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2012 SRNL-EM VANE RHEOLOGY RESULTS

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EXECUTIVE SUMMARY

The work described in this document supports the Department of Energy Environmental Management and Technology Development in furthering the capability of the vane method to assess the rheological properties of homogeneous and settled slurries in a larger bed as compared to bench top data. The scope of work covers the following items:

- Fabricate vane instrument.
- Bench top testing to further characterize the effect of cohesive and non-cohesive simulants.
- Data from measurement of homogenized and settled bed of Kaolin sludge and assessment of the technology.

The vane method was used to characterize the yield stress of four different non-cohesive glass beads as a function of depth and forced settling (tapping) using bench top equipment. The results indicate the following:

- Surface measurement results are insensitive to tapping or particle size distribution.
- Tapping increases the yield stress for a given submergence for all beads.
- Yield stress response is somewhat linear with depth other than the deepest measurement. The deepest measurement may be impacted by the bottom of the container resulting in a much higher response than expected for a linear relationship.
- In all cases, the glass beads easily poured out of the containers upon completion of testing, indicating the measured yield stress is a "confined" yield stress created by the wall of this container and the mechanical (hard body) interactions of the solids.

The vane was used to characterize the rheology of xanthan gum using both the vane method and vane flow curve. These results were compared to the traditional flow curve (concentric cylindrical method). All measurements were bench top and the results are:

- The traditional flow curve yielded the highest yield stress, followed by the vane flow curve and final the vane method. The reason for this is the range of shear rate measured and the range in which the data were fitted in the individual flow curves. The traditional flow curve had a much large shear rate range of measurement.
- The vane method showed an elastic modulus that was very short and a viscoelastic response that was long before the dynamic yield stress was reached. This response could be typical for such a fluid, where the continuous phase is non-Newtonian.

A conventional mixer (Rushton impeller) was used to prepare 15 to 32.5 weight percent (wt%) kaolin slurries and they were continuously mixed for up to 22 hours. Samples at 2 hour intervals were pulled and analyzed using the vane method, vane flow curve, and traditional flow curves as well as for wt% total solids and density. A 22.5 wt% slurry was prepared using a high shear mixer and analyzed using the traditional flow curve. Finally, 22.5 and 25 wt% slurries were analyzed for particle size distribution at 2 and 9 hours of mixing. All measurements were bench top and the results are:

- The traditional flow curve yielded the highest yield stress, followed by the vane flow curve and finally the vane method. The reason for this is the range of shear rate measured and the range in which the data were fitted in the individual flow curves. The traditional flow curve had a much large shear rate range of measurement.

- As the wt% solids increased, the difference between the vane measurements and traditional flow curve yield stresses increased. This is attributed to an increase in a more power law response at the lower shear rate range in the traditional flow curve as the wt% solids increased and curve fitting the linear region of the flow curve.
- For 20 wt% or greater kaolin concentration, the yield stress tends not to change much after 14 to 16 hours of mixing, given the mixing system used in this task.
- The vane method for the less than 22.5 wt% kaolin slurries does not show the typical or expected vane response, though the yield stresses as measured using the other methods are very similar.
- The vane method response to the kaolin slurries was different than that of the xanthan gum, where for the kaolin slurries there was a very small viscoelastic response region.
- An exponential model was used to fit the Bingham Plastic parameters of the traditional flow curve as a function of wt% TS for the different mixing times. The curve fit was good. One data set was assessed by fitting the data with the same model but using a limited number of data points to see the effect of interpolation and extrapolation. Interpolation fitted well with the actual data points whereas extrapolation in this case over-estimated the yield stress.
- The 22.5 wt% high sheared slurry resulted in rheological properties that were a factor of two greater as compared to the Rushton mixed sample and mixing times were reduced over a hundred fold. The sample was sheared at both high and very high shear rates and the rheological properties increased at the very high shear rates. The rate of applied shear and the time of shearing affect the rheological properties of kaolin.
- The particle size distribution shifted to a smaller distribution when continuously mixed using the Rushton impeller. The shift to a smaller particle size distribution is one of the parameters that is most likely affecting the rheological properties of kaolin. Sonication of these samples showed even a further shift to a smaller particle size distribution.

A large scale vane was designed, fabricated, and tested. The vane had the following capabilities:

- Measure up to 50 inches of slurry, homogenized or settled.
- Two different torque sensors, 0 to 0.5 N-m and 0 to 5 N-m.
- Five different vane sizes with A factors ranging between 139 to 1720 m^{-3} for subsurface measurements and 159 to 2148 m^{-3} for surface measurements.
- Vertical vane position and the rate of insertion in and out of the fluid are controlled.
- Rotational rate between 0.05 to 28 revolutions per minute.
- A 5 foot tall by 12 inch inside diameter tank for loading simulants.

The large scale vane was benchmarked against the bench top rheometer using 30 and 35 wt% kaolin slurries using both the vane method and vane flow curve with the following results:

- The vane method results for the 6x6 vane compared well with the bench top (up to $\pm$ 5%) over a range of 0.05 to 0.6 RPM. The vane method results for the 3x5 vane slightly under-estimated the 30 wt% and slightly over-estimated the 35 wt% as compared to the bench top (up to $\pm$ 20%) over a range of 0.05 to 0.6 RPM.
- The 3x5 and 6x6 vane flow curves are similar.
- The 3x5 and 6x6 vane flow curves yield smaller Bingham Plastic parameters as compared to the bench top results.
- The 3x5 and 6x6 vanes produced a circular cut through the fluid, supporting the vane method assumption (cylindrical shape) used in assessing the vane for yield stress.

The large scale vane was tested using a 3 wt% xanthan gum solution. The xanthan gum filled the 5 foot tank and three data points at any given elevation were obtained using the 3x5 or 6x6 vane with the following results:

- The vertical yield stress distribution was fairly flat using either the 3x5 or 6x6 vanes based on the initial vane measurement. The effect of depth did not impact the vane method result.
- The 2nd set of vane measurements showed that xanthan gum is highly impacted by shear history and this was supported by the bench top vane results.
- The bench top vane results were greater than the 3x5 or 6x6 vane results.

The large scale vane was tested using a 35 wt% kaolin slurry. The 3x5 vane was selected for this testing since it could obtain more vertical data points than the 6x6 vane. Both fresh (just mixed and placed kaolin slurry) and settled (3 month) 35 wt% data were obtained with the following results:

- The vertical yield stress distribution for the fresh slurry was fairly flat, indicating that slurry depth had no impact on the vane results for fresh properties. This was consistent with the xanthan gum results.
- The initial large scale vane results were comparable to the initial bench results.
- Subsequent vane method measurements showed the 35 wt% kaolin slurry to be somewhat thixotropic and this was evident in both the large scale vane and bench scale.
- After 3 months of settling, the average calculated solids concentration in the settled bed of kaolin increased by 2.36 wt%.
- The vertical yield stress distribution for the settled bed showed a vertical yield stress distribution, becoming thicker as the depth increased. The yield stress at 8 inches from the top of the settled bed was 43 Pa and at 53 inches it was 123 Pa. Six vertical data points were obtained and these data fit well to an exponential model.
- The second vane method measurement showed the settled bed to be much more thixotropic as compared to the fresh state. The initial measurements are important in determining the bed yield stress.
- Vane flow curves were obtained at 17 and 53 inches below the surface. Thixotropic properties were removed using the vane at 25 RPM. The results clearly show the flow curve at the 53 inch level to be much thicker than that at the 17 inch level.

The use of xanthan gum or other rheology modifiers that directly dissolve and become part of the continuous phase to make the solution non-Newtonian is not recommended for future testing. In the DOE realm of waste, the continuous phase is a solution that only has Newtonian properties and the undissolved solids is the phase that contributes to the non-Newtonian behavior.

The following recommendations are to further develop the capabilities of the vane for use in measuring the rheological properties of slurries and implementation for in situ measurements of both settled and homogenized slurries in actual tank farm operations or test programs:

- Compare the bench top and large scale using the vane method to see whether the bench top measurements can be used to assess for settled solids or aging effects that could occur in a large settled bed. The bench top container and vane must be modified such that depth measurements on the bench scale can be made. Simple single point bench scale vane method measurements are not sufficient.
- Quantify whether the vane can be used to determine the flow properties of non-Newtonian fluids on the bench scale. Only cover the rheological range of properties that can typically be mixed or transferred in the DOE complex. This work should initially be performed on the bench scale and then taken to the large scale vane.
- Perform bench scale tests with cohesive slurries containing non-cohesive materials to determining how the non-cohesive materials settle out over time and how they impact the rheological properties. The cohesive materials should have a range of rheological

properties. The non-cohesive materials should include solids that have different densities and particle size distributions. The concentration of these non-cohesive materials should also be a variable. These properties can be determined at a later date.

- Use the existing large scale vane to investigate whether the settled bed of cohesive solids packs differently if the initial starting wt% solids concentration of the slurry is a variable. Obtain settled bed material to quantify both density and wt% solids so as to relate these data back to the yield stress measurements. The effect of settling time should also be included. The initial cohesive simulant should be a simple simulant. Bench scale tests should be run concurrently to determine whether scale is an issue, e.g. the height of the settled bed is a factor.
- Use the existing large scale vane to determine when shaft contributions start to impact the vane measurement.
- Use the existing large scale vane and results from the bench scale testing to determine the effect of non-cohesive solids on the settled bed of cohesive solids. These data must be compared to bench top data to determine whether bench top data can be used to assess settling or aging.
- Design, fabricate and test a large vane that has attributes that can be deployed to a full scale vane for plant measurements. Such attributes would include how to extend the shaft, easy replacement of components, and upgrading instrumentation and equipment capability.

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LIST OF ABBREVIATIONS

DOE	Department of Energy
SRNL	Savannah River National Laboratory
EM	Environmental Management
TDD	Technology Development and Deployment
TS	Total Solids
NIST	National Institute of Standards and Technology
LSV	Large Scale Vane Platform
PV	Plastic Viscosity (from Bingham Plastic model)
BPYS	Bingham Plastic Yield Stress
PSD	Particle Size Distribution

1.0 Introduction

The vane method has been shown to be an effective tool in measuring the yield stress of both settled and mixed slurries in laboratory bench scale conditions in supporting assessments of both actual and simulant waste slurries. [1], [2], [3], [4] The vane has also been used to characterize dry powders and granular solids[5], the effect of non-cohesive solids with interstitial fluids [3], [6], [7] and used as a guide to determine if slip is present in the geometries typically used to perform rheological flow curve measurements.[8] The vane has been extensively characterized for measuring the shear strength in soils in both field and laboratory studies.[9]

The objectives for this task are stated below and are from the Department of Energy (DOE) Environmental Management (EM)-30 Technology Development and Deployment (TDD) Program Task Plan, Task 3.2.1. [10]

- Fabricate vane instrument.
- Bench top testing to further characterize the effect of cohesive, non-cohesive, and blends of cohesive/non-cohesive simple simulants.
- Data from measurement of homogenized and settled bed of Kaolin sludge and assessment of the technology.

In this document, the assessment using bench scale measurements of non-cohesive materials (beads) and cohesive materials (kaolin) is discussed. The non-cohesive materials include various size beads and the vane was assessed for depth and deaeration (or packing) via tapping measurements. For the cohesive (or non-Newtonian) materials, flow curves and yield stress measurements are performed using the vane and this data is compared to the traditional concentric cylinder flow curve measurement. Finally, a large scale vane was designed, fabricated, and tested with the cohesive (or non-Newtonian) materials to determine how a larger vane performs in measuring the yield stress and flow curve of settled cohesive solids.

2.0 Experimental Procedure

The experimental procedure section consists of the following sections: (2.1) simulant selection description and preparation, (2.2) measurement techniques, (2.3) full scale vane, (2.4) bench scale simulant testing, and (2.5) full scale simulant testing.

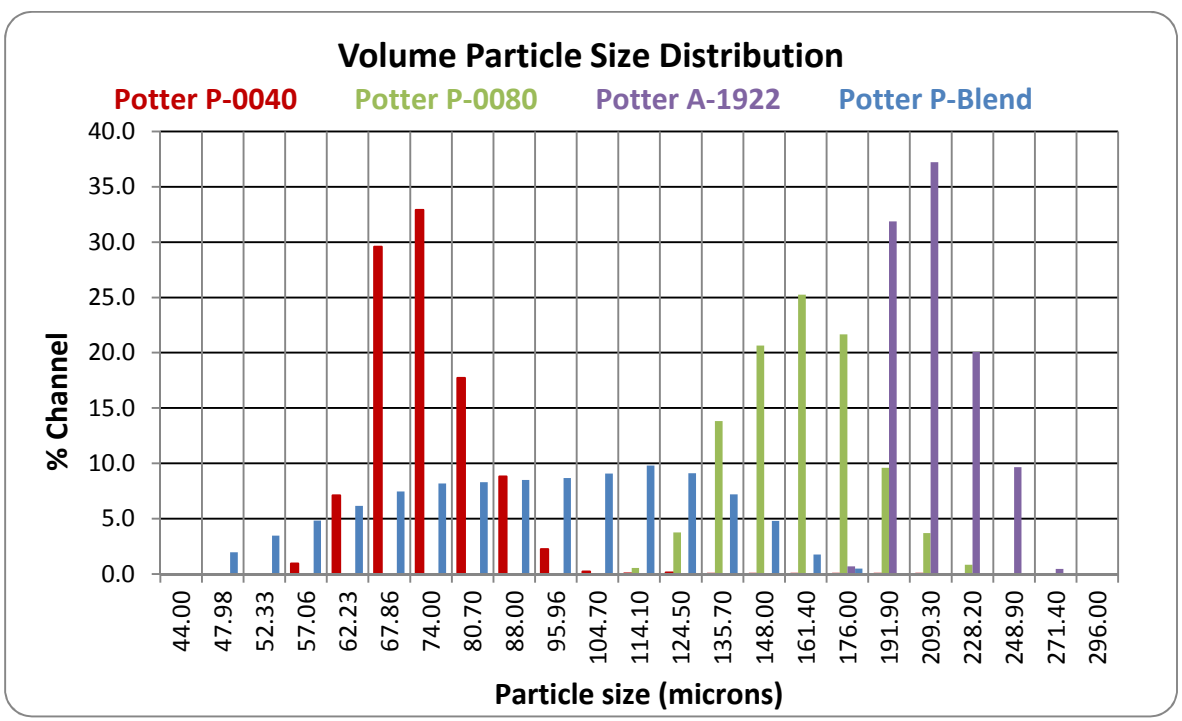
2.1 Simulants

The non-cohesive simulants are type A and P glass beads made by Potters and at least 90% are spherical[i]. These beads have been used in previous programs, hence were readily available for testing. The particle size distribution and analysis of these beads were performed with a Microtrac S3000 using DI water as the carrier fluid. The densities of the beads are 2.5 g/cm^3 and the volume, area, and number means are provided in Table 2-1. The particle size distribution is provided in Figure 2-1. The distribution of the P-blend is broad compared to the other beads.

Mean Variable	Potter Bead Designation			
	P-0040	P-0080	A-1922	P - Blend
Volume (μm)	75.2	164.0	207.4	115.9
Area (μm)	73.6	161.2	205.7	108.8
Number (μm)	71.4	155.8	202.4	92.3

Table 2-1 Mean Volume, Area and Number of Potter Glass Beads Used

Figure 2-1 Volume Distribution of Potter Beads Used



[i] Per vendor description of their products. This was not validated using visual microscopy.

The beads were used as is, where they were taken directly from their container and placed into the measuring container. No effort was made to remove any residual moisture that may have been present on the beads.

Two types of non-Newtonian simulants were used, xanthan gum from Sigma-Aldrich and EPK kaolin from Edgar Minerals. The xanthan gum has been used in previous conventional mixing studies and the EPK kaolin has been used to support Hanford jet mixing activities. These two materials can produce non-Newtonian fluids, though through different mechanisms. The xanthan gum effects the continuous phase of the liquid (in this case, water) and the resulting product is a homogenous product, where no settling occurs due to the dissolution of the xanthan gum into the continuous phase. There is a concentration at which dissolved xanthan gum makes the fluid non-Newtonian. The concentration of xanthan gum in water has little effect on density. The EPK kaolin is also blended with water, but unlike xanthan gum, the kaolin does not dissolve. Kaolin has a very broad distribution of solids and the particles are typically in the micron range or smaller. The density of the kaolin particles is 2.65 g/cm^3.[ii] The kaolin is blended with water and non-Newtonian properties occur at some minimum solids concentration. Unlike xanthan gum, if this kaolin-water slurry is allowed to remain at rest (no mixing), the kaolin solids will separate, resulting in a clear standing water on top of the settled solids. There is a solids concentration where no visual separation (settling) will occur, but such a case was not tested.

2.2 Measurement Techniques

The following bench scale measurements were used in this task, (1) solids analysis, (2) density, (3) particle size, and (4) rheology.

2.2.1 *Solids Analysis*

Samples used for solids analysis were homogenized (shaking of the bottle) prior to performing the analyses.

The Mettler Toledo HR83 Halogen Moisture analyzer, Figure 2-2, was used to analyze for weight percent (wt%) total solids (TS). This moisture analyzer uses a load cell that continuously measures the mass placed on the cell. Water and volatiles are evaporated using a halogen heat lamp that is controlled by an infrared thermometer that measures the temperature of the surface of the sample. The mass of the sample pan and sample mesh is first measured and the weight tared. The sample is homogenized via rapid shaking of the sample and approximately 1.5 to 3 grams of a sub-sample is placed onto the mesh (which helps absorb and distribute the liquid) and this mass is recorded by the analyzer. The temperature of the sample is then ramped to 105°C and maintained throughout the measurement. The measurement stops when the weight of the sample does not change more than 1 milligram over a 20 second period and this final mass is recorded by the analyzer. The wt% TS is the ratio of the final mass (M_{TS}) to initial mass (M_T)multiplied by 100%, equation (2-1). The analyzer load cell is checked on a daily basis (when used) using a 2.0 gram weight and functionally checked using a 8.0 wt% TS NaCl solution. Duplicate samples are run and the data averaged.

$$\text{wt\% TS} = \frac{M_{TS}}{M_T} \cdot 100\% \qquad \textbf{(2-1)}$$

[ii] Per vendor MSDS 43685.

Figure 2-2 Mettler Toledo HR83 Halogen Moisture Analyzer

2.2.2 *Density*

Densities were measured using an Anton Paar DMA 4500 Density analyzer, Figure 2-3. A sample is pushed into the density analyzer glass u-tube and the sample temperature controlled to 25°C. A vibration is then induced on one end of the u-tube and the frequency is measured at the other end. The density of the sample is determined based on the measured frequency shift. The density analyzer is functionally checked on a daily basis (when used) with DI water. Duplicate samples are run and the data averaged.

Figure 2-3 Anton Paar DMA 4500 Density Analyzer

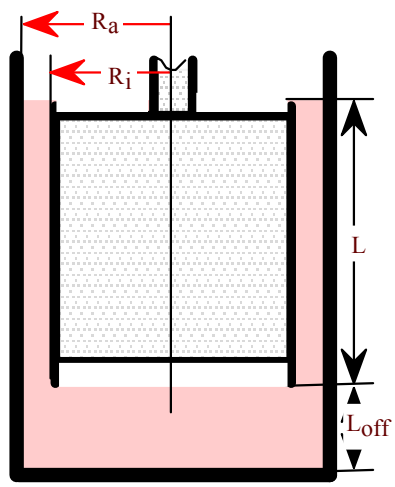
2.2.3 *Rheology*

Rheological measurements were obtained using the Haake RS600 rheometer. The flow curve measurements were obtained using the Z41 cylindrical rotor and their specifications are shown in Table 2-2. The cup and rotor are initially installed onto the rheometer and then the zero reference point is

determined by the rheometer by raising the cup until the bottom of the cup makes contact with the rotor. The cup is then lowered and the rotor and cup are removed. The appropriate sample volume is added to the cup and the cup and rotor are then reinstalled onto the rheometer. The rheometer drives the rotor into the predetermined bottom off-set position based on the rotor. A cooling/heating bath is used to control the temperature of the rotor/sample/cup at 25°C. The rheometer is programmed to control the rate at which the rotor spins and measures both the rotational speed and the torque (the resistance to shear), and this method is known as the control shear rate. The shear stress at the wall of the rotating rotor is then calculated (internally by the Haake™ software) based on the product of the measured torque and geometry (A-factor) of the rotor. The shear rate of the rotating rotor is calculated as the product of the measured speed and geometry (M-factor) of the rotor/cup and assumes the fluid is Newtonian. The A-factor, M-factor, and flow curve (shear rate range and the linear ramp up time, hold time at maximum shear rate, and linear ramp down time) are provided in Table 2-2. The linear ramp rates (or acceleration) is $\pm$ 30 sec^{-1} per minute.

Table 2-2 Z41 Rotor Specification and Program Ramp Rates

Design of Rotor



Z41 Rotor Specifications

Rotor	Z41
Rotor radius (mm)	R_i = 20.710
Cup Radius (mm)	R_a = 21.700
Height of rotor (mm)	L = 55
Sample Volume (cm^3)	V = 14
Bottom off-set (mm)	L_{off} = 3
A factor (Pa/(N·m))	6750
M factor (s^{-1}/rad s^{-1})	22.4
Shear rate measuring range (s^{-1})	0 – 1000
Ramp up time (min)	5
Hold time (min)	1
Ramp down time (min)	5

Prior to any flow curve measurement, the rotor and cup are inspected for visual damage that could potentially impact the rheological measurement. A National Institute of Standards and Technology (NIST) traceable Newtonian oil standard is then used to verify the operability of the rheometer at a measurement temperature of 25°C. The NIST flow curves are analyzed as a Newtonian fluid and the calculated viscosity is compared to that of the NIST traceable Newtonian oil standard. The rheometer is considered operable if the calculated viscosity is within $\pm$ 10% of the NIST traceable Newtonian oil standard viscosity. The NIST traceable Newtonian oil standard was run each day that a flow curve or vane measurements was required. The measured viscosities were always within the $\pm$ 10% of the standard. Upon completion of a flow curve measurement, the bottom of the rotor is inspected to determine if the sample completely fills the void space, and if so noted. This void space is an air buffer, where the shear stress contribution is negligible compared to the shear stress contribution from the cylindrical section of the rotor, which is in complete contact with the fluid during the flow curve measurement. The effect of the bottom void being completely filled is an increase in the measured shear stress. In all cases, the void was never completely filled.

For all baseline samples, a minimum of two flow curve measurements were performed. The non-Newtonian fluids are analyzed as a Bingham Plastic fluid, equation (2-2). Because these fluids are not true Bingham Plastic fluids, the shear rate range in which the data is fitted are also provided.

$$\tau = \tau_o + \eta_\infty \dot{\gamma} \qquad \textbf{(2-2)}$$

Where: τ = the shear stress (Pa)
τ_o = the Bingham Plastic yield stress (Pa)
η_∞ = the plastic viscosity (Pa-sec)
$\dot{\gamma}$ = shear rate (1/sec)

The rheological properties can be estimated given another physical property, such as wt% undissolved solids, which for cohesive or micron size particles are typically the controlling parameter for a salt based slurry. In this case, where only kaolin and water will be used, this relationship will be related to total solids, which is that of the kaolin itself.. The simplest relationship relating rheological to wt% TS is the exponential model, equation (2-3) and requires at least two data points, though at least three is recommended as a minimum to fit this equation. Other models which have additional fitting parameters have been used, but as the number of parameters increase, more data points are required.

$$\tau_o = \mathrm{a}e^{b \cdot wt\%TS}. \qquad \textbf{(2-3)}$$

Vanes have been used to measure the yield stress (or shear strength or settled solids yield stress) of non-Newtonian fluids.[11,12,13,14,15,16,17] For laboratory measurements, the conditions shown in Figure 2-4 must be satisfied. The vane is inserted into the fluid and is rotated at a very slow speed, unlike in flow curve measurement, typically between 0.1 to 0.7 rpm. The cylindrical surface area cut by the vane is used to determine the shear stress. It has been shown that this assumption is adequate for determining the yield stress of the fluid using the vane.[16, 17] Equation (2-4) is used to determine the yield stress and it assumes the yield stress is uniform. If there is not sufficient sample and the other geometric conditions are met, the yield stress can be determined using equation (2-5) where the vane is submerged to a point where it is flush with the surface of the sample. In this case, stress contribution from the top circular surface is that from air and is negligible.

$$\tau_y = \frac{\Gamma}{\frac{\pi \cdot D^3}{2}\left(\frac{H}{D}+\frac{1}{3}\right)} = A \cdot \Gamma,\ A = \frac{2}{\pi \cdot D^3\left(\frac{H}{D}+\frac{1}{3}\right)} \qquad \textbf{(2-4)}$$

$$\tau_{y,sur} = \frac{\Gamma}{\frac{\pi \cdot D^3}{2}\left(\frac{H}{D}+\frac{1}{6}\right)} = A_{sur} \cdot \Gamma,\ A_{sur} = \frac{2}{\pi \cdot D^3\left(\frac{H}{D}+\frac{1}{6}\right)} \qquad \textbf{(2-5)}$$

Where τ_y= yield stress, shear strength or settled solids yield stress (Pa)
$\tau_{y,suf}$ = yield stress, shear strength or settled solids yield stress measured at surface (Pa)
Γ = measured torque (N·m)
D = diameter of vane (m)
H = height of vane (m)
A = geometric constant (m^{-3})

A typical stress versus time (or displacement) curve for a vane measurement is shown in Figure 2-5. The initial vane response for a non-Newtonian fluid having a yield stress is typically linear with a slope that is called the Hookean elastic modulus (G). The point of departure from this linear region, called the static

yield stress,[11] occurs when the fluid starts to transition from a fully elastic to viscoelastic behavior. At the maximum stress, the behavior of the material transitions between viscoelastic and fully viscous and is called the yield stress (also known as the dynamic yield stress). This maximum shear stress is the reported yield stress using the vane.

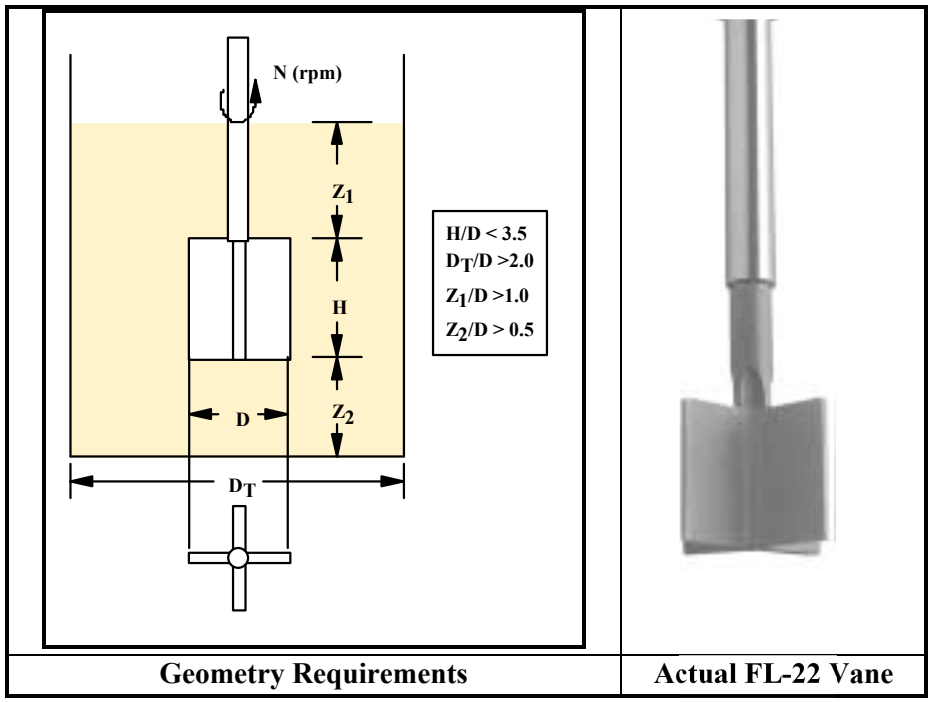


Figure 2-4 Vane Requirements and Actual Vane

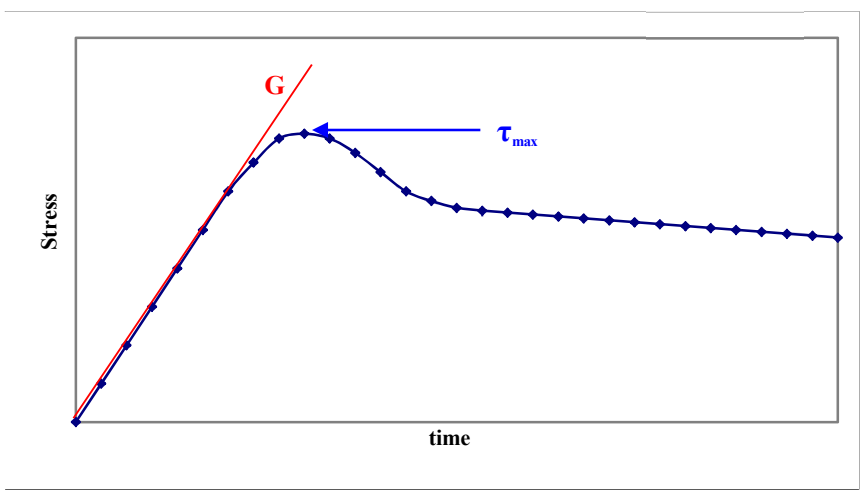


Figure 2-5 Typical Vane Torque Versus Time/Displacement Curve

All bench scale measurements were performed using the dimension of the Haake FL-22 vane. SRNL fabricated additional vanes using the same vane dimensions to allow measurements of varying depths and to investigate how a bent shaft could impact the measurement, see Figure 2-6. Time did not permit investigating the bent shaft.

The height and diameter of the FL-22 vane are 16 mm and 22 mm respectively. The A factor for surface and submerged measurements are 66,881 m^{-3} and 56,371 m^{-3} respectively, using equations (2-4) and (2-5). For submerged depth measurement, no correction of the submerge shaft was considered, which would have slightly reduced the yield stress.

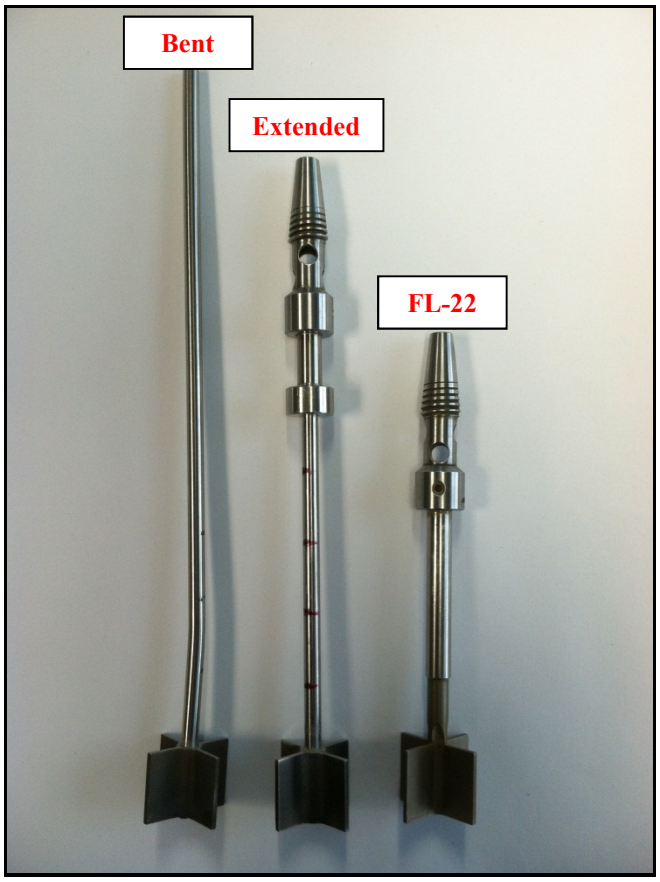


Figure 2-6 Bench Scale Vanes with The Same Vane Geometry (A-Factor)

The rotational speed for measuring the yield stress using the vane was 0.3 RPM for all the simulants used in this task. The vane has been used to measure the yield stress of dry/wet beads/granular solids,[3,5,6,7] but the results are questionable in how they should be applied to the various process operations in the DOE complex, if any.

Finally, vane flow curves were obtained for the non-Newtonian fluids by rotating the shaft between 0 to 40 sec^{-1} (M factor of 1.7 was used in the Haake software) and this data was fitted to a Bingham Plastic model, without correcting for the shear rate. Due to the complex geometry of the vane and the large gap between the vane and the wall, correcting the shear rate was not performed. Simplistic methods, such as the Otto-Metzner method where a linear relationship between the rotational speed is obtained (such as that of an M factor) for the average shear rate were not performed or used.[18] This method is independent of the diameter and can either be obtained from literature (if previously analyzed) or determined using a range of NIST traceable Newtonian fluids.

2.2.4 *Particle Size Distribution*

Particle size distributions (PSD) were measured using a Microtrac S3500 particle size analyzer. The S3500 uses a Tri-Laser system that uses angular measurement of scattered light through a full 180 degree angular range with three lasers and two detector arrays. The Tri-Laser System analyzes the scattered light to determine particle size using the Mie based unified angular scattering theory from large particle analysis to small particle analysis. For the kaolin simulants, the samples were analyzed and then sonicated and re-analyzed. DI water was used as the carrier fluid for all the simulants. Triplicate measurements were made and averaged.

2.3 Full Scale Vane

A large scale vane platform (LSV) was designed and fabricated to permit measuring about 5 vertical feet of fluid (see Figure 2-7 and Figure 2-8). The LSV is predominately made of aluminum and the vanes were all made of stainless steel. The LSV used a Baldor servo driven linear actuator that controlled the vertical position and rate at which the vane traveled into and out of the fluid. A 17 MDSI stepper motor controlled the rotational rate of the vane, between 0.05 to 28 RPM. Two different sized inline torque transducers were procured, one providing a range between 0 to 0.5 Nm and the other between 0 to 5 Nm. These transducers were calibrated at the factory. A data acquisition and control system was used to control the LSV and record the linear and rotating speed settings, torque measurement, and vertical location. Five different vanes were fabricated and their nominal dimensions and the subsurface and surface A factors are provided in Table 2-3. All vane shafts are ½ inch in diameter and connect to the torque transducer via a coupling. Care was used to minimize balance issues during the fabrication of the vane, since there was no method readily available to balance the vanes. All vanes had a slight wobble that was noticeable at the higher RPMs. At 0.1 to 0.7 RPM, wobble was not noticeable. The various vanes can be loaded onto the LSV chassis for storage (Figure 2-8). The torque sensor, drive length, and vane/torque connection are shown in Figure 2-9 and Figure 2-10. To mitigate any potential tipping issues with this design, 400 pounds of counterweights were used as shown in Figure 2-8. The tank used to hold the simulants is 59 inches tall and has an inside diameter of 12 inches and can be loaded and drained from the bottom drain valve (Figure 2-8). This tank was selected to minimize simulant usage given the maximum vane size. Modification to the LSV can be performed to extend the vertical track away from the base.

During the vane method measurements, a baseline air reference torque measurement is first made (there is no zeroing capability of the torque sensors used) and then the vane is inserted into the fluid to make the vane measurement. The baseline data is averaged and then subtracted from the vane measurement, yielding the measured torque of the vane going through the fluid. There was little difference between the baseline air measurements for a given day of measurements for a given vane set. Changing of the vane set can shift the zero position. For the vane flow curve, only one baseline air reference is made.

Table 2-3 Large Scale Vane Platform Vane Dimensions and A Factors

Vane Designator (in "x" in)	Height (cm)	Width (cm)	Subsurface A (m^{-3})	Surface A_{sur}(m^{-3})
1.5 x 3	3.835	7.62	1720	2148
2 x 4	5.08	11.584	531	677
3 x 3	7.62	7.62	1079	1233
3 x 5	7.62	12.497	346	420
6 x 6	15.24	15.037	139	159

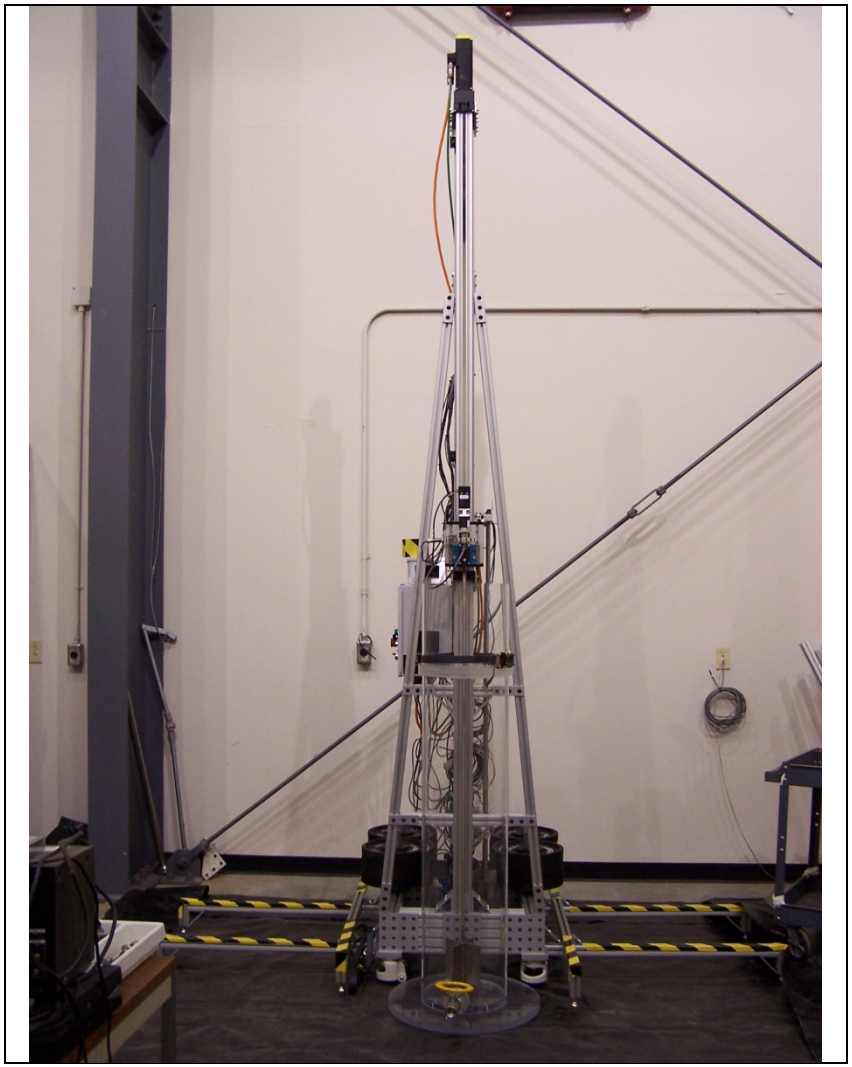


Figure 2-7 Full Vane – Front View, 6x6 Vane Installed

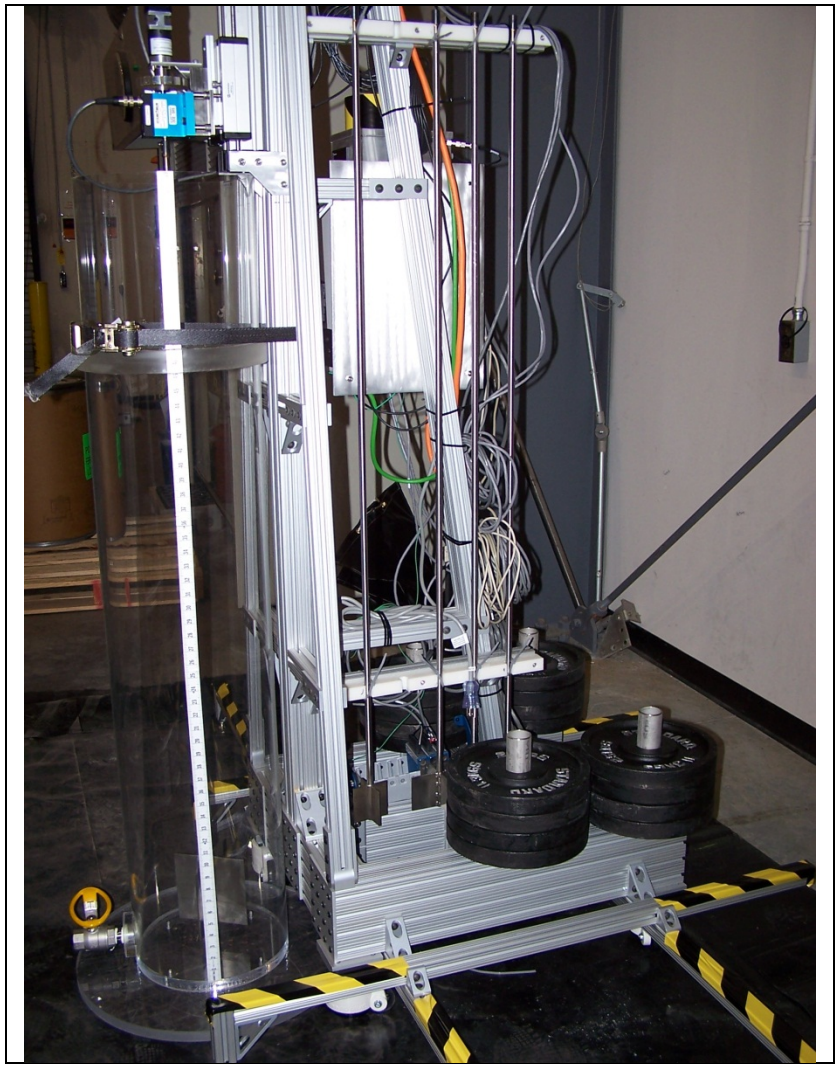


Figure 2-8 Full Vane – Side View, 6x6 Vane Installed

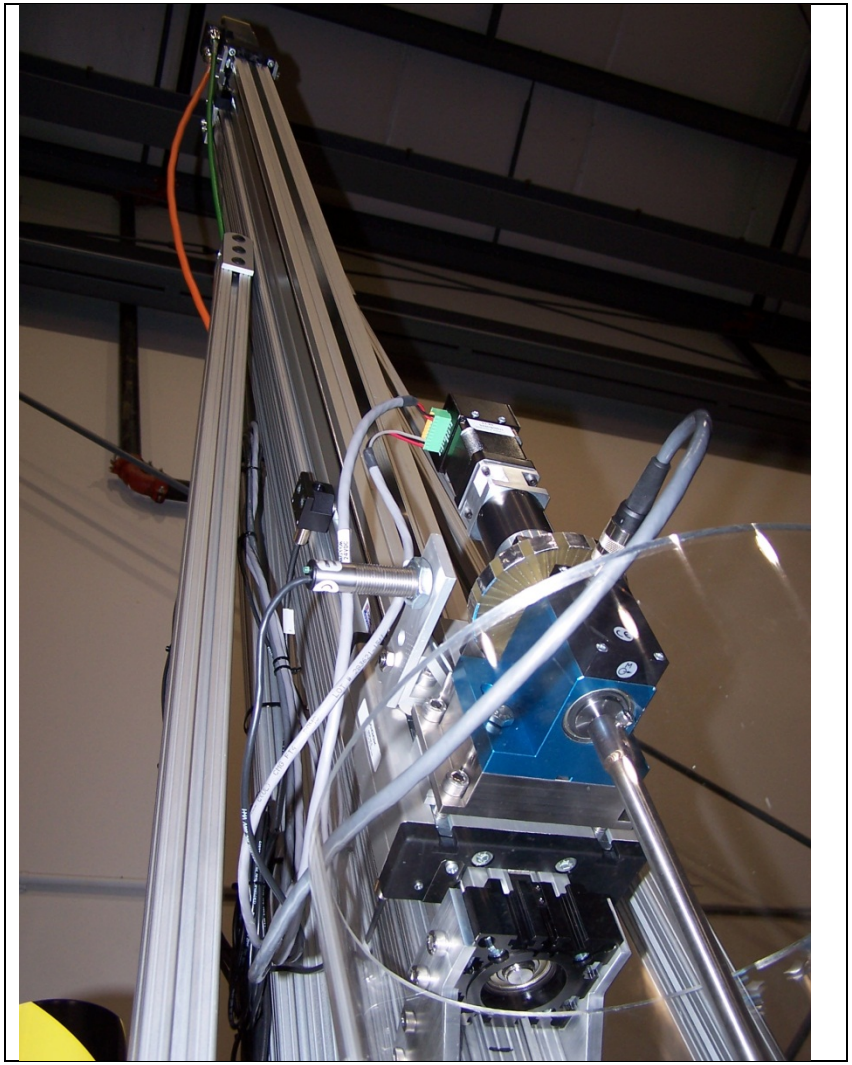


Figure 2-9 Full Vane – View of Vertical Track

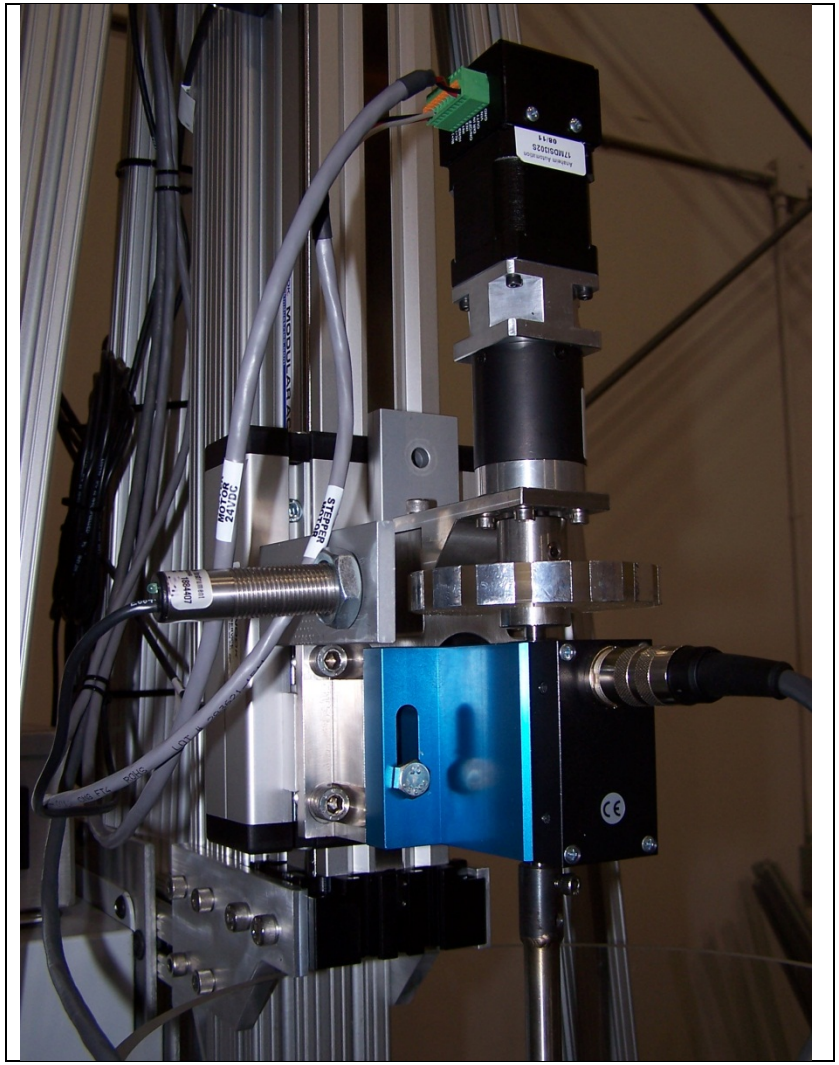


Figure 2-10 Full Vane – Torque Transducer

Unlike the bench scale vanes, the shafts on the LSV vanes are long, with a maximum immersion depth of 50 inches. The shaft can contribute to the torque measurements as the shaft is immersed further into the fluid. In this analysis, it is assumed that the stress contribution of the fluid is constant on all surfaces of the shaft and vane and there is no twisting of the shaft. The measured torque is the sum of the torque contribution from the vane and shaft. The shaft has a submerged diameter d and height h. The vane has a diameter D and height H. The total torque is:

$$\Gamma_{total} = \Gamma_{shaft} + \Gamma_{vane} \qquad \textbf{(2-6)}$$

The torque from the shaft is due to the shearing on the sides of the cylinder (e.g. no end contributions) and is given as:

$$\Gamma_{shaft} = \frac{\pi}{2} d^2 h \tau_s = \frac{1}{A_s} \tau_s, \qquad \textbf{(2-7)}$$

Where $A_s = \frac{2}{\pi d^2 h}$ (m^{-3})

The torque from the submerged vane is given by equation (2-4), hence the total shaft torque is:

$$\Gamma_{total} = \frac{1}{A_s} \tau_s + \frac{1}{A} \tau_y \qquad \textbf{(2-8)}$$

For constant fluid properties (e.g. yield stress), the above equation reduced to:

$$\Gamma_{total} = \left(\frac{1}{A_s} + \frac{1}{A} \right) \tau \qquad \textbf{(2-9)}$$

The fraction of torque contributed by the shaft is:

$$\mathrm{f}_{\Gamma_{shaft}} = \frac{\frac{1}{A_s}}{\frac{1}{A_s} + \frac{1}{A}} = \frac{A}{A + A_s} \qquad \textbf{(2-10)}$$

The fractional torque shaft contributions as a function of submerged shaft length for a constant properties fluid for the various fabricated vanes for the LSV are provided in Table 2-4. Given the potential range of yield stress of the non-Newtonian materials that will be tested, the 3x5 and 6x6 vanes were selected for testing. Shaft contributions will not be corrected in this task and the reported results will be an over-estimate of the yield stress. The fractional torque shaft contributions listed in Table 2-4 are most likely an overestimate due to the shear history and settling effects not being considered.

If the fluid properties are such that they are a function of depth (or from shear history or settling), then the shaft contribution can be determined using either equations (2-11) or (2-12). If the yield stress of the fluid is discrete for any given height (h_i), then equation (2-11) should be used. If the yield stress is a continuous function of fluid height, then equation (2-12) is the preferred equation.

$$\Gamma_{shaft} = \frac{\pi}{2} d^2 \sum_i h_i \tau_{s,i} \quad \textbf{(2-11)}$$

$$\Gamma_{shaft} = \frac{\pi}{2} d^2 \int_0^h \tau_{s,i}(h)\, dh \quad \textbf{(2-12)}$$

Table 2-4 Fraction of Torque Contribution Due to Shaft Immersion for the LSV Vanes

h (in)	Vane Designation					h (in)	Vane Designation				
	1.5 x 3	2 x 4	3 x 3	3 x 5	6 x 6		1.5 x 3	2 x 4	3 x 3	3 x 5	6 x 6
1	0.0109	0.0069	0.0034	0.0022	0.0009	26	0.2234	0.1529	0.0815	0.0547	0.0227
2	0.0217	0.0137	0.0068	0.0044	0.0018	27	0.2301	0.1579	0.0844	0.0567	0.0236
3	0.0321	0.0204	0.0101	0.0066	0.0027	28	0.2366	0.1628	0.0873	0.0587	0.0244
4	0.0424	0.0270	0.0135	0.0088	0.0036	29	0.2430	0.1676	0.0901	0.0606	0.0253
5	0.0524	0.0336	0.0168	0.0110	0.0045	30	0.2493	0.1724	0.0929	0.0626	0.0261
6	0.0623	0.0400	0.0201	0.0132	0.0053	31	0.2554	0.1771	0.0957	0.0645	0.0270
7	0.0719	0.0464	0.0233	0.0153	0.0062	32	0.2615	0.1818	0.0985	0.0665	0.0278
8	0.0813	0.0526	0.0266	0.0175	0.0071	33	0.2675	0.1864	0.1013	0.0684	0.0287
9	0.0906	0.0588	0.0298	0.0196	0.0080	34	0.2734	0.1910	0.1040	0.0704	0.0295
10	0.0996	0.0649	0.0330	0.0218	0.0089	35	0.2792	0.1955	0.1068	0.0723	0.0304
11	0.1085	0.0710	0.0362	0.0239	0.0097	36	0.2849	0.2000	0.1095	0.0742	0.0312
12	0.1172	0.0769	0.0394	0.0260	0.0106	37	0.2905	0.2044	0.1122	0.0761	0.0320
13	0.1258	0.0828	0.0425	0.0281	0.0115	38	0.2960	0.2088	0.1149	0.0780	0.0329
14	0.1342	0.0886	0.0456	0.0302	0.0124	39	0.3015	0.2131	0.1175	0.0799	0.0337
15	0.1424	0.0943	0.0487	0.0323	0.0132	40	0.3068	0.2174	0.1202	0.0818	0.0345
16	0.1504	0.1000	0.0518	0.0344	0.0141	41	0.3121	0.2216	0.1228	0.0836	0.0354
17	0.1583	0.1056	0.0549	0.0365	0.0150	42	0.3173	0.2258	0.1254	0.0855	0.0362
18	0.1661	0.1111	0.0579	0.0385	0.0158	43	0.3224	0.2299	0.1280	0.0874	0.0370
19	0.1737	0.1166	0.0609	0.0406	0.0167	44	0.3275	0.2340	0.1306	0.0892	0.0379
20	0.1812	0.1220	0.0639	0.0426	0.0176	45	0.3324	0.2381	0.1332	0.0910	0.0387
21	0.1886	0.1273	0.0669	0.0447	0.0184	46	0.3373	0.2421	0.1358	0.0929	0.0395
22	0.1958	0.1325	0.0699	0.0467	0.0193	47	0.3422	0.2461	0.1383	0.0947	0.0404
23	0.2029	0.1377	0.0728	0.0487	0.0202	48	0.3469	0.2500	0.1408	0.0965	0.0412
24	0.2099	0.1429	0.0757	0.0507	0.0210	49	0.3516	0.2539	0.1433	0.0983	0.0420
25	0.2167	0.1479	0.0787	0.0527	0.0219	50	0.3562	0.2577	0.1458	0.1001	0.0428

2.4 Bench Scale Simulant Tests

For the non-cohesive simulants (beads only), the beads were placed into two different sized beakers (smaller beaker D=1.9" H=2.25", large beaker D=3.25", H=4"). The smaller beaker allowed for a surface and one sub-surface measurement. The larger beaker allowed for a surface and four sub-surface measurements. The beakers once filled with beads were tapped once manually or placed on a tapper and tapped 100 times using a Quantachrome Autotap (Figure 2-11). The 100 taps was randomly selected, since the purpose was to see how settling (forced in this case) can effect non-cohesive vane measurements. For plotting purposes, half the vane height minus the total submergence depth will be used, since this is the center location of the vane relative to its measurement. The distances for the surface, 1st subsurface, 2nd subsurface, 3rd subsurface, and 4th surface measurements are 8, 24, 40, 56, and 72 mm respectively. Due to the vane requirements for measurement, the smaller beaker had to be reloaded for each

measurement. For the large beaker, the surface, 2nd subsurface and 4th subsurface measurements were made and the beaker had to reloaded for the other set of measurements. At least 2 measurements of each depth and condition were made.

Figure 2-11 Quantachrome Auto Tapper

For the xanthan gum solutions, 20 and 30 Pa Bingham Plastic yield stress fluids were selected for testing. The concentration of xanthan gum used was 2 grams and 2.67 grams per 1000 grams of DI water for a 20 and 30 Pa fluid respectively. These solutions were made using conventional mixers (Rushton blade) and the solution was mixed until all the solids dissolved. Flow curve, subsurface vane, and vane curves were measured.

For the EPK kaolin, 15, 17.5, 20, 22.5, 25, 27.5, 30, and 32.5 wt% kaolin batches were made. These batches were mixed between 16 to 22 hours. Batches were made such that a small vortex was maintained throughout the mixing time for all the blends and the agitator speed was dependent on the rheology of the sample and changed as the rheology changed. The mixing containers were two liter bottles with drilled out holes so that the agitator shaft could pass though so as to minimize evaporative losses. Mixing only occurred when staffing was available to perform the necessary measurements and mixing occurred for two consecutive days for each mix. Samples were pulled every two hours and analyzed for flow curve, subsurface vane, vane curves, total solids, and density. A set of 22.5 and 25 wt% kaolin batches were made and samples pulled at 2 and 9 hours of mixing and analyzed for particle size analysis, without and with sonication to determine the effect of mixing on PSD. Another set of 22.5 wt% kaolin was made using a high shear Ross HSM L100 laboratory mixer to mix the slurry for 7 minutes at high shear and for another 2 minutes at very high shear. Rheology measurements were made at 2, 3 5, 7 and at the end of the very high shear mixing.

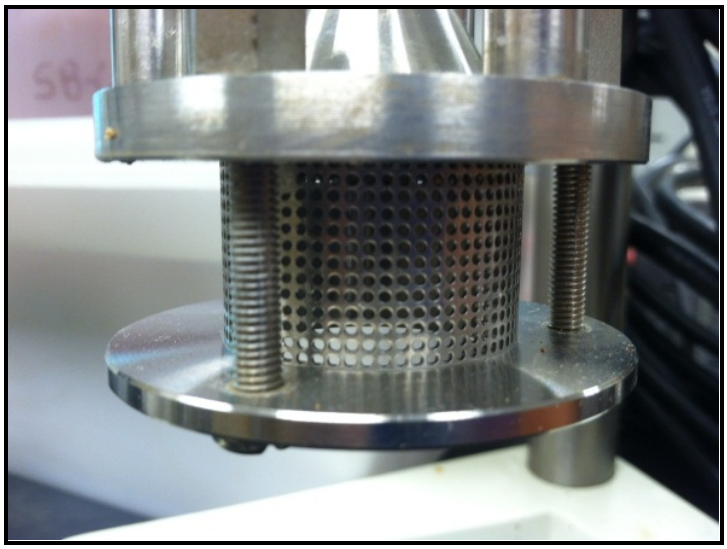


Figure 2-12 Cage used on Ross High Shear Mixer

2.5 Large Scale Vane (LSV) Tests

In the initial LSV tests, 5 gallon bucket tests were performed using 3 wt% xanthan gum and 30 wt% and 35 wt% EPK kaolin. In these tests, the RS600 was used to obtain rheological data for comparison. Vane and vane curve measurements were obtained from the LSV. The RS600 also captured the traditional flow curve. In these 5 gallon bucket tests, the non-Newtonian fluids in the bucket were mixed between measurements, so as to remove shear history on the measuring surfaces. In these tests, the 6x6 and 3x5 vanes were used.

A 3 wt% xanthan gum solution and 35 wt% kaolin slurry were used for the large scale vane tests. These fluids were mixed in a 55 gallon drum using a propeller blade and mixed for at least 24 hours prior to use. The fluids were transferred to the LSV tank, filling this tank using the bottom drain valve. During these transfers, air entrainment was kept to a minimum (suction was taken from the bottom of the 55 gallon drum) so as not to effect the measurements in the LSV tank. The 3x5 vane was primarily used in these measurements. Variable depth vane measurements were made of the simulants once they were completely loaded into the LSV tank so as to minimize aging effects in the measurements. A second set of measurements were performed to obtain additional data. The measurements started from the top and then down. Vane curve measurements were also obtained near the top and bottom of the LSV upon completion of the vane measurements. Subsamples were pulled while filling the LSV from the 55 gallon drum and measured by the RS600 for comparison. In these tests, due to how the vane measurements are performed, shear history was taken into consideration and RS600 data as generated for comparison.

The 35 wt% kaolin slurry was allowed to settle undisturbed for 3 months (12/8/2011 to 3/11/2012). This test was to show the capabilities of the vane to measure the settled solids shear strength as a function of depth. Vane curve measurements were also obtained for the 2nd and deepest subsurface measurements upon completion of the vane measurements. There was no RS600 data taken during these measurements.

3.0 Results and Discussion

The results are broken into the bench and full scale tests.

3.1 Bench Scale Results

The results are broken into the dry beads, xanthan gum solution, and EPK kaolin slurries.

3.1.1 *Dry Beads*

The vane yield stress results for the glass beads for the small and large cups are provided in Table 3-1. The vane results for the large cup is shown in Figure 3-1 and for the surface and 1st subsurface vane measurements are shown in Figure 3-2.

Table 3-1 Vane Yield Stress Measurements of Glass Beads

Depth Location (mm)	Potters P-0040							
	Small Cup (8-24-2011)				Large cup (9-21-2011)			
	1 tap		100 Tap		1 tap		100 Tap	
	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
8	200	20	196	3	215	7	220	12
24	573	6	782	1	498	84	702	42
40	-	-	-	-	821	266	1269	32
56	-	-	-	-	978	115	1815	29
72	-	-	-	-	2032	1502	3198	87
Depth Location (mm)	Potters P-0080							
	Small Cup (8-23-2011)				Large cup (9-21-2011)			
	1 tap		100 Tap		1 tap		100 Tap	
	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
8	208	5	223	9	213	57	313	23
24	586	3	1055	9	670	39	1005	148
40	-	-	-	-	720	29	1519	76
56	-	-	-	-	952	70	2125	105
72	-	-	-	-	1459	66	3710	154
Depth Location (mm)	Potters A-1922							
	Small Cup (8-23-2011)				Large cup (8-23-2011)			
	1 tap		100 Tap		1 tap		100 Tap	
	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
8	169	13	164	1	181	8	179	2
24	563	15	674	4	670	39	652	27
40	-	-	-	-	746	3	1107	111
56	-	-	-	-	1067	71	1865	128
72	-	-	-	-	1566	94	3190	412
Depth Location (mm)	Potters P-Blend							
	Small Cup (9-21-2011)							
	Avg.	Std.	Avg.	Std.				
	1 tap		100 Tap					
8	173	14	161	1				
24	618	49	736	11				

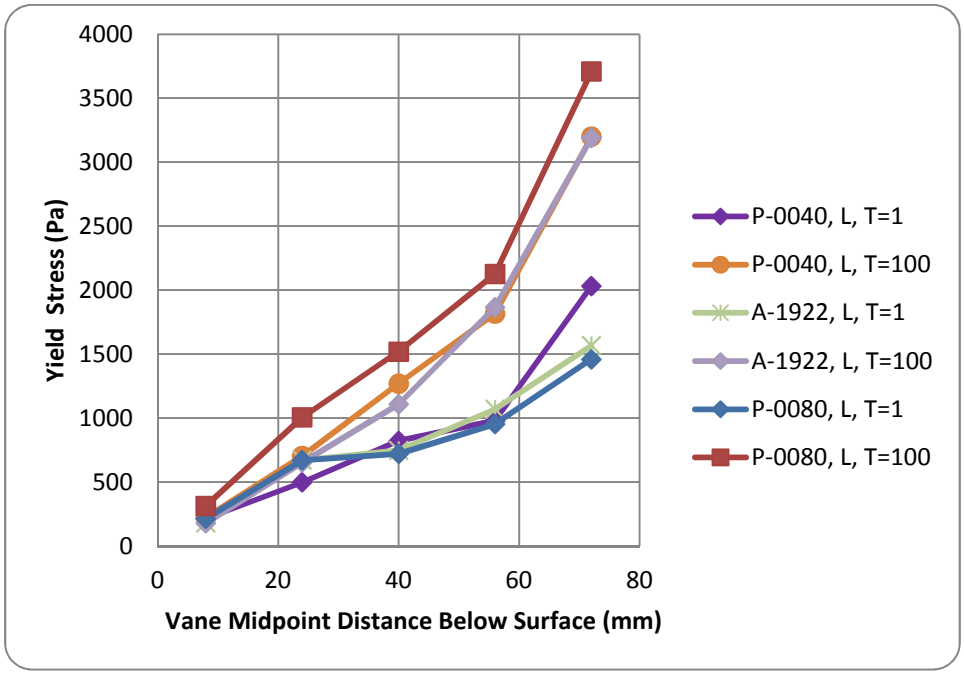


Figure 3-1 Vane Yield Stress – Large Vessel Results For Glass Beads

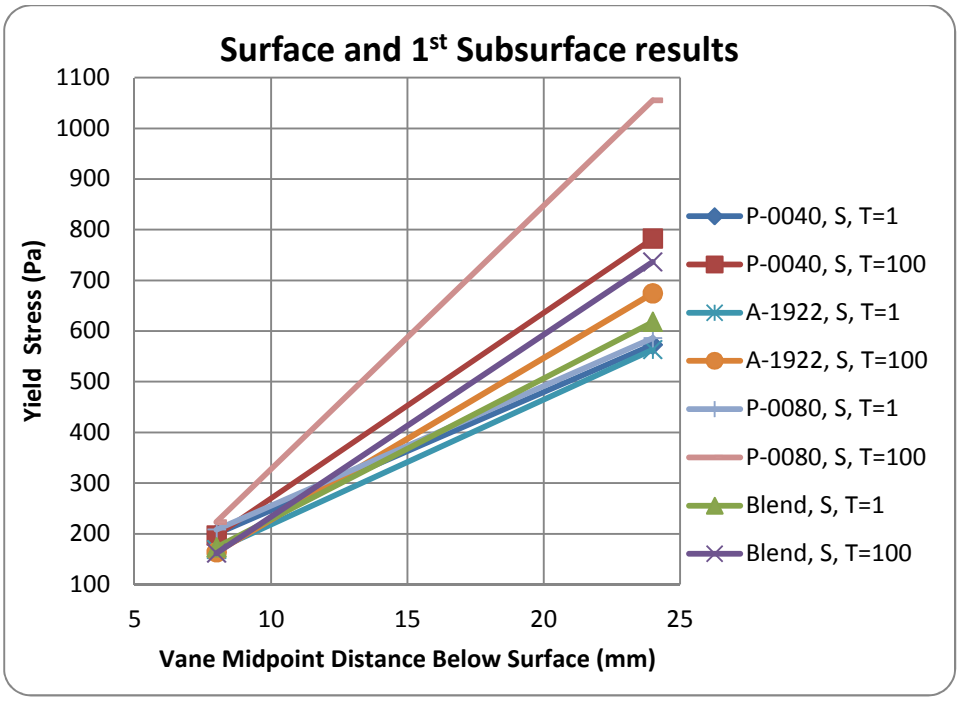


Figure 3-2 Vane Yield Stress – Glass Bead Surface and Subsurface Measurement Results

The yield stress response is somewhat linear with respect to depth (Figure 3-1), other than the deepest measurement. The yield stress response for the deepest measurement could indicate that the vane is too close to the bottom of the container. Tapping (compaction) results in a higher yield stress and was expected for all submerged depth measurements. The surface yield stress measurements seem to be

insensitive to tapping or particle size. The P-0080 glass beads (mean particle size falls between the P-0040 and A-1922) has a higher yield stress response as compared to the other beads. This could be attributed to this material having less spherical particles, more moisture, or has a higher packing density, all of which were not characterized. In all cases, the solids easily poured out of the containers (by tilting the containers) upon completion of testing, indicating the measured yields stress is a "confined" yield stress created by the wall of this container and the mechanical (hard body) interactions of the solids. Hence the use of such measurements is questionable in its application to DOE waste processes. Individual yield stress vane measurements and particles size number and volume distributions can be found in reference 19.

3.1.2 *Xanthan Gum*

The flow curve, vane curve and vane yield stress data for the 20 and 30 Pa xanthan gum fluids are provided in Table 3-2. Typical flow curve, vane curve and vane yield stress curve for the xanthan gum solutions are provided in Figure 3-3, Figure 3-4, and Figure 3-5 respectively. The traditional flow curve provides the highest yield stress, followed by the vane flow curve and then finally the vane yield stress. The 30 Pa xanthan gum fluid is more thixotropic as compared to the 20 Pa xanthan gum fluid as shown in Figure 3-3 and Figure 3-4 if one observes the first part of the up curves. The Bingham Plastic fit to the flow and vane curves cannot be compared, since correction to the vane curve shear rate was not determined in this task. Figure 3-6 is a plot of the 20 Pa xanthan gum Z41 and vane curves in the lower shear rate range. Inspection of this curve indicates that increasing the M factor (geometric shear rate factor) could potentially result in similar flow curve assessments while targeting a common maximum shear stress common to both sets of data. The vane yield stress curves for the these xanthan gum solutions show that this fluid has an elastic modulus that is a very short and the viscoelastic response is long before the dynamic yield stress is reached. This response could be typical for such a fluid, where the continuous phase is non-Newtonian. Individual xanthan gum rheological measurements can be found in reference 20 for bench top measurements.

Table 3-2 Xanthan Gum Flow Curve, Vane Curve, and Vane Results

Target	Traditional Z41 Flow Curve			Vane Curve			Vane Yield Stress (Pa)
	PV (cP)	BPYS (Pa)	Fitted Range (sec-1)	PV (cP)	BPYS (Pa)	Fitted Range (sec^{-1})	
20 Pa	36.3	23.8	50 - 1000	370	15.4	1 - 40	10.8
	37.9	23.6	1000 - 50	347	15.9	40 - 5	
30 Pa	43.2	40.6	50 - 1000	412	27.8	2 - 40	18.0
	49.8	35.7	1000 - 50	484	24.9	40 - 5	

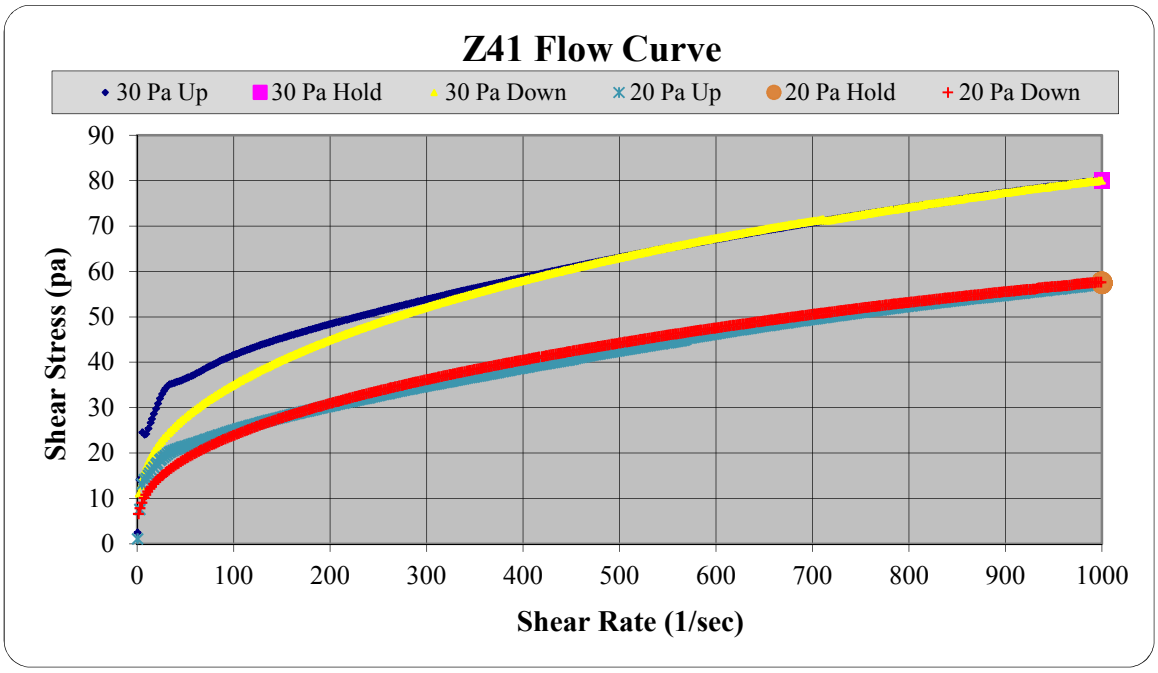


Figure 3-3 Typical Xanthan Z41 Flow Curve

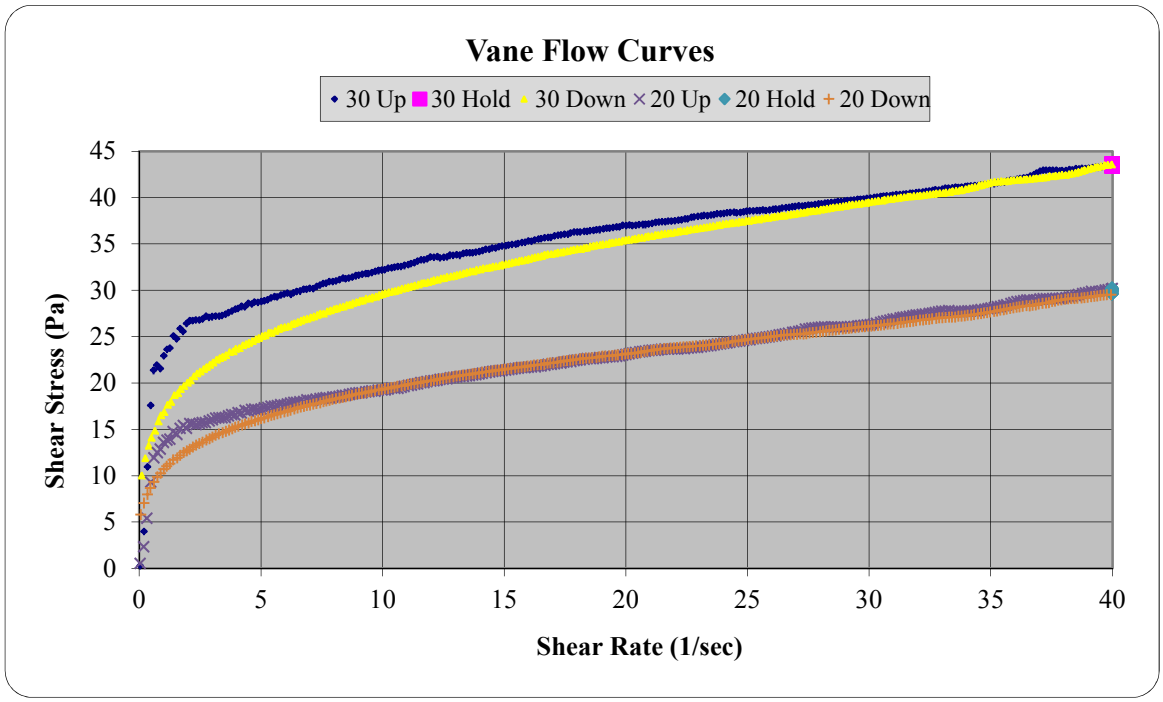


Figure 3-4 Typical Xanthan Vane Flow Curve

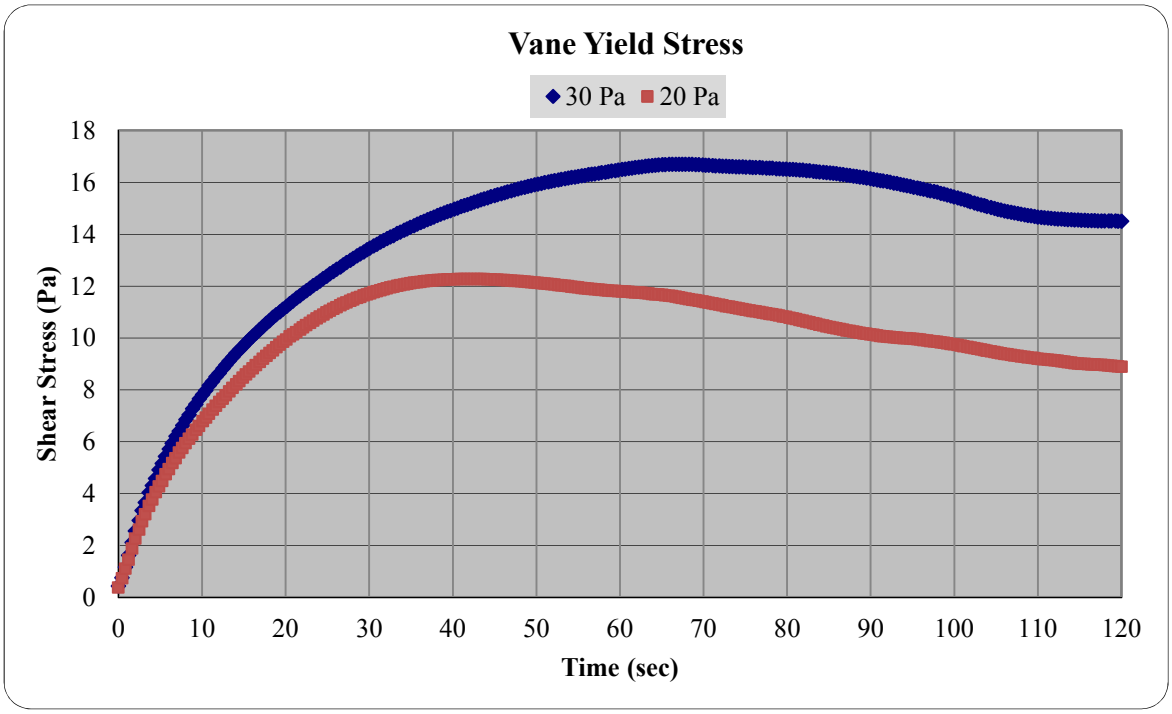


Figure 3-5 Typical Xanthan FL-22 Vane Yield Stress Curve, 0.3 RPM

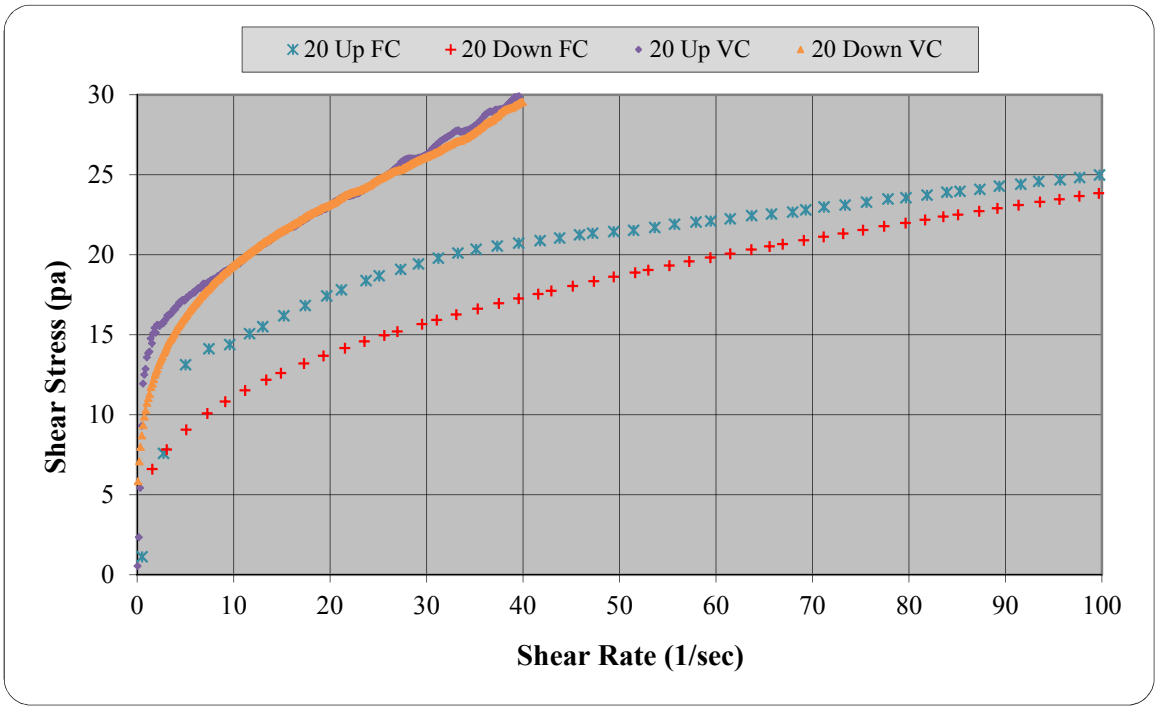


Figure 3-6 20 Pa Xanthan Gum Flow Curve (FC) and Vane Curve (VC)

3.1.3 *Kaolin Slurries*

The up and down Bingham Plastic parameters for both conventional and vane flow curves, vane yield stress, wt% total solids and density data for the 15, 17.5, 20, 22.5, 25, 27.5, 30, and 32.5 wt% Kaolin slurries are provided in Table 3-3, Table 3-4, Table 3-5, Table 3-6, Table 3-7, Table 3-8, Table 3-9, and Table 3-10 respectively. These tables provide all these properties for the various mixing times these slurries were mixed. The wt% and density data indicate that during the mixing and sampling activities, the mixtures were maintained such that evaporative losses were minimized. The wt% data were all below target. The EKP kaolin source was analyzed for water content using the halogen loss and weight instrument and was determined to contain 2.8 wt % water, explaining the difference in target and actual. The Bingham Plastic yield stresses and vane data for 15, 17.5, 20, and 22.5 wt% kaolin is shown in Figure 3-7 and for the 25, 27.5, 30, and 32.5 wt% Kaolin slurries they are shown in Figure 3-8. Typical flow curves from both the concentric (Z41) and vane are shown in Figure 3-9 for a rheologically thin and viscous kaolin slurries. For the 15 wt% kaolin, Taylor vortices are present in the Z41 flow curve and the same type of response (or instability) is shown in the vane flow curve as well. Due to these instabilities, the flow curves were fitted in the initial linear region and the region of curve fit for each flow curve is provided in Table 3-3 through Table 3-10. The BPYS response is consistent with each data set, where the Z41 flow curve BPYS's are larger than either the vane flow curve or vane yield stress measurements. Additionally, the up curve BPYS is lower than the down curve BPYS and the plastic viscosity of the up curve BPYS is greater than the down curve BPYS. As the wt% increases, the vane yield stress measurement tends to the lowest yield stress value and this is due to how the flow curves were fitted. This is the same issue that was observed with the xanthan solutions. Furthermore, the yield stress response for the EKP kaolin slurries is different than that of the xanthan gum and this can be observed in Figure 3-10, where there is a very small viscoelastic component. For 20 wt% or greater kaolin concentration, the yield stress tends not to change much after 14 to 16 hours of mixing, given the mixing system used in this task. The use of the vane method to determine the yield stress for the thinner rheological materials needs further assessment to determine its viability using field type equipment.

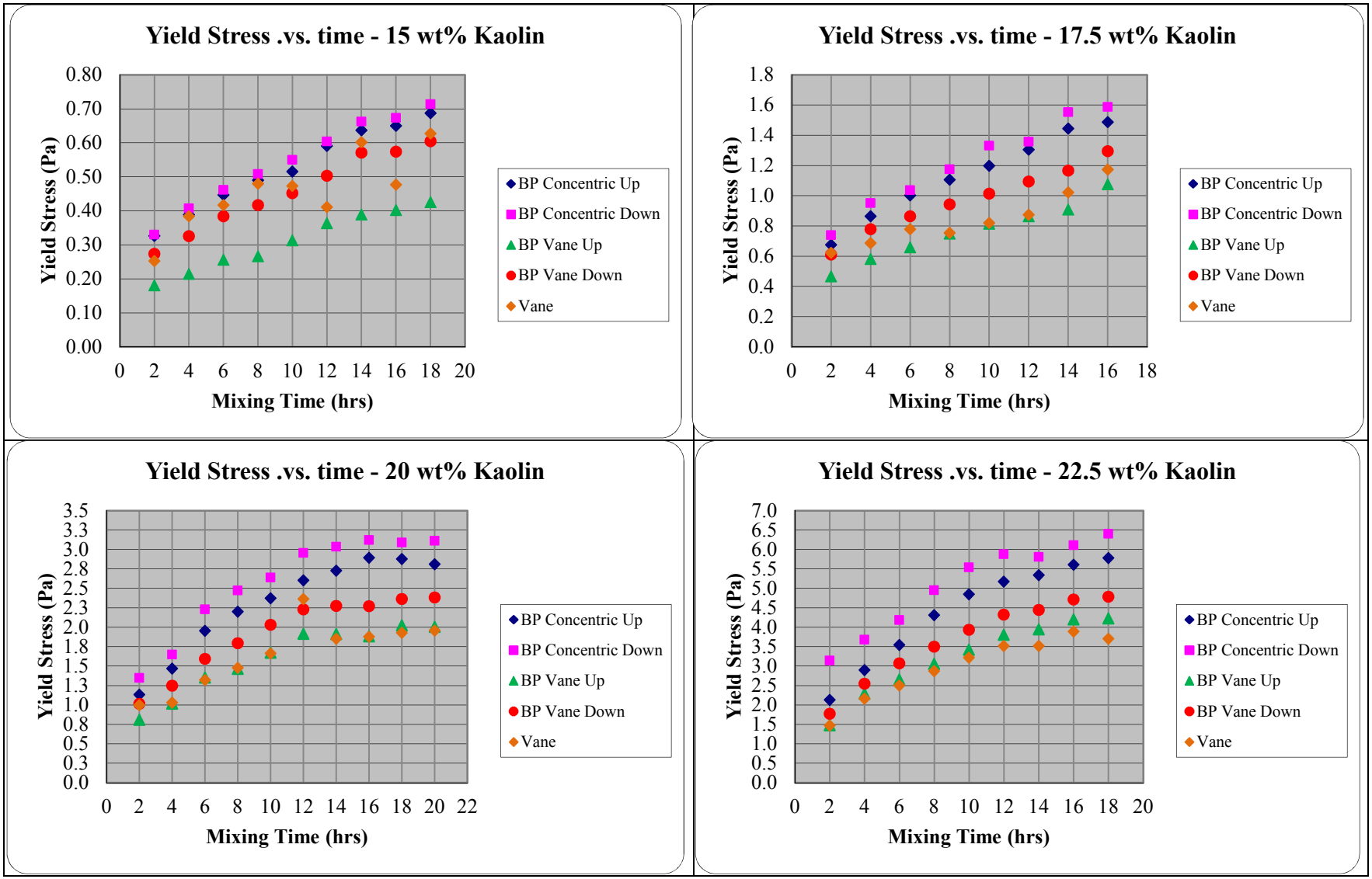


Figure 3-7 15, 17.5, 20, and 22.5 Wt% TS Kaolin Yield Stress Versus Time

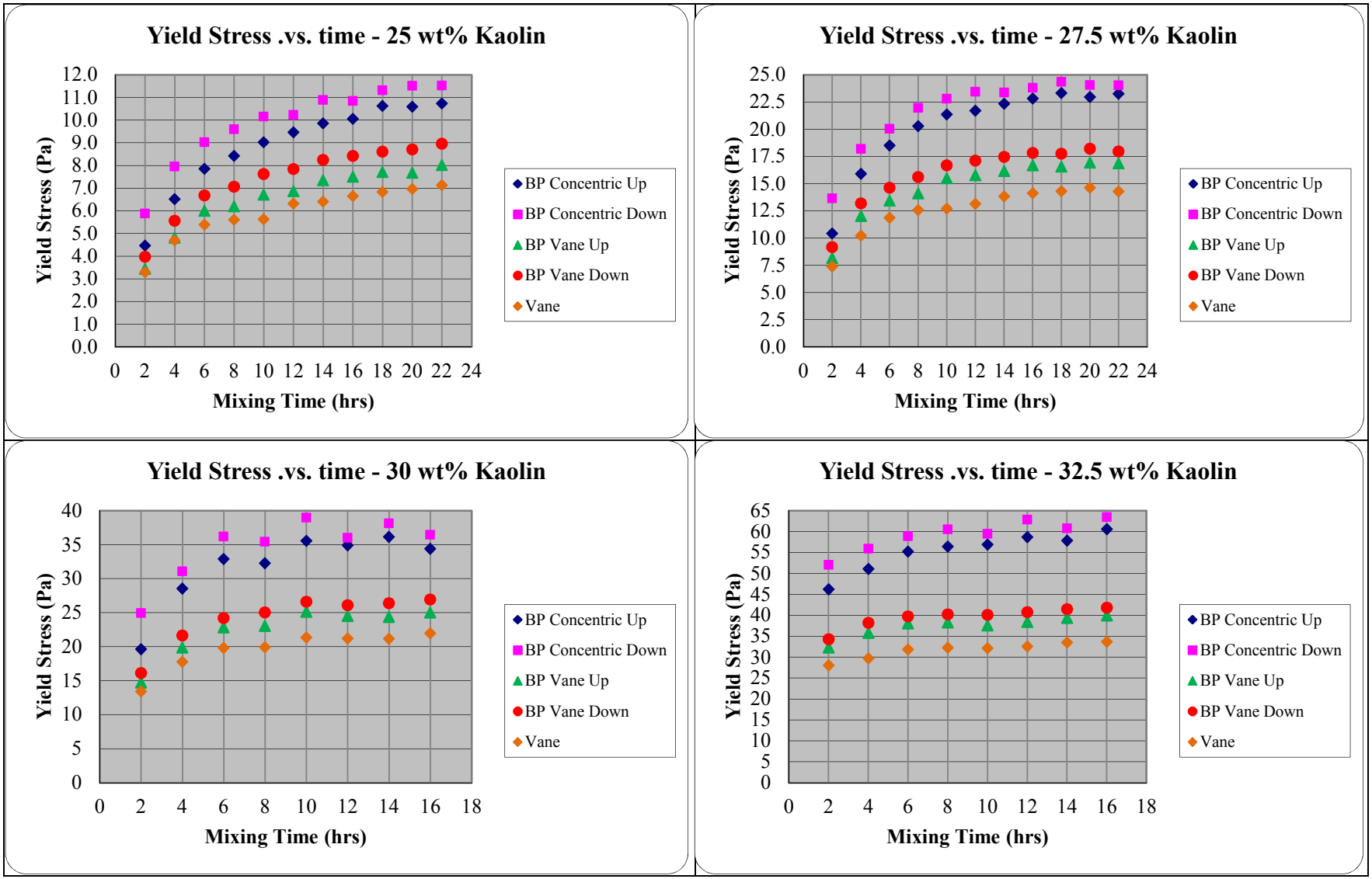


Figure 3-8 25, 27.5, 30, and 32.5 Wt% TS Kaolin Yield Stress Versus Time

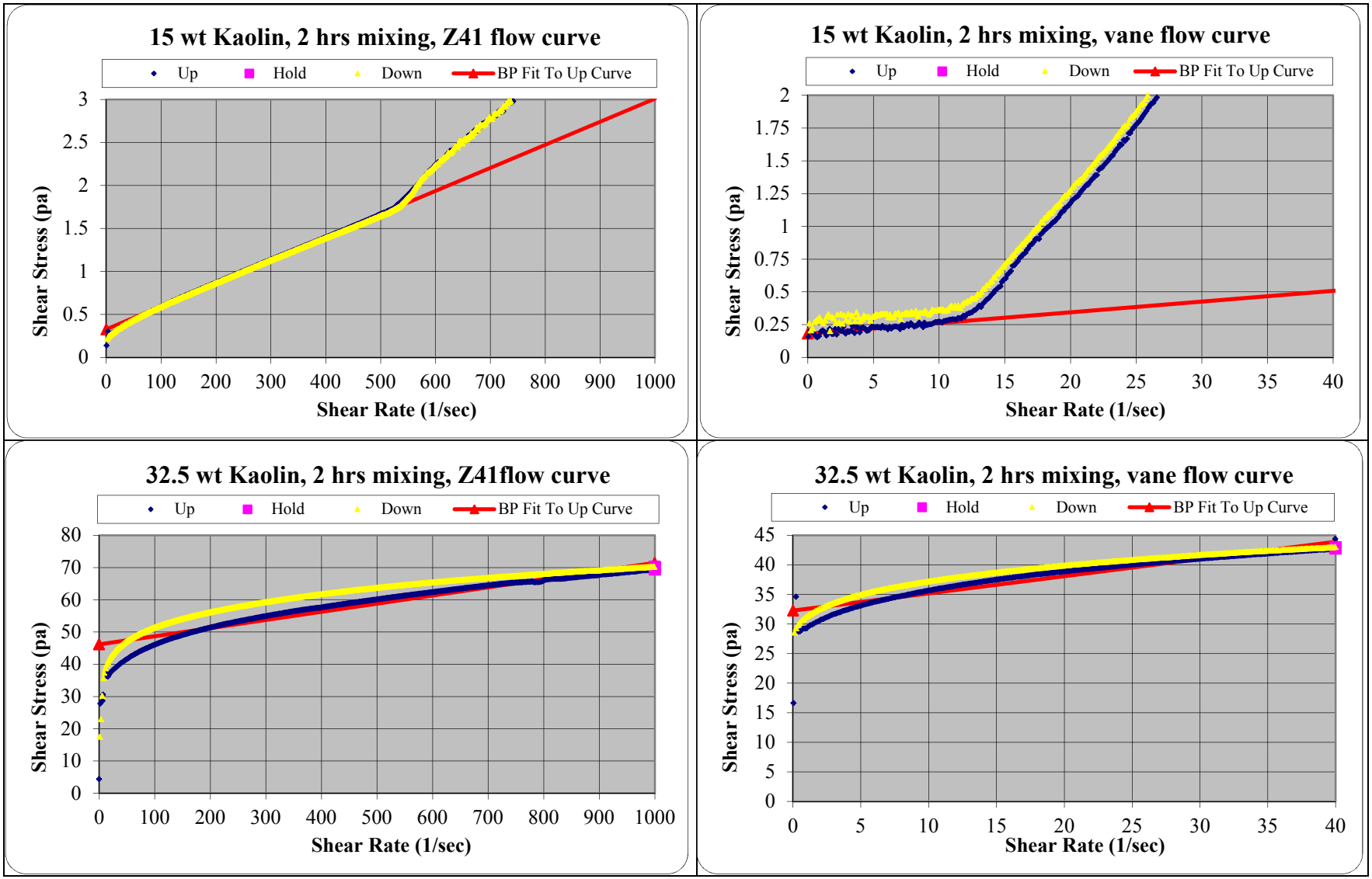


Figure 3-9 Typical Kaolin Slurry Z41 and Vane Flow Curves

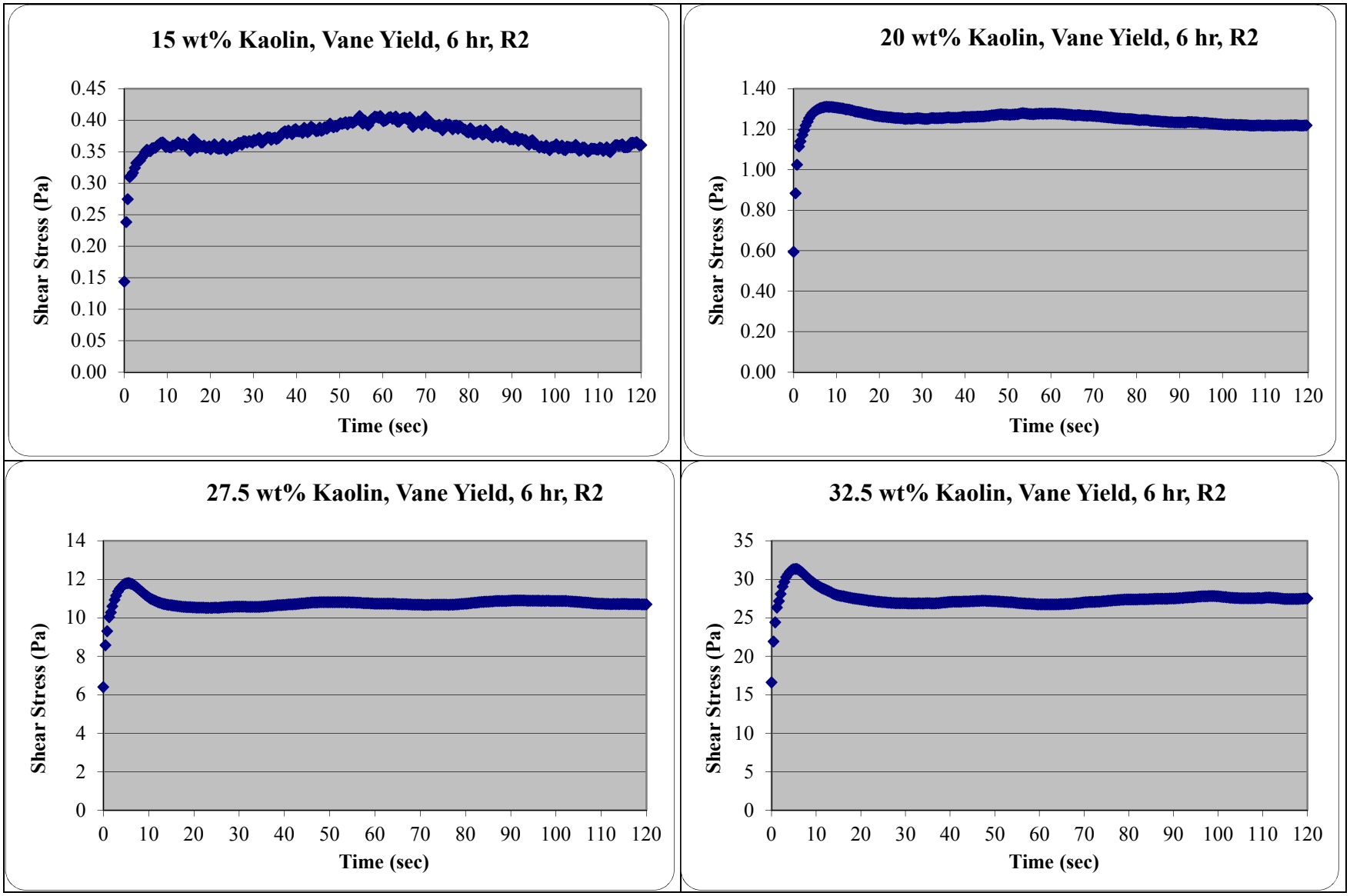


Figure 3-10 15, 20, 27.5 and 32.5 wt% Kaolin Vane Yield Stress Measurements

Table 3-3 15 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	2.68	0.33	0.9996	50 - 500	8.19	0.18	0.7225	1 - 10	0.25	14.34	1.0935
	down	2.65	0.33	0.9996	500 - 50	8.02	0.27	0.4981	10 - 1			
4	up	2.78	0.39	0.9993	50 - 500	9.13	0.21	0.7603	1 - 10	0.38	14.46	1.0938
	down	2.73	0.41	0.9995	500 - 50	7.38	0.33	0.5774	10 - 1			
6	up	2.89	0.45	0.9992	50 - 600	10.44	0.26	0.8100	1 - 10	0.42	14.34	1.0945
	down	2.82	0.46	0.9994	600 - 50	9.56	0.38	0.7574	10 - 1			
8	up	2.92	0.49	0.9992	50 - 600	10.91	0.27	0.8032	1 - 10	0.48	14.39	1.0944
	down	2.85	0.51	0.9995	600 - 50	8.46	0.42	0.6644	10 - 1			
10	up	2.99	0.52	0.9991	50 - 600	11.92	0.31	0.8578	1 - 10	0.47	14.42	1.0946
	down	2.93	0.55	0.9995	600 - 50	10.48	0.45	0.8042	10 - 1			
12	up	2.82	0.59	0.9974	50 - 600	13.64	0.36	0.8375	1 - 15	0.41	14.52	1.0948
	down	2.80	0.60	0.9989	600 - 50	12.18	0.50	0.9176	15 - 1			
14	up	3.11	0.64	0.9985	50 - 600	15.26	0.39	0.9476	1 - 15	0.60	14.43	1.0941
	down	3.03	0.66	0.9993	600 - 50	11.75	0.57	0.9221	15 - 1			
16	up	3.10	0.65	0.9982	50 - 600	15.55	0.40	0.9652	1 - 15	0.48	14.37	1.0947
	down	3.02	0.67	0.9991	600 - 50	12.33	0.57	0.9491	15 - 1			
18	up	3.24	0.69	0.9982	50 - 600	15.32	0.43	0.9513	1 - 15	0.63	14.49	1.0947
	down	3.15	0.71	0.9992	600 - 50	12.35	0.60	0.9339	15 - 1			

Table 3-4 17.5 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	3.33	0.67	0.9989	50 - 600	14.44	0.47	0.9544	1 - 15	0.62	16.88	1.1122
	down	3.28	0.74	0.9992	600 - 50	12.61	0.61	0.9482	15 - 1			
4	up	3.48	0.86	0.9986	50 - 700	18.96	0.58	0.9729	1 - 15	0.69	16.88	1.1128
	down	3.41	0.95	0.9986	500 - 50	13.75	0.78	0.9393	15 - 1			
6	up	3.35	1.00	0.9966	50 - 700	19.62	0.66	0.9716	1 - 15	0.78	16.87	1.1129
	down	3.32	1.04	0.9983	500 - 50	15.43	0.86	0.9582	15 - 1			
8	up	3.77	1.10	0.9980	50 - 700	20.51	0.75	0.9698	1 - 15	0.75	16.87	1.1130
	down	3.70	1.17	0.9986	500 - 50	16.43	0.94	0.9449	15 - 1			
10	up	3.90	1.20	0.9981	50 - 700	21.09	0.81	0.8272	1 - 15	0.82	16.93	1.1132
	down	3.78	1.33	0.9982	500 - 50	18.29	1.01	0.9487	15 - 1			
12	up	3.83	1.30	0.9981	50 - 800	23.05	0.86	0.9859	1 - 20	0.87	16.85	1.1135
	down	3.77	1.36	0.9988	800 - 50	17.90	1.09	0.9752	20 - 1			
14	up	4.00	1.44	0.9974	50 - 800	24.52	0.91	0.9855	1 - 20	1.02	16.85	1.1131
	down	3.88	1.55	0.9978	800 - 50	18.71	1.17	0.9735	20 - 1			
16	up	4.06	1.49	0.9978	50 - 800	23.97	1.08	0.9872	1 - 20	1.17	16.88	1.1122
	down	3.94	1.59	0.9985	800 - 50	19.33	1.29	0.9708	20 - 1			

Table 3-5 20 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	3.94	1.13	0.9989	50 - 800	22.26	0.81	0.9702	1 - 15	1.00	19.23	1.1309
	down	3.88	1.34	0.9980	800 - 50	16.64	1.01	0.9638	15 - 1			
4	up	4.20	1.47	0.9983	50 - 800	24.54	1.02	0.9844	1 - 20	1.03	19.43	1.1310
	down	4.10	1.65	0.9984	800 - 50	19.38	1.25	0.9721	20 - 1			
6	up	4.54	1.95	0.9983	50 - 900	27.76	1.35	0.9882	1 - 25	1.32	19.36	1.1313
	down	4.37	2.23	0.9971	900 - 50	22.11	1.59	0.9809	25 - 1			
8	up	4.66	2.20	0.9979	50 - 1000	31.89	1.46	0.9846	1 - 25	1.48	19.33	1.1320
	down	4.48	2.47	0.9973	1000 - 50	23.57	1.80	0.9731	25 - 1			
10	up	4.68	2.37	0.9976	50 - 1000	34.75	1.67	0.9814	1 - 30	1.66	19.26	1.1322
	down	4.59	2.64	0.9975	1000 - 50	25.36	2.03	0.9702	30 - 1			
12	up	5.01	2.60	0.9974	50 - 1000	34.97	1.91	0.9785	1 - 30	2.36	19.25	1.1323
	down	4.87	2.96	0.9972	1000 - 50	26.90	2.23	0.9685	30 - 1			
14	up	5.03	2.73	0.9970	50 - 1000	36.72	1.91	0.9772	1 - 30	1.85	19.24	1.1322
	down	4.91	3.03	0.9973	1000 - 50	27.46	2.27	0.9656	30 - 1			
16	up	5.05	2.89	0.9967	50 - 1000	37.74	1.88	0.9771	1 - 30	1.88	19.08	1.1312
	down	5.03	3.12	0.9972	1000 - 50	27.40	2.27	0.9641	30 - 1			
18	up	4.96	2.88	0.9964	50 - 1000	37.33	2.02	0.9743	1 - 30	1.93	19.12	1.1319
	down	4.84	3.09	0.9972	1000 - 50	28.63	2.36	0.9662	30 - 1			
20	up	4.87	2.81	0.9960	50 - 1000	38.19	2.00	0.9769	1 - 30	1.96	19.12	1.1316
	down	4.68	3.11	0.9962	1000 - 50	28.44	2.38	0.9624	30 - 1			

Table 3-6 22.5 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	5.08	2.13	0.9991	50 - 1000	30.67	1.48	0.9874	1 - 25	1.47	21.68	1.1510
	down	4.80	3.14	0.9908	1000 - 50	23.14	1.77	0.9800	25 - 1			
4	up	4.99	2.90	0.9972	50 - 1000	33.77	2.29	0.9864	1 - 30	2.16	21.75	1.1512
	down	4.68	3.68	0.9910	1000 - 50	27.66	2.54	0.9771	30 - 1			
6	up	5.51	3.54	0.9961	50 - 1000	42.97	2.65	0.9760	1 - 30	2.50	21.71	1.1515
	down	5.15	4.18	0.9929	1000 - 50	32.71	3.07	0.9671	30 - 1			
8	up	5.99	4.31	0.9961	50 - 1000	44.91	3.06	0.9770	1 - 35	2.87	21.67	1.1524
	down	5.66	4.95	0.9934	1000 - 50	34.20	3.50	0.9688	35 - 1			
10	up	6.21	4.84	0.9952	50 - 1000	49.40	3.42	0.9727	1 - 35	3.22	21.63	1.1525
	down	5.81	5.54	0.9924	1000 - 50	36.77	3.93	0.9607	35 - 1			
12	up	6.61	5.18	0.9946	50 - 1000	49.33	3.81	0.9734	1 - 40	3.52	21.63	1.1529
	down	6.18	5.87	0.9931	1000 - 50	37.35	4.32	0.9645	40 - 1			
14	up	6.43	5.34	0.9947	50 - 1000	50.76	3.95	0.9701	1 - 40	3.52	21.66	1.1514
	down	6.18	5.81	0.9926	1000 - 50	38.90	4.44	0.9627	40 - 1			
16	up	6.57	5.61	0.9937	50 - 1000	52.49	4.20	0.9683	1 - 40	3.89	21.63	1.1529
	down	6.26	6.11	0.9925	1000 - 50	40.31	4.71	0.9607	40 - 1			
18	up	6.60	5.78	0.9934	50 - 1000	53.68	4.22	0.9701	1 - 40	3.70	21.80	1.1528
	down	6.19	6.40	0.9910	1000 - 50	40.60	4.78	0.9591	40 - 1			

Table 3-7 25 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	6.47	4.46	0.9969	50 - 1000	49.64	3.44	0.9765	1 - 30	3.29	24.19	1.1724
	down	5.64	5.88	0.9866	1000 - 50	36.42	3.96	0.9651	30 - 1			
4	up	7.57	6.51	0.9945	50 - 1000	62.16	4.81	0.9660	1 - 35	4.69	24.27	1.1738
	down	6.58	7.95	0.9886	1000 - 50	44.63	5.56	0.9525	35 - 1			
6	up	7.86	7.85	0.9926	50 - 1000	63.85	6.00	0.9665	1 - 40	5.39	24.14	1.1728
	down	7.02	9.02	0.9872	1000 - 50	50.26	6.68	0.9480	40 - 1			
8	up	8.29	8.42	0.9899	50 - 1000	71.59	6.20	0.9612	1 - 40	5.61	24.21	1.1725
	down	7.34	9.59	0.9873	1000 - 50	53.17	7.06	0.9409	40 - 1			
10	up	8.56	9.02	0.9884	50 - 1000	77.51	6.70	0.9584	1 - 40	5.62	24.09	1.1740
	down	7.65	10.15	0.9865	1000 - 50	56.31	7.62	0.9439	40 - 1			
12	up	8.41	9.45	0.9882	50 - 1000	79.36	6.86	0.9604	1 - 40	6.31	24.06	1.1715
	down	7.82	10.22	0.9882	1000 - 50	57.91	7.84	0.9405	40 - 1			
14	up	8.87	9.85	0.9866	50 - 1000	81.63	7.35	0.9542	1 - 40	6.41	24.11	1.1740
	down	7.99	10.88	0.9863	1000 - 50	60.96	8.25	0.9406	40 - 1			
16	up	8.37	10.05	0.9846	50 - 1000	84.22	7.50	0.9532	1 - 40	6.64	24.09	1.1721
	down	7.78	10.83	0.9810	1000 - 50	62.37	8.42	0.9402	40 - 1			
18	up	8.84	10.62	0.9866	50 - 1000	85.09	7.70	0.9538	1 - 40	6.83	23.96	1.1736
	down	8.30	11.31	0.9874	1000 - 50	64.52	8.60	0.9390	40 - 1			
20	up	9.14	10.59	0.9848	50 - 1000	88.04	7.68	0.9533	1 - 40	6.96	24.13	1.1726
	down	8.25	11.51	0.9874	1000 - 50	64.16	8.71	0.9370	40 - 1			
22	up	8.91	10.73	0.9855	50 - 1000	90.21	8.01	0.9499	1 - 40	7.12	24.11	1.1721
	down	8.28	11.52	0.9835	1000 - 50	67.42	8.95	0.9404	40 - 1			

Table 3-8 27.5 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	10.04	10.41	0.9927	50 - 1000	89.95	8.15	0.9573	1 - 40	7.37	26.57	1.1937
	down	7.74	13.64	0.9628	1000 - 50	68.03	9.16	0.9453	40 - 1			
4	up	11.64	15.89	0.9832	50 - 1000	123.31	12.01	0.9444	1 - 40	10.20	26.68	1.1941
	down	9.90	18.17	0.9685	1000 - 50	96.74	13.17	0.9334	40 - 1			
6	up	12.13	18.50	0.9783	50 - 1000	137.22	13.43	0.9432	1 - 40	11.84	26.58	1.1948
	down	11.00	20.03	0.9674	1000 - 50	110.12	14.62	0.9312	40 - 1			
8	up	13.04	20.27	0.9761	50 - 1000	151.37	14.09	0.9484	1 - 40	12.56	26.65	1.1944
	down	11.62	21.94	0.9701	1000 - 50	117.40	15.59	0.9260	40 - 1			
10	up	13.29	21.36	0.9732	50 - 1000	156.83	15.47	0.9388	1 - 40	12.70	26.36	1.1934
	down	12.07	22.78	0.9697	1000 - 50	128.04	16.68	0.9258	40 - 1			
12	up	13.85	21.69	0.9717	50 - 1000	164.24	15.77	0.9359	1 - 40	13.13	26.5	1.1942
	down	12.28	23.42	0.9681	1000 - 50	132.95	17.10	0.9261	40 - 1			
14	up	13.26	22.34	0.9726	50 - 1000	167.50	16.16	0.9313	1 - 40	13.81	26.58	1.1948
	down	12.45	23.36	0.9678	1000 - 50	136.86	17.45	0.9272	40 - 1			
16	up	13.37	22.82	0.9710	50 - 1000	167.18	16.68	0.9332	1 - 40	14.11	26.55	1.1943
	down	12.56	23.79	0.9673	1000 - 50	140.53	17.82	0.9251	40 - 1			
18	up	13.81	23.32	0.9716	50 - 1000	166.48	16.55	0.9336	1 - 40	14.30	26.59	1.1943
	down	12.95	24.35	0.9676	1000 - 50	138.78	17.74	0.9258	40 - 1			
20	up	13.69	22.96	0.9707	50 - 1000	173.34	16.93	0.9359	1 - 40	14.62	26.62	1.1949
	down	12.78	24.05	0.9664	1000 - 50	143.41	18.21	0.9244	40 - 1			
22	up	13.38	23.24	0.9717	50 - 1000	172.12	16.85	0.9290	1 - 40	14.27	26.5	1.1941
	down	12.82	24.03	0.9659	1000 - 50	143.92	17.96	0.9257	40 - 1			

Table 3-9 30 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)	Curve	Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
		PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	14.79	19.61	0.9876	50 - 1000	143.01	14.72	0.95	1 - 40	13.40	29.02	1.2166
	down	11.09	24.92	0.9400	1000 - 50	113.10	16.12	0.94	40 - 1			
4	up	16.22	28.54	0.9692	50 - 1000	201.54	19.87	0.94	1 - 40	17.76	29.06	1.2164
	down	14.36	31.06	0.9532	1000 - 50	158.67	21.64	0.93	40 - 1			
6	up	19.17	32.88	0.9662	50 - 1000	213.19	22.83	0.94	1 - 40	19.82	28.99	1.2157
	down	16.22	36.17	0.9508	1000 - 50	181.72	24.18	0.93	40 - 1			
8	up	18.94	32.26	0.9633	50 - 1000	234.44	23.04	0.94	1 - 40	19.90	28.97	1.2159
	down	16.24	35.40	0.9549	1000 - 50	188.07	25.03	0.92	40 - 1			
10	up	20.14	35.55	0.9660	50 - 1000	238.98	25.15	0.94	1 - 40	21.32	29.08	1.2152
	down	16.97	38.96	0.9502	1000 - 50	206.08	26.61	0.92	40 - 1			
12	up	17.62	34.89	0.9576	50 - 1000	247.93	24.50	0.93	1 - 40	21.18	29.01	1.2139
	down	16.69	35.99	0.9561	1000 - 50	207.22	26.09	0.92	40 - 1			
14	up	19.01	36.15	0.9558	50 - 1000	254.41	24.37	0.93	1 - 40	21.14	29.07	1.2163
	down	17.12	38.12	0.9522	1000 - 50	204.58	26.40	0.92	40 - 1			
16	up	18.70	34.38	0.9557	50 - 1000	258.58	25.03	0.93	1 - 40	21.95	29.11	1.2175
	down	16.65	36.43	0.9551	1000 - 50	212.38	26.93	0.92	40 - 1			

Table 3-10 32.5 Wt. % Kaolin Slurry Mixing Physical Data

Mixing Time (hr)		Z41 Flow Curve				Vane Flow Curve				Vane Yield (Pa)	Wt % TS	Density (g/cm^3)
	Curve	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)	PV (cP)	BPYS (Pa)	R^2	Curve Fit (1/s)			
2	up	25.25	46.17	0.9566	50 - 1000	290.41	32.28	0.94	1 - 40	28.00	31.43	1.2347
	down	20.43	52.03	0.9312	1000 - 50	246.82	34.24	0.93	40 - 1			
4	up	27.27	51.03	0.9417	50 - 1000	345.62	35.78	0.93	1 - 40	29.67	31.44	1.2393
	down	22.42	55.84	0.9351	1000 - 50	292.25	38.16	0.92	40 - 1			
6	up	27.46	55.24	0.9384	50 - 1000	345.81	38.05	0.93	1 - 40	31.80	31.55	1.2395
	down	23.89	58.81	0.9354	1000 - 50	308.90	39.69	0.92	40 - 1			
8	up	29.31	56.38	0.9384	50 - 1000	356.71	38.27	0.93	1 - 40	32.26	31.54	1.2382
	down	25.39	60.52	0.9421	1000 - 50	315.64	40.19	0.92	40 - 1			
10	up	27.69	56.90	0.9499	50 - 1000	384.46	37.57	0.92	1 - 40	32.15	31.48	1.2396
	down	25.52	59.41	0.9458	1000 - 50	323.22	40.05	0.92	40 - 1			
12	up	30.19	58.65	0.9371	50 - 1000	385.09	38.39	0.93	1 - 40	32.53	31.49	1.2406
	down	26.65	62.82	0.9380	1000 - 50	326.98	40.73	0.92	40 - 1			
14	up	28.63	57.82	0.9285	50 - 1000	384.37	39.37	0.92	1 - 40	33.48	31.59	1.2405
	down	25.74	60.71	0.9401	1000 - 50	334.31	41.44	0.92	40 - 1			
16	up	28.96	60.55	0.9506	50 - 1000	382.71	39.95	0.92	1 - 40	33.66	31.55	1.2409
	down	26.42	63.39	0.9402	1000 - 50	338.24	41.78	0.92	40 - 1			

The exponential model, equation (2-3) was used to fit the 2 through 16 hour data sets for each set. The results for both the Bingham Plastic parameters are provided in Table 3-11. This equation fits both the BPYS and plastic viscosity, where there R^2 shows a better fit to the BPYS. An issue with using such an equation is that there can be problem using this data for interpolation or extrapolation. For example, the 8 hour data set was fitted between the 15 to 27.5 wt% data and using three data points (15, 25, and 32.5 wt%) using equation (2-3). The 15 to 27.5wt% data set was used to interpolate/extrapolate. The 15, 25, and 32.5 data was used to interpolate only. The results are shown in Table 3-12, including the fit to the exponential model, which shows that extrapolation can be problematic, while interpolation of data shows a much better fit.

Table 3-11 Curve Fitting Rheological Data as a Function of Wt.% Total Solids

Mixing Time (hrs)	Bingham Plastic Yield Stress Fit (Pa)			Plastic Viscosity Fit (cP)		
	a	b	r^2	A	b	r^2
2	4.76E-03	0.2877	0.9969	0.339	0.1279	0.9660
4	5.87E-03	0.291	0.9969	0.347	0.1327	0.9717
6	7.66E-03	0.2866	0.9967	0.342	0.1357	0.9789
8	9.63E-03	0.2803	0.9958	0.367	0.1349	0.9834
10	1.07E-02	0.2787	0.9945	0.392	0.133	0.9860
12	1.34E-02	0.2713	0.9954	0.380	0.1344	0.9878
14	1.57E-02	0.2664	0.9949	0.431	0.1297	0.9882
16	1.67E-02	0.2646	0.9957	0.436	0.1291	0.9850

Table 3-12 Curve Fitting Rheological Data as a Function of Wt.% Total Solids

Wt% TS	Measured BPYS (Pa)	All Data $\tau = 9.63 \cdot 10^{-3} e^{0.2803 \cdot wt\%TS}$	Interpolate/Extrapolate (15 to 27.5 wt% TS) $\tau = 6.77 \cdot 10^{-3} e^{0.299 \cdot wt\%TS}$	Interpolate (3 points) (15, 25, and 32.5 wt% TS) $\tau = 9.22 \cdot 10^{-3} e^{0.2785 \cdot wt\%TS}$
14.42	0.49	0.55	0.50	0.51
16.88	1.10	1.09	1.05	1.01
19.24	2.20	2.12	2.13	1.96
21.68	4.31	4.20	4.43	3.87
24.12	8.42	8.32	9.18	7.63
26.56	20.27	16.49	19.04	15.04
29.04	32.26	33.01	39.93	29.98
31.51	56.38	65.97	83.56	59.65

The type of mixer used to prepare a slurry or sample can impact its rheological properties. A 22.5 wt% kaolin sample was made using a high shear mixer for a total of 9 minute of mixing, where the first 7 minutes was at high shear and the final two minutes was at very high shear. Samples were pulled throughout and analyzed using the Z41 flow curve program and the plastic viscosity and BPYS results are shown in Figure 3-11 and Figure 3-12 respectively. The higher shear mixer increased the rheological properties by a factor of two and reduced mixing time over a hundred fold. The very high shear sample was more viscous than the high shear sample, further indicating shear rate dependency in kaolin rheology. The 22.5 wt% high sheared kaolin has similar rheological properties of the 25 wt% conventional agitator mixing kaolin. High shear mixing does not always result in a more viscous fluid.[21]

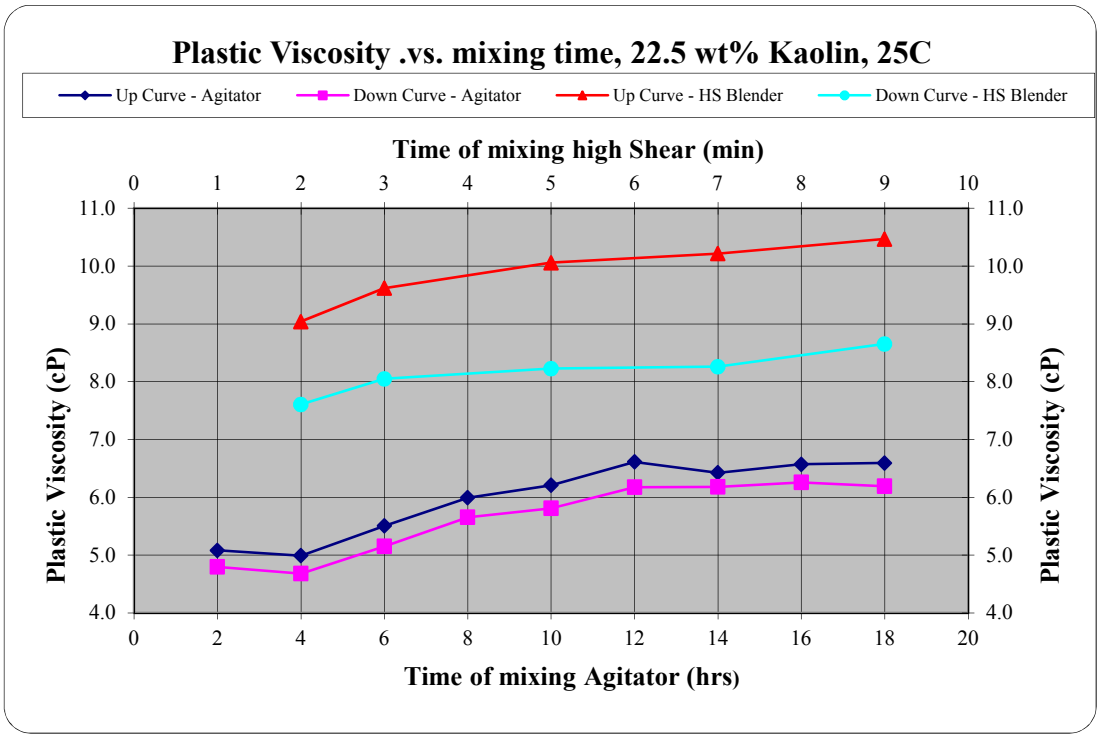


Figure 3-11 Mixer Effect on Plastic Viscosity, 22.5 wt% Kaolin

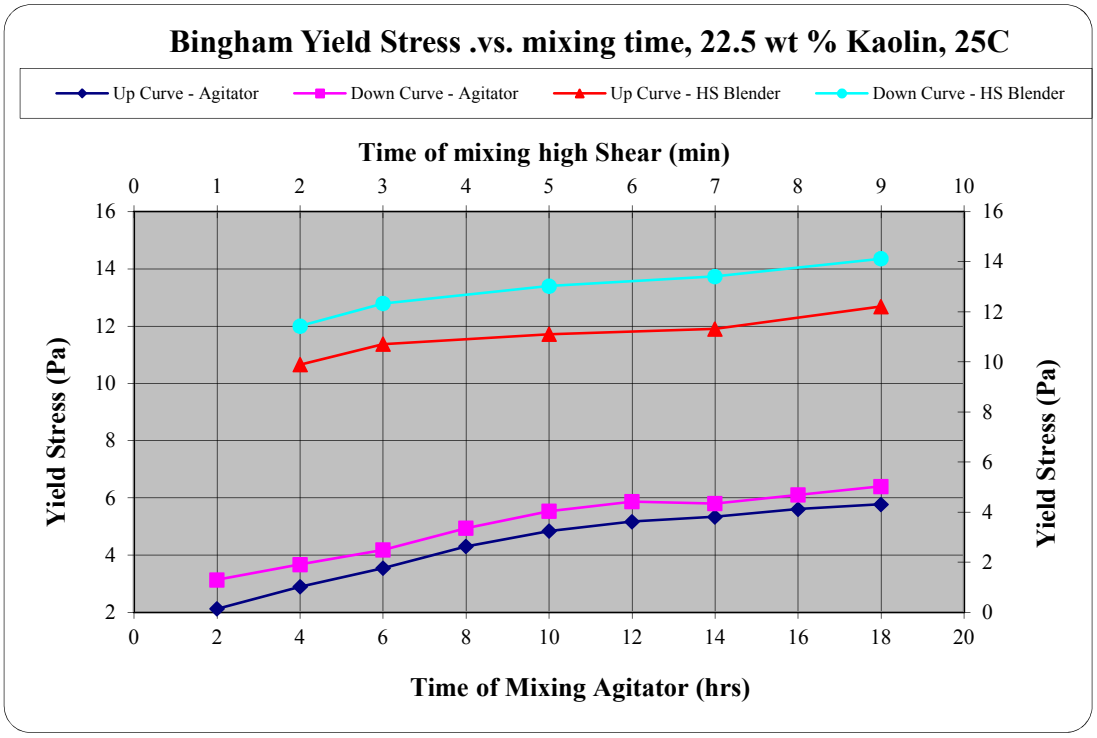


Figure 3-12 Mixer Effect on Bingham Plastic Yield Stress, 22.5 wt% Kaolin

One of the other physical properties that could potentially affect the rheological properties during the conventional mixing process is the particle size distribution. A 22.5 and 25 wt% kaolin samples were prepared, mixed and sampled at 2 hours and 9 hours of mixing. These samples were analyzed for particle size distribution without and with sonication and the results are provided in Table 3-13, clearly showing that the particle distribution is shifting to a smaller PSD due to mixing (shearing). Figure 3-13 is for the 22.5 wt% kaolin sample, showing a definite shift to a smaller PSD during mixing and is consistent with the 25 wt% kaolin sample data. Sonication further reduces the PSD to a much smaller distribution, showing that the shearing applied by the conventional mixers has a limit in reducing the PSD. No particle size distribution measurements were obtained from the 22.5 wt% kaolin high shear mixes. Individual rheological measurements and number and volume particle size distributions can be found in reference 22 for bench top kaolin measurements..

Table 3-13 Curve Fitting Rheological Data as a Function of Wt.% Total Solids

Sample	Mean Values (microns)		
	Volume	Number	Area
22.5 wt% Kaolin - 2hrs - Not Sonicated	17.56	0.686	3.55
22.5 wt% Kaolin - 2hrs - Sonicated	8.85	0.506	1.879
22.5 wt% Kaolin - 9hrs - Not Sonicated	14.57	0.596	2.821
22.5 wt% Kaolin - 9hrs - Sonicated	8.86	0.507	1.883
25 wt% Kaolin - 2hrs - Not Sonicated	17.19	0.653	3.330
25 wt% Kaolin - 2hrs - Sonicated	8.26	0.507	1.856
25 wt% Kaolin - 2hrs - Not Sonicated	13.7	0.582	2.550
25 wt% Kaolin - 2hrs - Sonicated	8.28	0.505	1.849

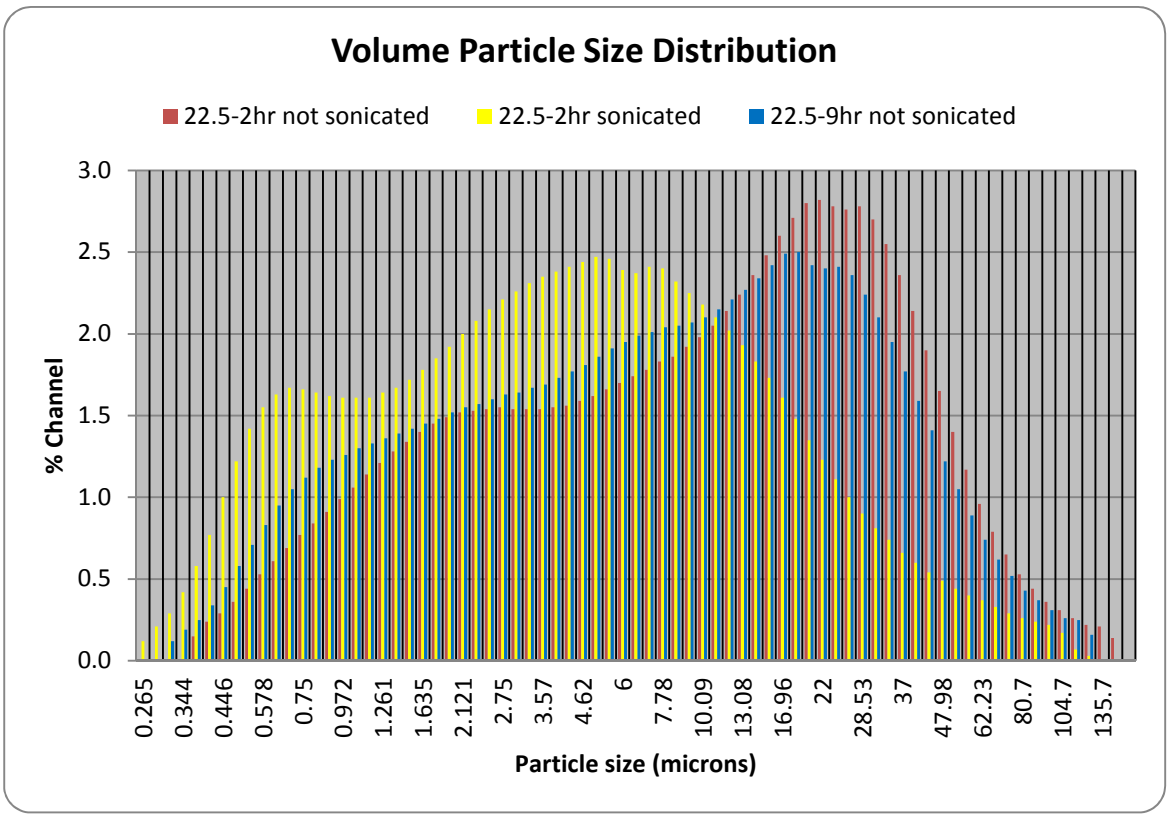


Figure 3-13 Mixer Effect on Bingham Plastic Yield Stress, 22.5 wt% Kaolin

3.2 Large Scale Vane Results

3.2.1 *Kaolin 5 Gallon Bucket Tests*

The large scale vane was functionally checked using a 5 gallon bucket for the 6x6 and 3x5 vanes with 30 and 35 wt% EPK kaolin slurries. The most sensitive torque sensor (max 0.5 Nm) was used in almost all of these activities due to the selected simulant having been rheologically thin compared to the capabilities of the LSV. Only one data point was taken with the larger torque sensor. Rheological measurements were also obtained using the RS600 rheometer. A 30 wt% Kaolin slurry was tested and the results of the vane and vane flow curve are provided in Table 3-14 using the 6x6 vane and the data shows good comparison given the different rotational speed tested. The flow curve (note that shear rate is now replaced with RPM) is also provided in Figure 3-14 and this data shows that the RS600 response yields a higher plastic viscosity and slightly high BPYS, though inspection of this figure indicates that the starting point of the curves originate from about the same yield stress.

Table 3-14 6 x 6 Vane, 0.5 Nm Sensor, 30 wt% Kaolin Rheology Results (11-29-2011)

Vane Data				Flow Curve Data					
Device	RPM	Yield Stress (Pa)	Stdev. (Pa)	Device	Curve	Fitted Range (RPM)	PV (cP)	BPYS (Pa)	R^2
RS600	0.3	17.2	0.21	RS600	up	1 – 23.5	337	20.7	0.9478
LSV	0.05	16.3	0.29		down	23.5 - 1	275	22.2	0.9420
	0.1	17.1	1.30	LSV	up	1 - 28	166	17.1	0.9322
	0.3	16.5	0.71		Down	5 - 28	99	19.4	0.9862
	0.6	17.7	0.48						

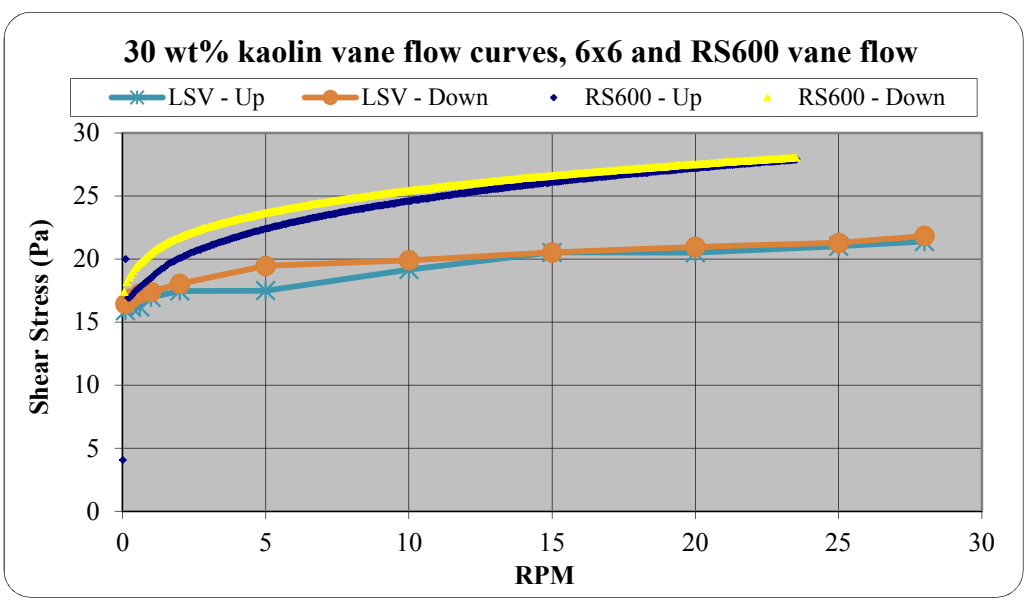


Figure 3-14 6x6 Vane LSV and FL-22 Vane RS600 Flow Curves, 30 wt% Kaolin

The results for the 30 wt% and 35 wt% kaolin using the 3x5 vane are provided in Table 3-15 and Table 3-16 respectively. The vane data indicates that the 3x5 vane slightly underestimated the yield stress for the 30 wt% kaolin and slightly overestimated the yield stress for the 35 wt% kaolin. The larger torque sensor was tested for only one data point (Table 3-15) and compares well to the more sensitive torque sensor. The flow curve for the 35 wt% kaolin using the LSV and RS600 is shown in Figure 3-15 and the response is similar to the previous comparison between the two instruments.

Table 3-15 3 x 5 Vane, 0.5 Nm Sensor, 30 wt% Kaolin Rheology Results (11-30-2011)

Vane Data				Flow Curve Data					
Device	RPM	Yield Stress (Pa)	Stdev. (Pa)	Device	Curve	Fitted Range (RPM)	PV (cP)	BPYS (Pa)	R^2
RS600	0.3	17.2	0.21	LSV	up	1 - 28	147	16.4	0.7810
LSV	0.1	13.6	0.49		Down	1 - 28	126	15.9	0.8167
	0.3	16.0	0.96						
	0.6	18.3	0.09						
	0.1**	14.2	0.86						

** This measurement was performed using the 5 Nm sensor

Table 3-16 3 x 5 Vane, 0.5 Nm Sensor, 35 wt% Kaolin Rheology Results (11-30-2011)

Vane Data				Flow Curve Data					
Device	RPM	Yield Stress (Pa)	Stdev. (Pa)	Device	Curve	Fitted Range (RPM)	PV (cP)	BPYS (Pa)	R^2
RS600	0.3	36.6	0.43	RS600	up	3 -23.5	648	48.7	0.9739
LSV	0.05	40.7	0.71		down	23.5 – 3	571	51.0	0.9589
	0.1	38.8	1.53	LSV	up	1 - 28	319	41.5	0.9695
	0.3	41.0	1.76		Down	1 - 28	279	42.5	0.8941
	0.6	44.2	1.20						

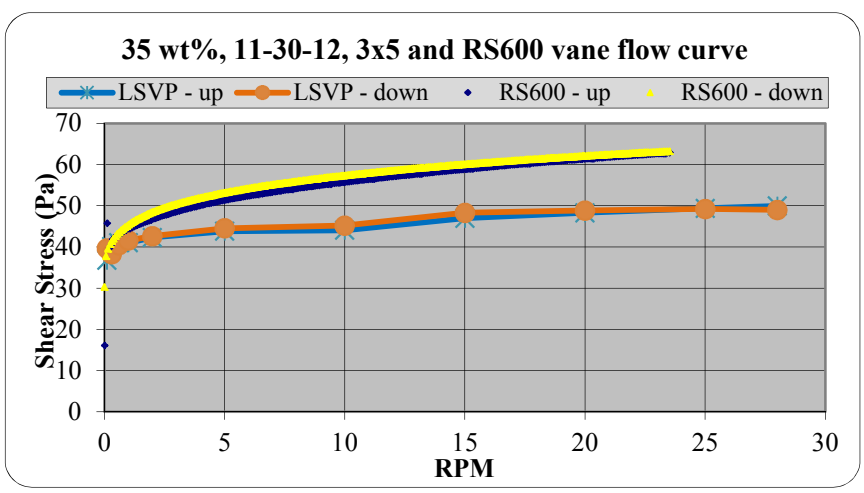


Figure 3-15 3x5 Vane LSV and FL-22 Vane RS600 Flow Curves, 35 wt% Kaolin

The 6x6 vane was also tested using the 35 wt% kaolin slurry and its results are provided in Table 3-17 and it shows a good comparison with the RS600 results. The 3x5 and 6x6 vane flow curves are shown in Figure 3-16, where the 3x5 is slightly more viscous, but the curve are close to each other, unlike the RS600 results.

Table 3-17 6x6 Vane, 0.5 Nm Sensor, 35 wt% Kaolin Rheology Results (11-30-2011)

Vane Data				Flow Curve Data					
Device	RPM	Yield Stress (Pa)	Stdev. (Pa)	Device	Curve	Fitted Range (RPM)	PV (cP)	BPYS (Pa)	R^2
RS600	0.3	36.6	0.43	RS600	up	3 -23.5	648	48.7	0.9739
LSV	0.1**	34.8	0.88		down	23.5 – 3	571	51.0	0.9589
	0.1	37.5	0.91	LSV	up	1 - 25	395	38.2	0.9494
	0.3	36.3	0.40		Down	25 - 1	342	39.4	0.9144
	0.6	38.0	0.30						

** Surface Measurement

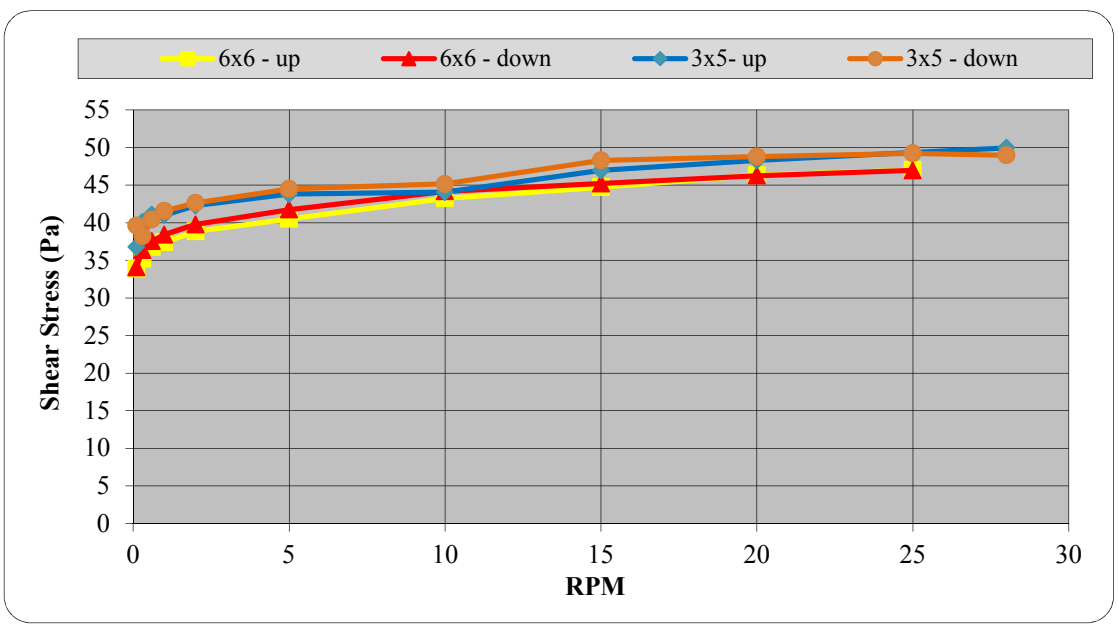


Figure 3-16 3x5 and 6x6 Vanes LSV Flow Curves, 35 wt% Kaolin

Figure 3-17 shows a surface measurement using the 6x6 inch vane upon completion of the 35 wt% kaolin measurement. The figure shows the outline of the vane after it has sliced through the material and further supports the assumption (cylindrical shape) used in assessing the vane for yield stress measurements. Individual kaolin rheological measurements can be found in reference 23 for large vane measurements.

Figure 3-17 3x5 Vane Cutting through 35 wt% Kaolin at Surface in 5 Gallon Bucket

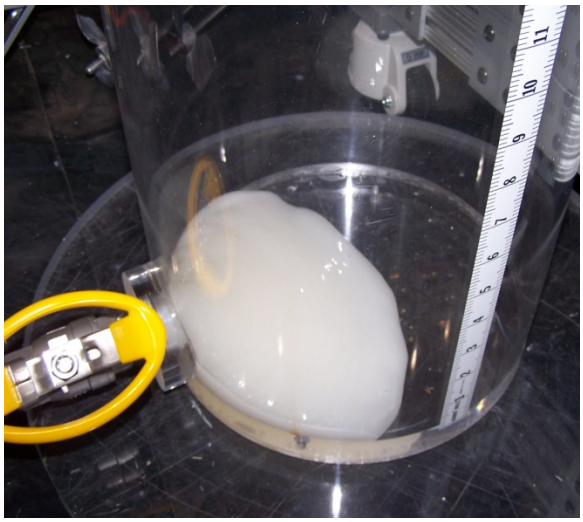
3.2.2 *Xanthan Gum LSV Depth Measurements*

Xanthan gum was the next material used to assess the performance of the LSV. As stated previously, the 3 wt% xanthan gum was mixed in a 55 gallon drum and transferred. The fluid was transferred using a peristaltic pump from the drum to the LSV and the initial and final loading of the LSV can be seen in Figure 3-18. The 3 wt% xanthan gum was very viscous and took over an hour and a half to load the LSV.

The first day of measurements used the 3x5 vane and the results are provided in Table 3-18 and shown in Figure 3-19. The first set of measurements was performed at 0.1 RPM and the second set was performed at 0.3 RPM. The first set of measurement results show that after the 1st vane measurement was taken, subsequent vane results were lower, indicating shear history might be a factor for xanthan gum solutions and the fact that the xanthan gum is more of a gel and the time between measurements were not adequate for the yield stress to recover by diffusion only. This was verified by RS600 data by the 2nd vane measurement. The second set of vane measurements still shows shear history. Figure 3-19 shows a very slight increase in yield stress as a function of immersion depth. The 3x5 vane slightly under-estimated the yield stress as compared to the RS600 data. Upon completion of the second set, the vane was rotated at its maximum rotation speed and slow raised through the xanthan gum so as to provide a consistent shear history for the 2nd day of measurements using 6x6 vanes. The reference xanthan gum samples for the RS600 were also sheared at the same time to remove any history.

The 6x6 xanthan gum results are provided in Table 3-19 and shown in Figure 3-20. The 6x6 vane also reported a lower yield stress than the RS600 and subsequent vane measurements after the 1st were lower in value indicating shear history as previously stated.

Figure 3-21 shows a typical vane response as compared to the RS600. Due to the slower rotational speed of the LSV (0.1RPM) as compared to the RS600 (0.3 RPM), the viscoelastic region was much greater. This response is also typical of other materials when changing the rotational speed; this is not a unique condition. Individual xanthan gum rheological measurements can be found in reference 20 for large scale xanthan gum measurements.



Initial Filling

LSV Filled

Figure 3-18 Filling the LSV with 3 wt% Xanthan Gum

Table 3-18 3 wt% Xanthan Gum – 3x5 Variable Depth Vane Measurements – Day 1

Point	First Set of Measurements						Second Set of Measurements		
	LSV at 0.1 RPM				RS600		LSV at 0.3 RPM		
	Height from surface	Measurement Sequence and Yield Stress (Pa)			Measurement and Yield Stress (Pa)		Measurement Sequence and Yield Stress (Pa)		
	(in)	1st	2nd	3rd	1st	2nd	1st	2nd	3rd
0	2.5	22.4	17.6	18.2	-	-	18.9	16.6	16.9
1	10.5	23.9	18.5	14.4	29.8	19.2	20.0	18.3	13.9
2	18.5	25.3	21.0	15.1	29.9	18.5	18.6	16.2	15.3
3	26.5	24.7	18.6	19.4	-	-	20.5	17.5	15.2
4	34.5	22.0	19.2	18.7	-	-	19.5	15.4	17.8
5	42.5	25.4	15.5	18.8	-	-	21.1	16.7	18.4
6	50.5	27.9	22.5	19.9	-	-	19.3	18.7	18.4

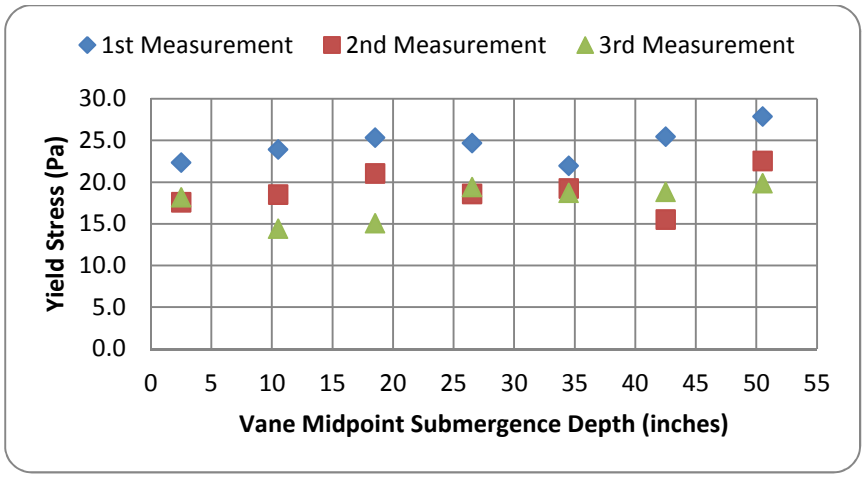


Figure 3-19 3 wt% Xanthan Gum – 3x5 Vane - Variable Depth – 1st Set of Measurements Day 1

Table 3-19 3 wt% Xanthan Gum – 6x6 Variable Depth Vane Measurements – Day 2

Point	First Set of Measurements						Second Set of Measurements		
	LSV at 0.1 RPM				RS600		LSV at 0.3 RPM		
	Height from surface	Measurement Sequence and Yield Stress (Pa)			Measurement and Yield Stress (Pa)		Measurement Sequence and Yield Stress (Pa)		
	(in)	1st	2nd	3rd	1st	2nd	1st	2nd	3rd
0	6	27.8	20.8	17.5	29.9	20.2	16.1	13.6	14.3
1	18	24.5	19.4	19.0	-	-	18.5	16.2	15.7
2	30	26.7	20.1	18.5	28.5	19.7	19.3	17.1	16.6
3	42	26.2	20.1	19.6	-	-	18.4	17.3	17.4
4	54	25.3	19.3	17.2	28.0	19.4	19.8	17.1	16.9

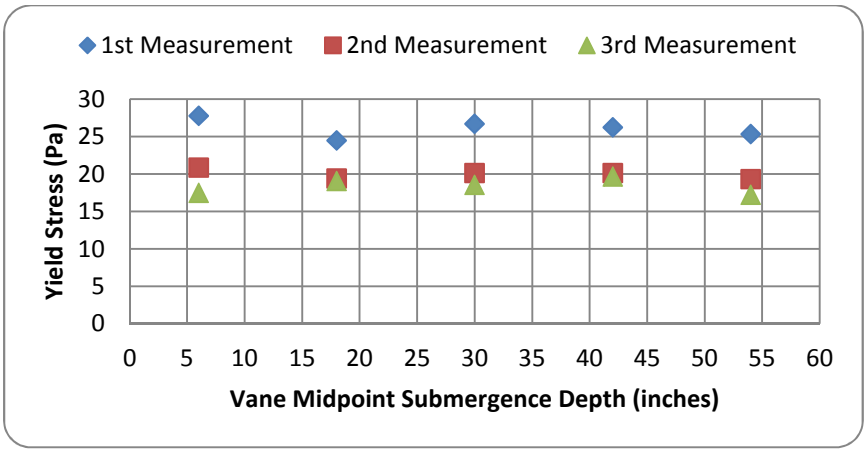


Figure 3-20 3 wt% Xanthan Gum – 6x6 Vane - Variable Depth – 2nd Set of Measurement Day 2

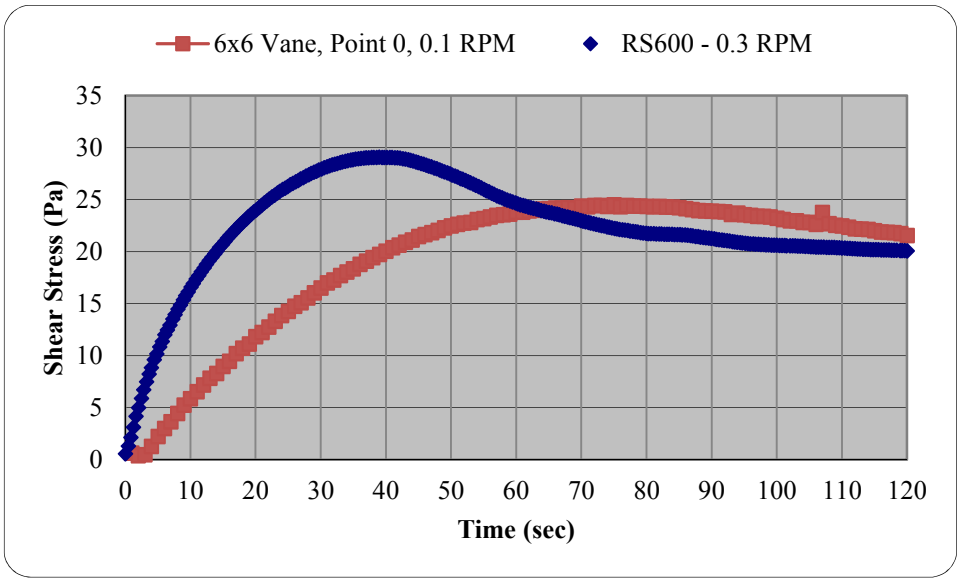
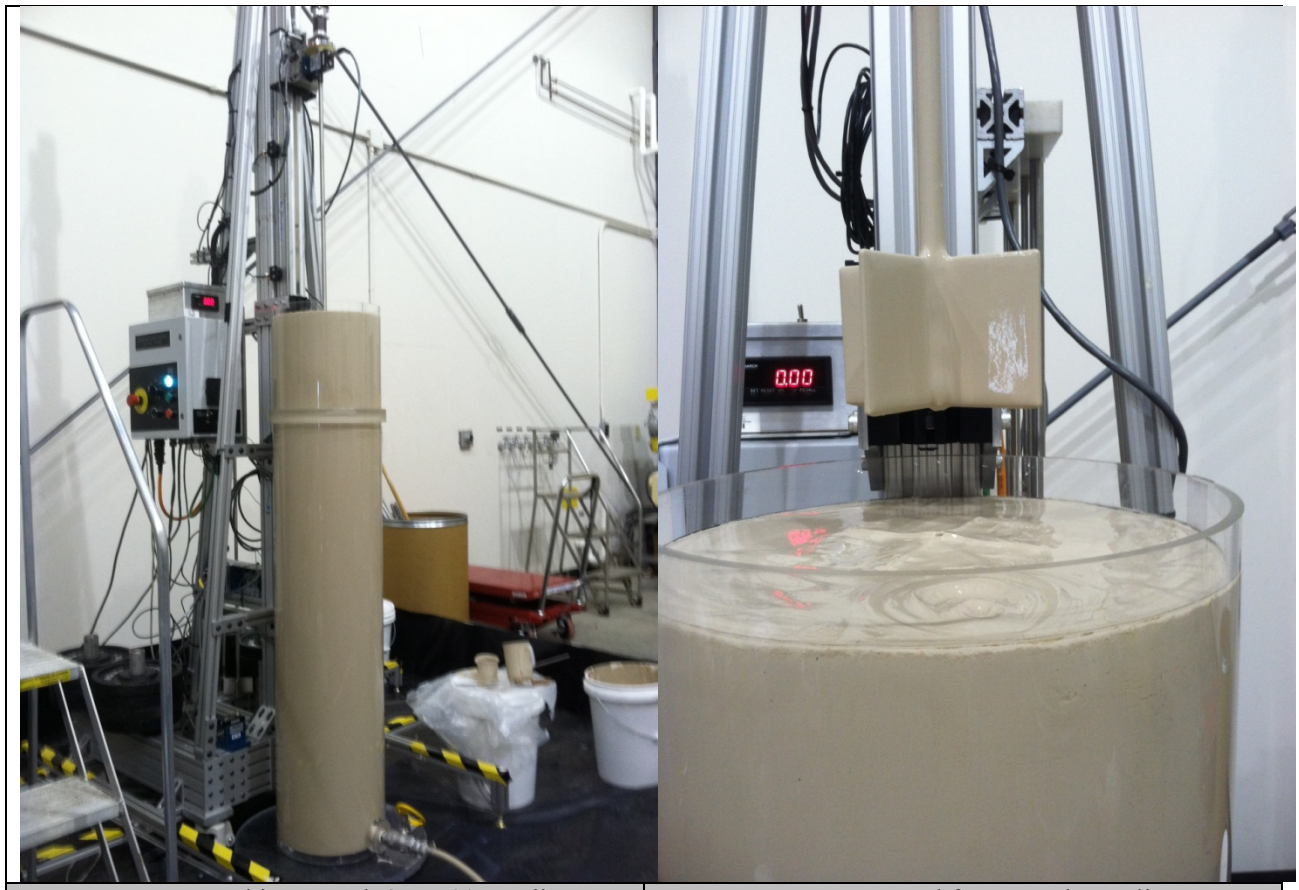


Figure 3-21 Typical Xanthan Gum Vane Response, LSV and RS600

3.2.3 *35 wt% Kaolin LSV Initial Depth Measurements*

A 35 wt% (calculated concentration of 34.02 wt%) was mixed in a 55 gallon drum and transferred to the LSV using the same pumping configuration used for the 3 wt% xanthan gum. Unlike the xanthan gum, the 35 wt% kaolin was transferred in less than 30 minutes. Figure 3-22 shows the LSV tank filled to 58.25 inches and the vane submerged into the kaolin and the 3x5 vane after a measurement has been completed. The results for 35 wt% kaolin are provided in Table 3-20 and the depth measurements are plotted in Figure 3-23. The LSV vane results compared well with the RS600 results. Also, the distance between measurements was reduced to increase the number of data point and this did not seem to have an effect (thought additional testing will be required) on the response. Figure 3-23 shows little effect on vane immersion depth and yield stress. Figure 3-24 shows a typical vane response for the LSV using the 3x5 vane, where the initial measurement has the traditional vane response and the subsequent response coming to a flat plateau. This was consistent with all subsequent measurements, indicating that kaolin may also have some shear history effects but not like that of xanthan gum. Individual kaolin rheological measurements can be found in reference 23 for large vane measurements.



Vane Inserted into Fresh 35 wt% Kaolin	Vane Removed from Fresh Kaolin

Figure 3-22 35 wt% Kaolin Loaded into LSV and 3x5 Vane Measurement

Table 3-20 35 wt% Kaolin – 3x5 Variable Depth Vane Measurements – Day 1

Point	First Set of Measurements					
	LSV at 0.1 RPM				RS600	
	Height from surface	Measurement Sequence and Yield Stress (Pa)			Measurement and Yield Stress (Pa)	
	(in)	1st	2nd	3rd	1st	2nd
0	2.5	35.9	33.3	30.9	36.2	35.4
1	8.5	35.4	28.7	29.9	36.2	34.6
2	16.5	32.3	28.4	29.4	36.5	34.8
3	24.5	33.1	31.4	31.5	-	-
4	32.5	34.0	29.5	32.4	-	-
5	40.5	34.3	30.1	29.3	-	-
6	48.5	34.3	32.8	29.6	36.3	33.7
7	55.7	38.4	30.4	34.4	36.5	35.2

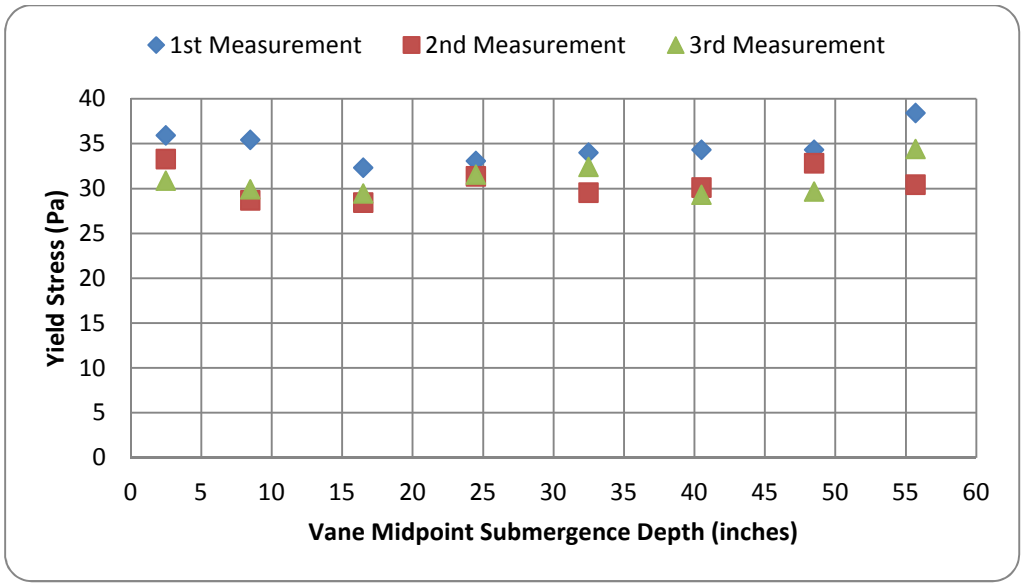


Figure 3-23 35 wt% Kaolin – 3x5 Vane - Variable Depth –1st Set of Measurement Day 1, 0.1RPM

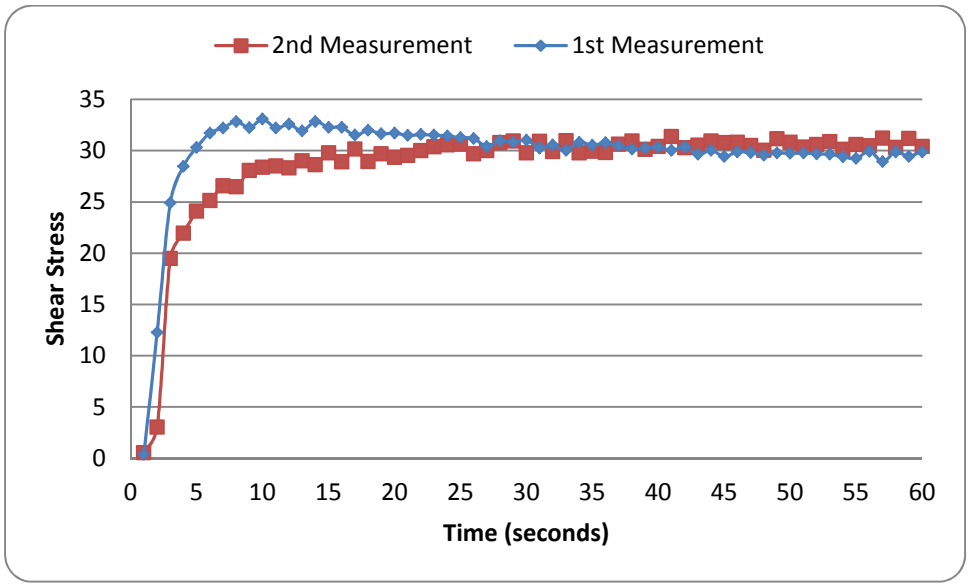
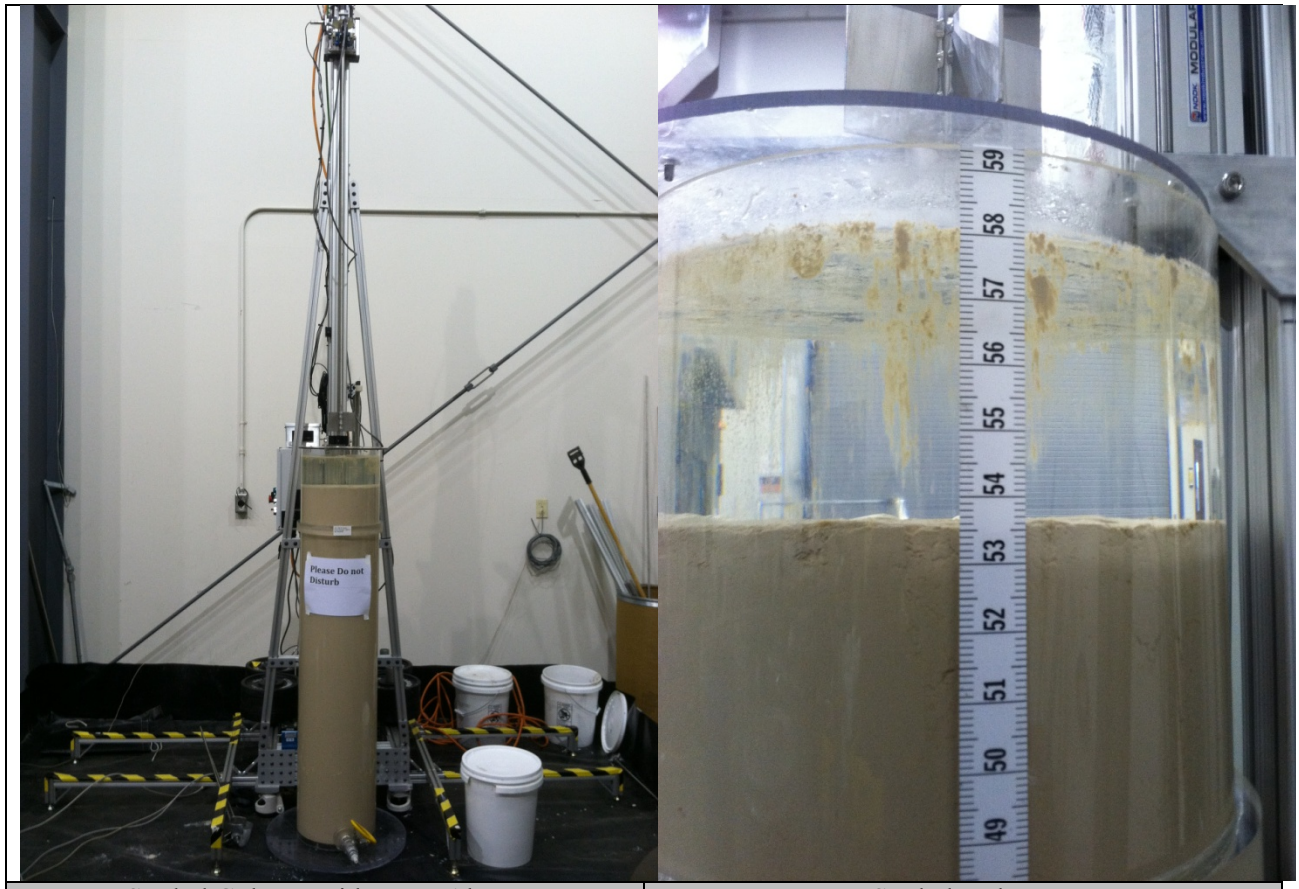


Figure 3-24 35 wt% Kaolin – 3x5 Vane - Variable Depth – Point 3 Measurement, 0.1 RPM

3.2.4 *Three Months of settled 35 wt% Kaolin LSV Depth Measurements*

The 35 wt% kaolin settled for 3 months prior to the last set of measurements. The kaolin settled from 58.25 inches to 53.5 inches, as shown in Figure 3-25. The "average" calculated wt% total solids in the settled bed went from 34.02 to 36.36 wt% and no settling (interfacial) rates were obtained during this period of time. The vane results are shown in Table 3-21 and in Figure 3-26. There is definitely a yield stress gradient in the settled bed and the data fits well to an exponential model as shown in Figure 3-26. There were no RS600 data for comparison, though it would have been useful as a comparison since the effect of a settled bed cannot be reproduced on small rheology samples. Figure 3-27 shows the vane

response for the deepest measurement, which is also consistent with the previous data set with respect to how the 2nd measurement response. In this case, the kaolin seems to be very thixotropic.



Settled Column with Vane Above	Settled Volume

Figure 3-25 35 wt% Kaolin 3 Months Of Settling

Table 3-21 35 wt% Kaolin – 3x5 Variable Depth Vane Measurements – 3 Months Settled, 0.1 RPM

Point	Height from surface (in)	Measurement Sequence and Yield Stress (Pa)	
		1st	2nd
0	7.75	42.7	25.5
1	16.75	62.0	42.5
2	25.75	69.8	43.0
3	34.75	82.7	56.0
4	43.75	97.1	68.7
5	52.75	123.2	88.7

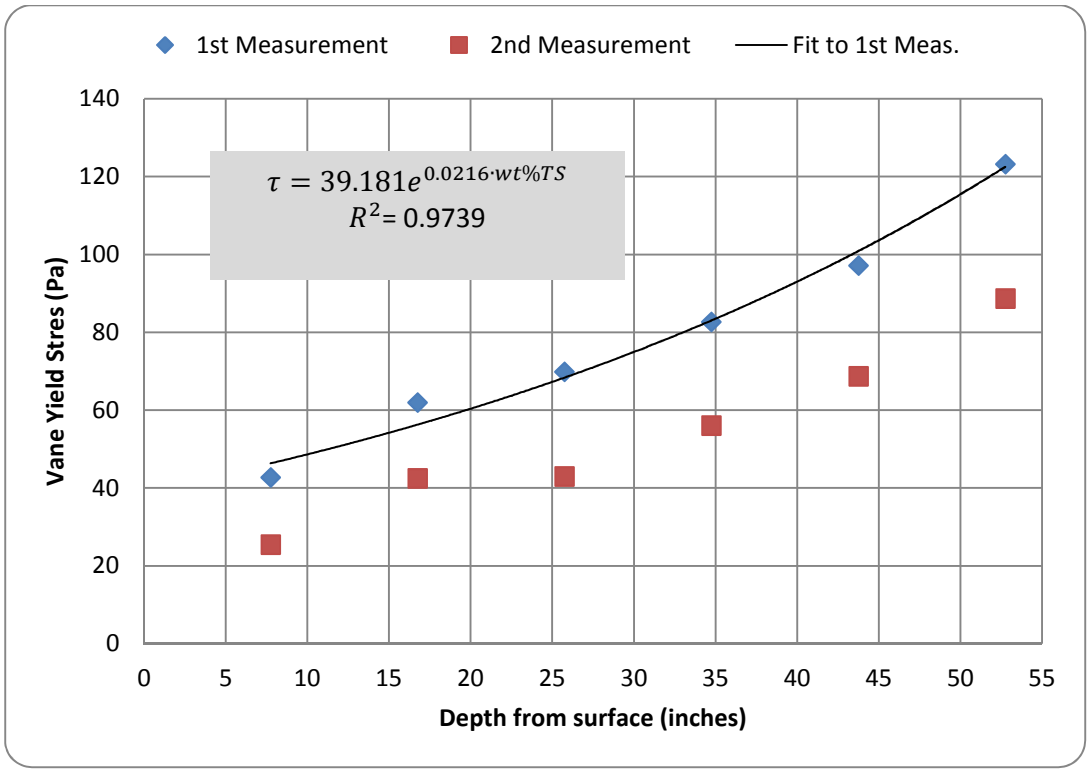


Figure 3-26 Settled Kaolin – 3x5 Vane - Variable Depth – 3 Months

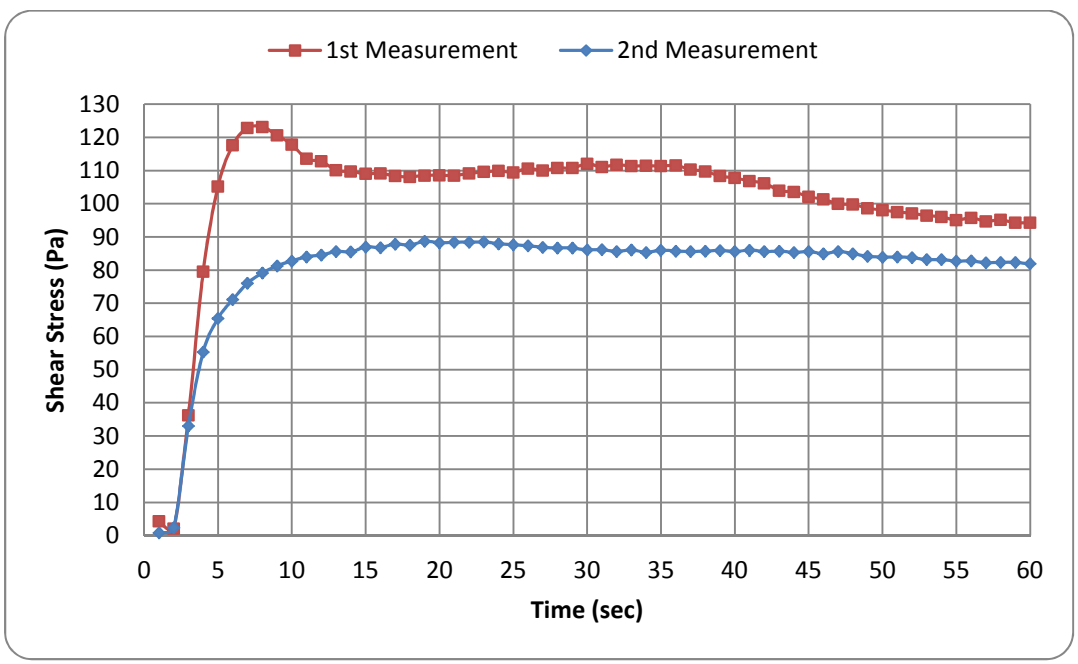


Figure 3-27 Settled Kaolin – 3x5 Vane Response - Variable Depth – 3 Months, 0.1 RPM

Prior to performing the flow curve measurements, the vane was allowed to rotate for three minutes at 25 RPM while measuring the shear stress to further remove any thixotropic properties given the range at which the LSV can measure. The shear stress response for the deepest insertion measurement shows that

most of the thixotropic properties have been removed (see Figure 3-28). Flow curves for immersion depths 16.75 and 52.75 inches are provided in Figure 3-29. This clearly shows that the lower section of settled solids is more viscous than the upper region and is consistent with the other vane measurements. There is no definitive answer for this gradient since other physical properties were not captured, such as density and solids concentration as a function of settled bed. Individual kaolin rheological measurements can be found in reference 23 for large vane measurements.

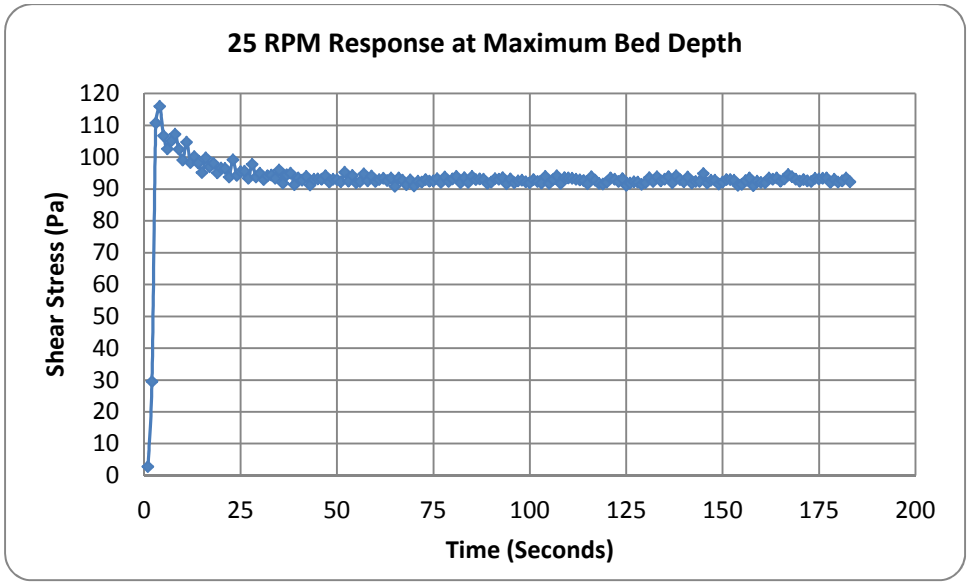


Figure 3-28 Settled Kaolin – 52.75 Inch Vane Immersion Depth, Thixotropic Removal Curve

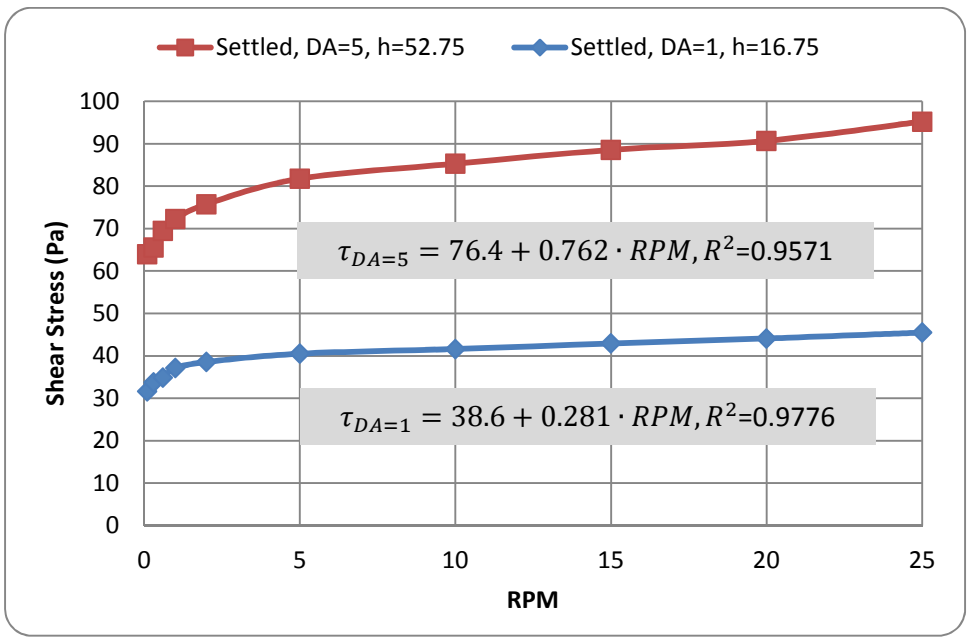


Figure 3-29 Settled Kaolin – Flow Curve at DA=1 and DA=5 Vane Immersion Depths

4.0 Conclusions

The vane method was used to characterize the yield stress of four different non-cohesive glass beads as a function of depth and forced settling (tapping) using bench top equipment. The results indicate the following:

- Surface measurement results are insensitive to tapping or particle size distribution.
- Tapping increases the yield stress for a given submergence for all beads.
- Yield stress response is somewhat linear with depth other than the deepest measurement. The deepest measurement may be impacted by the bottom of the container resulting in a much higher response than expected for a linear relationship.
- In all cases, the glass beads easily poured out of the containers upon completion of testing, indicating the measured yield stress is a "confined" yield stress created by the wall of this container and the mechanical (hard body) interactions of the solids.

The vane was used to characterize the rheology of xanthan gum using both the vane method and vane flow curve. These results were compared to the traditional flow curve (concentric cylindrical method). All measurements were bench top and the results are:

- The traditional flow curve yielded the highest yield stress, followed by the vane flow curve and final the vane method. The reason for this is the range of shear rate measured and the range in which the data were fitted in the individual flow curves. The traditional flow curve had a much large shear rate range of measurement.
- The vane method showed an elastic modulus that was very short and a viscoelastic response that was long before the dynamic yield stress was reached. This response could be typical for such a fluid, where the continuous phase is non-Newtonian.

A conventional mixer (Rushton impeller) was used to prepare 15 to 32.5 weight percent (wt%) kaolin slurries and they were continuously mixed for up to 22 hours. Samples at 2 hour intervals were pulled and analyzed using the vane method, vane flow curve, and traditional flow curves as well as for wt% total solids and density. A 22.5 wt% slurry was prepared using a high shear mixer and analyzed using the traditional flow curve. Finally, 22.5 and 25 wt% slurries were analyzed for particle size distribution at 2 and 9 hours of mixing. All measurements were bench top and the results are:

- The traditional flow curve yielded the highest yield stress, followed by the vane flow curve and finally the vane method. The reason for this is the range of shear rate measured and the range in which the data were fitted in the individual flow curves. The traditional flow curve had a much large shear rate range of measurement.
- As the wt% solids increased, the difference between the vane measurements and traditional flow curve yield stresses increased. This is attributed to an increase in a more power law response at the lower shear rate range in the traditional flow curve as the wt% solids increased and curve fitting the linear region of the flow curve.
- For 20 wt% or greater kaolin concentration, the yield stress tends not to change much after 14 to 16 hours of mixing, given the mixing system used in this task.
- The vane method for the less than 22.5 wt% kaolin slurries does not show the typical or expected vane response, though the yield stresses as measured using the other methods are very similar.
- The vane method response to the kaolin slurries was different than that of the xanthan gum, where for the kaolin slurries there was a very small viscoelastic response region.
- An exponential model was used to fit the Bingham Plastic parameters of the traditional flow curve as a function of wt% TS for the different mixing times. The curve fit was good. One data set was assessed by fitting the data with the same model but using a limited number of data points to see the effect of interpolation and extrapolation. Interpolation fitted well with the actual data points whereas extrapolation in this case over-estimated the yield stress.

- The 22.5 wt% high sheared slurry resulted in rheological properties that were a factor of two greater as compared to the Rushton mixed sample and mixing times were reduced over a hundred fold. The sample was sheared at both high and very high shear rates and the rheological properties increased at the very high shear rates. The rate of applied shear and the time of shearing affect the rheological properties of kaolin.
- The particle size distribution shifted to a smaller distribution when continuously mixed using the Rushton impeller. The shift to a smaller particle size distribution is one of the parameters that is most likely affecting the rheological properties of kaolin. Sonication of these samples showed even a further shift to a smaller particle size distribution.

A large scale vane was designed, fabricated, and tested. The vane had the following capabilities:

- Measure up to 50 inches of slurry, homogenized or settled.
- Two different torque sensors, 0 to 0.5 N-m and 0 to 5 N-m.
- Five different vane sizes with A factors ranging between 139 to 1720 m^{-3} for subsurface measurements and 159 to 2148 m^{-3} for surface measurements.
- Vertical vane position and the rate of insertion in and out of the fluid are controlled.
- Rotational rate between 0.05 to 28 revolutions per minute.
- A 5 foot tall by 12 inch inside diameter tank for loading simulants.

The large scale vane was benchmarked against the bench top rheometer using 30 and 35 wt% kaolin slurries using both the vane method and vane flow curve with the following results:

- The vane method results for the 6x6 vane compared well with the bench top (up to $\pm$ 5%) over a range of 0.05 to 0.6 RPM. The vane method results for the 3x5 vane slightly under-estimated the 30 wt% and slightly over-estimated the 35 wt% as compared to the bench top (up to $\pm$ 20%) over a range of 0.05 to 0.6 RPM.
- The 3x5 and 6x6 vane flow curves are similar.
- The 3x5 and 6x6 vane flow curves yield smaller Bingham Plastic parameters as compared to the bench top results.
- The 3x5 and 6x6 vanes produced a circular cut through the fluid, supporting the vane method assumption (cylindrical shape) used in assessing the vane for yield stress.

The large scale vane was tested using a 3 wt% xanthan gum solution. The xanthan gum filled the 5 foot tank and three data points at any given elevation were obtained using the 3x5 or 6x6 vane with the following results:

- The vertical yield stress distribution was fairly flat using either the 3x5 or 6x6 vanes based on the initial vane measurement. The effect of depth did not impact the vane method result.
- The 2nd set of vane measurements showed that xanthan gum is highly impacted by shear history and this was supported by the bench top vane results.
- The bench top vane results were greater than the 3x5 or 6x6 vane results.

The large scale vane was tested using a 35 wt% kaolin slurry. The 3x5 vane was selected for this testing since it could obtain more vertical data points than the 6x6 vane. Both fresh (just mixed and placed kaolin slurry) and settled (3 month) 35 wt% data were obtained with the following results:

- The vertical yield stress distribution for the fresh slurry was fairly flat, indicating that slurry depth had no impact on the vane results for fresh properties. This was consistent with the xanthan gum results.
- The initial large scale vane results were comparable to the initial bench results.
- Subsequent vane method measurements showed the 35 wt% kaolin slurry to be somewhat thixotropic and this was evident in both the large scale vane and bench scale.
- After 3 months of settling, the average calculated solids concentration in the settled bed of kaolin increased by 2.36 wt%.

- The vertical yield stress distribution for the settled bed showed a vertical yield stress distribution, becoming thicker as the depth increased. The yield stress at 8 inches from the top of the settled bed was 43 Pa and at 53 inches it was 123 Pa. Six vertical data points were obtained and these data fit well to an exponential model.
- The second vane method measurement showed the settled bed to be much more thixotropic as compared to the fresh state. The initial measurements are important in determining the bed yield stress.
- Vane flow curves were obtained at 17 and 53 inches below the surface. Thixotropic properties were removed using the vane at 25 RPM. The results clearly show the flow curve at the 53 inch level to be much thicker than that at the 17 inch level.

5.0 Recommendations, Path Forward or Future Work

The use of xanthan gum or other rheology modifiers that directly dissolve and become part of the continuous phase to make the solution non-Newtonian is not recommended for future testing. In the DOE realm of waste, the continuous phase is a solution that only has Newtonian properties and the undissolved solids is the phase that contributes to the non-Newtonian behavior.

The following recommendations are to further develop the capabilities of the vane for use in measuring the rheological properties of slurries and implementation for in situ measurements of both settled and homogenized slurries in actual tank farm operations or test programs:

- Compare the bench top and large scale using the vane method to see whether the bench top measurements can be used to assess for settled solids or aging effects that could occur in a large settled bed. The bench top container and vane must be modified such that depth measurements on the bench scale can be made. Simple single point bench scale vane method measurements are not sufficient.
- Quantify whether the vane can be used to determine the flow properties of non-Newtonian fluids on the bench scale. Only cover the rheological range of properties that can typically be mixed or transferred in the DOE complex. This work should initially be performed on the bench scale and then taken to the large scale vane.
- Perform bench scale tests with cohesive slurries containing non-cohesive materials to determining how the non-cohesive materials settle out over time and how they impact the rheological properties. The cohesive materials should have a range of rheological properties. The non-cohesive materials should include solids that have different densities and particle size distributions. The concentration of these non-cohesive materials should also be a variable. These properties can be determined at a later date.
- Use the existing large scale vane to investigate whether the settled bed of cohesive solids packs differently if the initial starting wt% solids concentration of the slurry is a variable. Obtain settled bed material to quantify both density and wt% solids so as to relate these data back to the yield stress measurements. The effect of settling time should also be included. The initial cohesive simulant should be a simple simulant. Bench scale tests should be run concurrently to determine whether scale is an issue, e.g. the height of the settled bed is a factor.
- Use the existing large scale vane to determine when shaft contributions start to impact the vane measurement.
- Use the existing large scale vane and results from the bench scale testing to determine the effect of non-cohesive solids on the settled bed of cohesive solids. These data must be compared to bench top data to determine whether bench top data can be used to assess settling or aging.
- Design, fabricate and test a large vane that has attributes that can be deployed to a full scale vane for plant measurements. Such attributes would include how to extend the shaft, easy replacement of components, and upgrading instrumentation and equipment capability.

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6.0 References

[1] Gauglitz, P. A., Fort, J. A., Wells, B. E., and Meyer, P. A., "An Approach to Understanding Cohesive Slurry Settling, Mobilization, and Hydrogen Gas Retention in Jet Mixed Vessels, PNNL-17707, May 2009

[2] Guerrero, H. N. and Restivo, M., "Final Report – UFP Restart and Sparger Testing", WSRC-TR-2004-00488, Rev. 0, October 2004

[3] Hansen, E. K. and Fellinger, T. L., "Yield Stress and Physical Data Results for the Tank 19F Radioactive Mound Sample and Tank 19F Simulant Samples", WSRC-TR-2002-00070, February 2002

[4] Pariezs, J. M. and Hansen, E. K., "Rheology and TIC/TOC Results of ORNL Tank Samples", SRNL-STI-2011-00754, In Review

[5] Poloski, A. P., and et al., "Characterization and Correlation of Particle-Level Interactions to the Macroscopic Rheology of Powders, Granular Slurries, and Colloidal Suspensions", PNNL-16133, Sept. 2006

[6] Higashi, N. and Sumita, I., "Experiments on granular rheology: Effects of particle size and fluid viscosity", Journal of Geophysical Research, Vol. 114, 2009

[7] Eibling, R. E., Hansen, E. K., and Pickenheim, "Potential Impact of Blending Residual Solids From Tanks 18/19 Mounds with Tank 7 Operations", WSRC-STI-2007-00113, Rev. 0, March 2007

[8] Hansen, E. K., "Summary of 2009 Rheology Modifier Program", SRNL-STI-2009-00697, December 2009

[9] Richards, A. F., "Vane Shear Strength Testing in Soils", ASTM, STP 1014, 1988

[10] WP3-3.2.1-FY2011, "EM-30 Technology Development and Deployment (TDD) Program Task Plan", June, 9, 2011

[11] Liddell, P.V. and Boger D.V., "Yield Stress Measurements with the vane", Journal of Non-Newtonian Fluid Mechanics, Vol. 63, pp 235-261, 1996

[12] Nguyen, Q.D. and Boger D.V., "Yield Stress Measurements for Concentrated Suspensions", Journal of Rheology, Vol. 27, pp 321-349, 1983

[13] Nguyen, Q.D. and Boger D.V., "Direct Yield Stress Measurement with the Vane Method", Journal of Rheology", Vol. 29, pp 335-347, 1985

[14] Barnes, H.A. and Nguyen, Q.D., "Review Rotating Vane Rheometry – a Review", Journal of Non-Newtonian Fluid Mechanics, Vol. 98, pp 1-14, 2001

[15] Yoshimura, A. S., and Prud'Homme, P.K., "A Comparison of Techniques for Measuring Yield Stresses", Journal of Rheology, Vol. 31, pp 699-710, 1987

[16] Steffe, J. F., "Rheological Methods in Food Processing Engineering", Freeman Press, 2nd edition, 1996

[17] Barnes, H. A. and Carnali, J. O., "The vane-in-cup as a novel rheometer geometry for shear thinning and thixotropic materials", Journal of Rheology, Vol. 34, pp 841-866, 1990

[18] Bjorkman, U., "Reflections over Metzner's method", Annual Transactions of the Nordic Rheology Society, Vol. 16, 2008

[19] Hansen, E. K., "Large SRNL Vane Data 2012 – Solid Spheres, - Bench Top", SRNL-L3100-2012-00128, Rev. 0, September, 2012

[20] Hansen, E. K., "Large SRNL Vane Data 2012 – Xanthan Gum – Bench and Large Scale", SRNL-L3100-2012-00130, Rev. 0, September, 2012

[21] Langton, C. A. and Hansen, E. K., "Saltstone Clean Cap Formulation", WSRC-TR-2005-00158, Rev. 0, April 22, 2005

[22] Hansen, E. K., "Large SRNL Vane Data 2012 – Kaolin Slurries - Bench Top", SRNL-L3100-2012-00129, Rev. 0, September, 2012

[23] Hansen, E. K., "Large SRNL Vane Data 2012 – Kaolin Slurries – Large Scale", SRNL-L3100-2012-00131, Rev. 0, September, 2012