00	100.00	3.57	0.00	8.68			
1184	0.00	100.00	62.23	0.00	100.00	3.27	0.00	8.68			
1086	0.00	100.00	57.06	0.00	100.00	2.999	0.00	8.68			
995.6	0.00	100.00	52.33	0.00	100.00	2.750	0.00	8.68			
913.0	0.00	100.00	47.98	0.00	100.00	2.522	0.00	8.68			
837.2	0.00	100.00	44.00	0.14	100.00	2.312	0.16	8.68			
767.7	0.00	100.00	40.35	0.21	99.86	2.121	0.24	8.52			
704.0	0.00	100.00	37.00	0.24	99.65	1.945	0.26	8.28			
645.6	0.00	100.00	33.93	0.32	99.41	1.783	0.28	8.02			
592.0	0.00	100.00	31.11	0.43	99.09	1.635	0.32	7.74			
542.9	0.00	100.00	28.53	0.62	98.66	1.499	0.36	7.42			
497.8	0.00	100.00	26.16	0.88	98.04	1.375	0.40	7.06			
456.5	0.00	100.00	23.99	1.23	97.16	1.261	0.45	6.66			
418.6	0.00	100.00	22.00	1.69	95.93	1.156	0.51	6.21			
383.9	0.00	100.00	20.17	2.21	94.24	1.060	0.56	5.70			
352.0	0.00	100.00	18.50	2.80	92.03	0.972	0.62	5.14			
322.8	0.00	100.00	16.96	3.48	89.23	0.892	0.66	4.52			
296.0	0.00	100.00	15.56	4.25	85.75	0.818	0.68	3.86			
271.4	0.00	100.00	14.27	5.22	81.50	0.750	0.67	3.18			
248.9	0.00	100.00	13.08	6.40	76.28	0.688	0.63	2.51			
228.2	0.00	100.00	12.00	7.69	69.88	0.630	0.56	1.88			
209.3	0.00	100.00	11.00	9.11	62.19	0.578	0.46	1.32			
191.9	0.00	100.00	10.09	9.84	53.08	0.530	0.38	0.86			
176.0	0.00	100.00	9.25	9.94	43.24	0.486	0.30	0.48			
161.4	0.00	100.00	8.48	8.80	33.30	0.446	0.18	0.18			
148.0	0.00	100.00	7.78	6.49	24.50	0.409	0.00	0.00			
135.7	0.00	100.00	7.13	4.40	18.01	0.375	0.00	0.00			
124.5	0.00	100.00	6.54	2.44	13.61	0.344	0.00	0.00			
114.1	0.00	100.00	6.00	1.26	11.17	0.315	0.00	0.00			
104.7	0.00	100.00	5.50	0.66	9.91	0.2890	0.00	0.00			
95.96	0.00	100.00	5.04	0.33	9.25	0.2650	0.00	0.00			
88.00	0.00	100.00	4.62	0.17	8.92						
80.70	0.00	100.00	4.24	0.07	8.75						

Figure 27: PSD of mMST used in current testing

Distribution:

T. B. Brown, 773-A
D. R. Click,
E. N. Hoffman,
F. M. Pennebaker, 773-42A
S. D. Fink, 773-A
S. L. Marra, 773-A
M. R. Poirier, 773-42A
F. F. Fondeur, 773-A
D. T. Hobbs, 773-A
W. R. Wilmarth, 773-A
D. C. Koopman, 999-W
C. J. Martino, 773-42A
C. A. Nash, 773-42A
T. B. Peters, 773-42A
T. C. Shehee, 773-A
K. M. L. Taylor-Pashow, 773-A
R. K. Leugemors, 704-67S
K. Hewitt,
W. B. Brasel, Parsons, 992-2W
T. D. Burns, Parsons, 992-5W
M. Brugh, Parsons,
K. D. Harp, 766-H
C. S. Weston, 766-H
D. J .Martin, 241-152H
C. Conner, Parsons
R. D. Lentsch, Parsons
A. N. Singer, Parsons
R. J. Schepens, Parsons
P. G. Suggs, 704-S
C. I. Aponte,