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Rheology Modifiers Applied to Kaolin-Bentonite Slurries for SRNL WTP Pulse Jets Tank Pilot Work in Support of RPP at Hanford

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ABSTRACT

Savannah River National Laboratory (SRNL) was tasked to find and characterize the impact of rheological modifiers to a clay (Kaolin-Bentonite) slurry having 23.1 total wt% solids, 1.165 g/ml, and Bingham Plastic yield stress of 13 Pa and plastic viscosity of 24 mPa-sec. The primary objective was to find rheological modifiers when blended with this clay slurry that would provide a vane yield stress of 300 Pa when the slurry was undisturbed for 24 hours. A secondary objective was to find a modifier that after shearing would produce a Bingham Plastic yield stress of 30 Pa and plastic viscosity of 30 mPa-sec. Two parallel paths were chosen with one examining a variety of organic/inorganic modifiers and another using just the inorganic modifier Laponite®. The addition of organic modifiers hydroxyethylcellulose, hydroxypropylmethylcellulose, and hydroxypropylcellulose at a target 0.50 wt% dramatically increased the vane yield stress over the range 311 - 724 Pa, and also increased the Bingham plastic yield stress and plastic viscosities over the range 33-112 Pa and 27-166 mPa-sec, respectively. The organic modifiers also showed elastic behavior, yielding a very unpredictable up flow curve. The 0.50 wt% addition of inorganic modifiers magnesium aluminum silicate and hydrate magnesium aluminum silicate only increased the vane yield stress to 36-46 Pa and had little impact on the Bingham Plastic parameters. A range of an inorganic (2-4 wt% magnesium aluminum silicate) and combination of a range of an inorganic (2-3 wt% magnesium aluminum silicate) and organic (0.03-0.05 wt% sodium carboxymethylcellulose) modifiers were then tested. These results showed that the target vane yield stress could be obtained but the Bingham Plastic yield stress and plastic viscosity were 3 times too high. Reducing the organic modifier weight percent by a few hundredths, the Bingham Plastic yield stress could be obtained, but then the vane yield stress would be too low. The addition of Laponite® (synthetic lithium aluminum silicate) increased the vane yield stress of the clay slurry to values as high as 1500 Pa. However, the flow curve behavior for the laponite samples was not predictable and the secondary objective was dropped based on customer needs and time constraints. Ultimately a 3-wt% addition of Laponite® was chosen to produce a 600 Pa vane yield stress mixture.

INTRODUCTION

SRNL was tasked with finding and testing commercially available rheological modifiers for a clay (Kaolin-Bentonite) slurry used for Waste Treatment Plant (WTP) Pulse Jet Mixer pilot work at SRNL in support of the River Protection Program (RPP) at Hanford.[1-2] The physical properties of the clay slurry were 23.1 wt% total solids, 1.165 g/ml, and a Bingham plastic yield stress of 13 Pa and plastic viscosity of 24 mPa-sec. The objective was to find rheological modifiers when blended with this clay slurry that would provide a vane yield stress of 300 Pa when the slurry was undisturbed for 24 hours and upon shearing and removal of thixotropic properties, a Bingham Plastic yield stress of 30 Pa and plastic viscosity of 30 mPa-sec. A program was developed to examine the impact of organic and inorganic modifiers on the clay slurry. Two parallel paths were chosen with one examining a variety of organic/inorganic modifiers and another using just the inorganic modifier Laponite®.

The modifiers were added to the clay slurry using high shear mixers with Rushton Turbine heads with 6 blades. To properly mix the small quantities required increasing the mixer speeds from 500 RPM to maximum speeds of 1800 RPM. Within minutes of adding the modifiers, the clay slurry was noticeably thicker. In some cases, the clay slurries had to be mixed like a milk shake by moving the container up, down, and around the mixing blades. After mixing the modified clay slurries were allowed to sit undisturbed for 24 hours to ensure the modifiers had time to form their various structures. Initial yield stresses were then measured on each sample using vane measurements on a Haake Rheometer 150. For these measurements the vane was gently lowered into the sample and then rotated slowly at constant speed while the torque was being recorded.[3] To further examine the flow properties of the clay slurries, cone and plate measurements were performed using a Haake Rheometer 600. As part of the cone and plate measurement, the material was re-sheared for both the up and down flow curves. Since the material was so thick (>150 Pa) the flow curves often exhibited pseudo-elastic behavior. The flow measurements were fitted to Bingham plastic models giving a yield stress and viscosity.

ORGANIC/INORGANIC RHEOLOGY MODIFIER STUDY

The clay slurry is to be blended with rheological modifiers to determine if the resulting slurry would have a vane yield stress of 300 Pa after being undisturbed for 24 hours and upon shearing and removal of thixotropic properties, yielding a Bingham Plastic fluid having a yield stress of 30 Pa and plastic viscosity of 30 mPa-sec.

The 1st phase of testing was conducted to narrow the selection of organic and inorganic modifiers for further testing. The results in testing six different rheology modifiers, resulting in a total of 18 tests are shown in Table 1. The organic modifiers hydroxyethylcellulose, hydroxypropylmethylcellulose, hydroxypropylcellulose, and sodium carboxymethylcellulose increased the vane shear stress significantly (724, 559, 311, 290 Pa, respectively) after just 24 hours with 0.50 wt% addition. During this phase of testing, the organic modifiers when blended with the clay slurry showed elastic behavior. This elastic behavior gave the material very unpredictable flow curve behavior during the initial up flow curve measurement. The clay slurries when blended with the organic modifiers were very thixotropic in behavior. The smectite modifiers, Hydrate Magnesium Aluminum Silicate and Magnesium Aluminum Silicate, at 0.50 wt% addition increased the vane yield stress to 36 and 46 Pa respectively or an order of magnitude less than the organic modifiers. These smectite modified slurries showed little to no thixotropic behavior. These results are also shown graphically in Figure 2 through Figure 4.

The results for the 1st phase of testing indicated that at blend of inorganic and organic modifiers could potentially provide the required rheological properties. A 2nd phase of testing then took combinations of the smectites to organic modifies in 10 to 1 ratios. The results from this testing are shown in Table 2, which show that the vane yield stress did increase to 300 Pa, but the plastic viscosity also increased to 3 times of the target 30 mPa-sec.

Figure 1 shows the structure of the clay slurry blended with 0.9 wt% magnesium aluminum silicate and 0.1 wt% sodium carboxymethylcellulose, after it had been allowed to sit undisturbed for 24 hours. The vane yield stress for this sample was 329 Pa and after shearing, the Bingham Plastic yield stress was 40 Pa and plastic viscosity was 80 mPa-sec. After 26 days, this clay slurry was like a thick bread pudding.

Based on these results, it appears that some combination of the smectites with the organic modifiers could produce a material with a vane yield stress (around 300 Pa) and after shearing the material, a Bingham Plastic yield stress between 30 to 40 Pa and plastic viscosity between 30 to 40 mPa-sec. The organic modifier portion added would most likely be kept extremely small and the material would have to be allowed to sit for a significant time (about a week) for the smectite modifiers to completely form their structures.

Table 1. Organic/inorganic Rheology Modifier Study Phase 1

Modifier		**Vane Yield Stress [Pa] After Blending is Completed**			**Bingham Plastic Properties after shearing**	
Type	**Wt% Added**	**24 hrs**	**48 hrs**	**144 hrs**	**Yield Stress [Pa]**	**Plastic Viscosity [mPa-sec]**
Hydrate Magnesium Aluminum Silicate	0.50%	36	53	68	12	28
Hydrate Magnesium Aluminum Silicate	1.50%	81	---	141	25	35
Hydroxyethylcellulose	0.10%	65	78	---	24	62
Hydroxyethylcellulose	0.50%	724	---	---	33	27
Hydroxypropylcellulose	0.10%	62	80	---	18	54
Hydroxypropylcellulose	0.50%	311	---	---	---	---
Hydroxypropylmethylcellulose	0.10%	60	74	---	17	51
Hydroxypropylmethylcellulose	0.50%	559	---	---	112	166
Magnesium Alumnium Silicate	0.50%	46	57	---	---	---
Magnesium Alumnium Silicate	1.50%	101	---	---	34	27
Sodium Carboxymethylcellulose-1	0.10%	127	---	---	---	---
Sodium Carboxymethylcellulose-1	0.50%	288	---	---	39	177
Sodium Carboxymethylcellulose-2	0.05%	190	---	---	12	57
Sodium Carboxymethylcellulose-2	0.10%	274	---	---	27	86
Sodium Carboxymethylcellulose-3	0.05%	191	---	---	---	---
Sodium Carboxymethylcellulose-3	0.10%	290	309	---	19	71
Xantham Gum	0.10%	26	35	---	---	---
Xantham Gum	1.00%	77	---	---	---	---

Figure 1. Kaolin Sample with 0.9 wt% magnesium aluminum silicate and 0.1 wt% sodium carboxymethylcellulose after 26 days

Table 2. Organic/inorganic Rheology Modifier Study Phase 2

Primary Modifier		Secondary Modifier		24 hr Vane Yield Stress [Pa] After Blending is Completed	Bingham Plastic Properties after shearing	
Type	Wt% added	Type	Wt% added		Yield Stress [Pa]	Plastic Viscosity [mPa-sec]
Magnesium Alumnium Silicate	1.36%	Hydroxypropyl-cellulose	0.14%	249	115	132
Magnesium Alumnium Silicate	1.36%	Hydroxypropyl-methylcellulose	0.14%	213	---	---
Magnesium Alumnium Silicate	1.36%	Hydroxyethyl-cellulose	0.14%	197	65	109
Magnesium Alumnium Silicate	1.36%	Sodium Carboxymethyl-cellulose-1	0.14%	222	21	79
Magnesium Alumnium Silicate	0.91%	Sodium Carboxymethyl-cellulose-2	0.09%	329	40	80
Magnesium Alumnium Silicate	0.91%	Sodium Carboxymethyl-cellulose-3	0.09%	316	---	---
Hydrate Magnesium Aluminum Silicate	1.36%	Hydroxypropyl-cellulose	0.14%	223	---	---
Hydrate Magnesium Aluminum Silicate	1.36%	Hydroxypropyl-methylcellulose	0.14%	200	---	---
Hydrate Magnesium Aluminum Silicate	1.36%	Hydroxyethyl-cellulose	0.14%	165	54	96
Hydrate Magnesium Aluminum Silicate	1.37%	Sodium Carboxymethyl-cellulose-1	0.14%	236	23	95
Hydrate Magnesium Aluminum Silicate	0.91%	Sodium Carboxymethyl-cellulose-2	0.09%	327	32	96
Hydrate Magnesium Aluminum Silicate	0.91%	Sodium Carboxymethyl-cellulose-3	0.09%	328	---	---
Xantham Gum	0.91%	Hydroxypropyl-cellulose	0.09%	141	---	---
Xantham Gum	0.91%	Hydroxypropyl-methylcellulose	0.09%	211	101	182
Xantham Gum	0.91%	Hydroxyethyl-cellulose	0.09%	86	---	---
Xantham Gum	0.91%	Sodium Carboxymethyl-cellulose-1	0.09%	129	---	---
Xantham Gum	0.91%	Sodium Carboxymethyl-cellulose-2	0.09%	252	---	---
Xantham Gum	0.91%	Sodium Carboxymethyl-cellulose-3	0.09%	186	---	---
Xantham Gum	0.50%	Magnesium Alumnium Silicate	0.50%	56	---	---
Xantham Gum	0.50%	Hydrate Magnesium Aluminum Silicate	0.50%	50	---	---

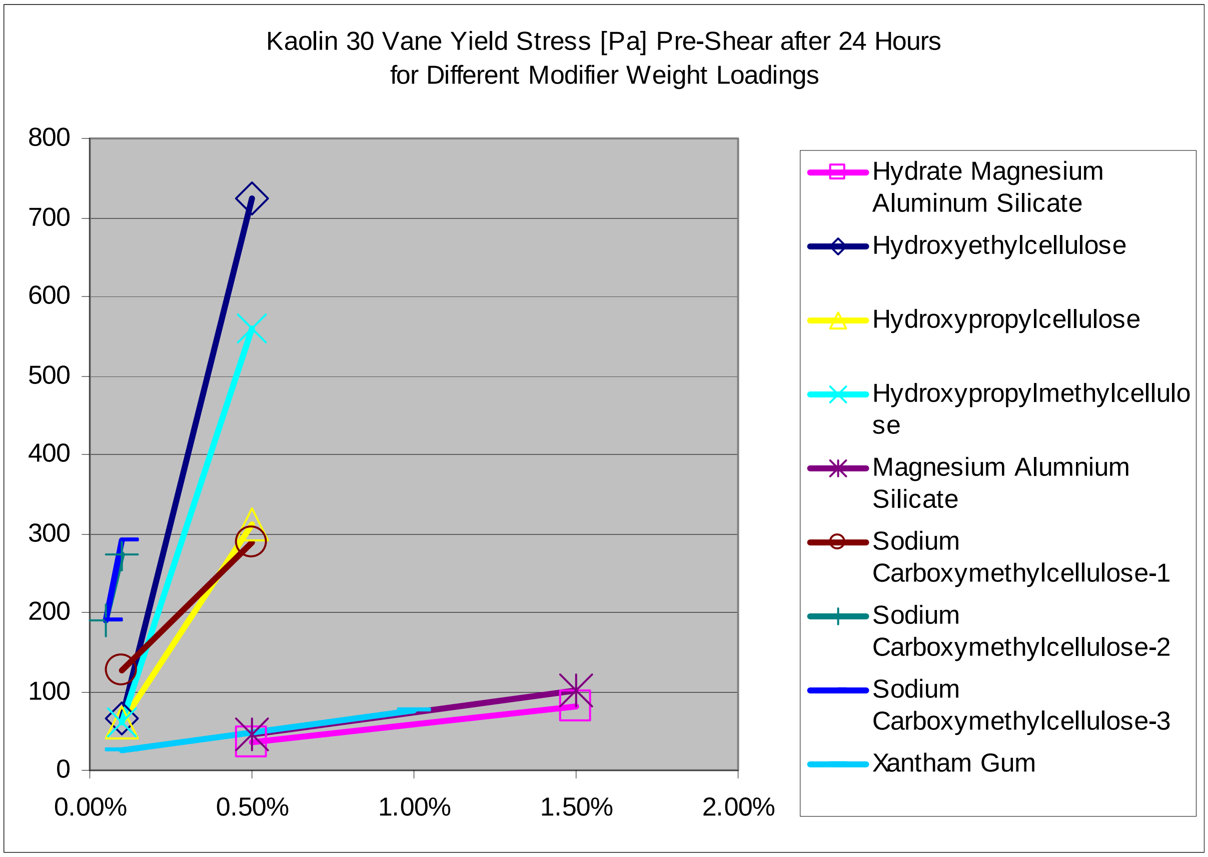

Figure 2. Kaolin 30 Vane Yield Stress [Pa] Pre-Shear after 24 Hours

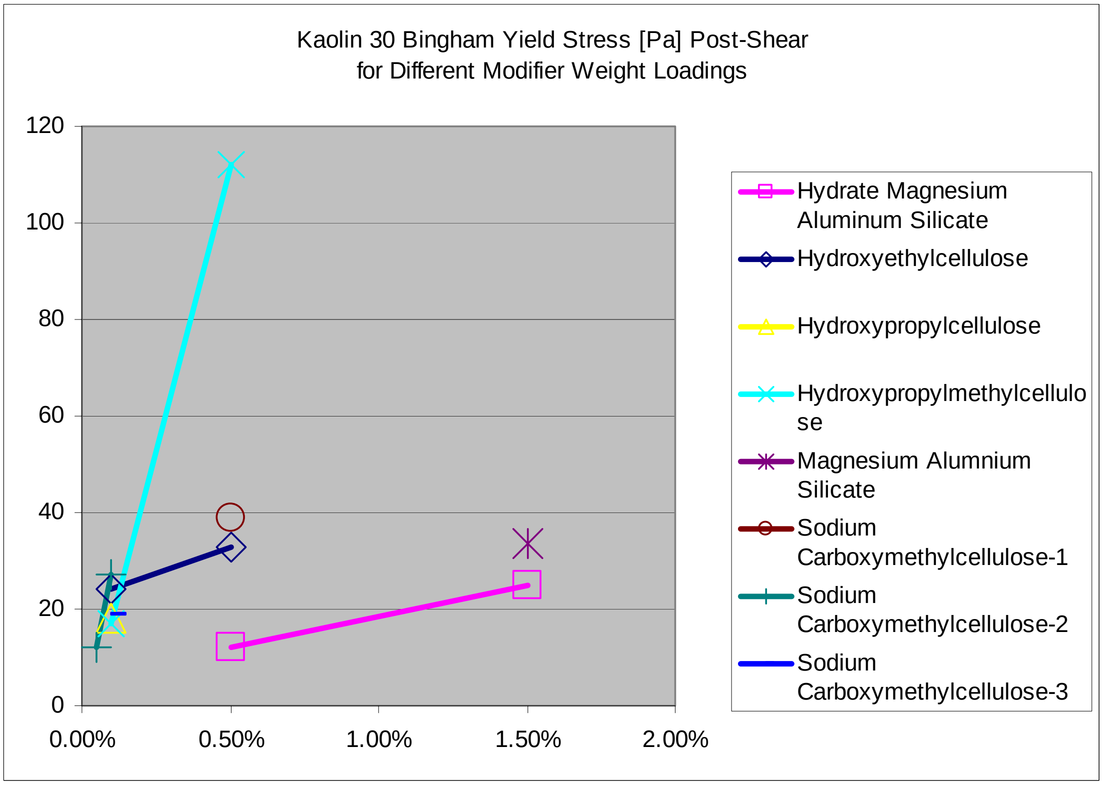

Figure 3. Kaolin 30 Bingham Yield Stress [Pa] Post-Shearing after 24 Hours

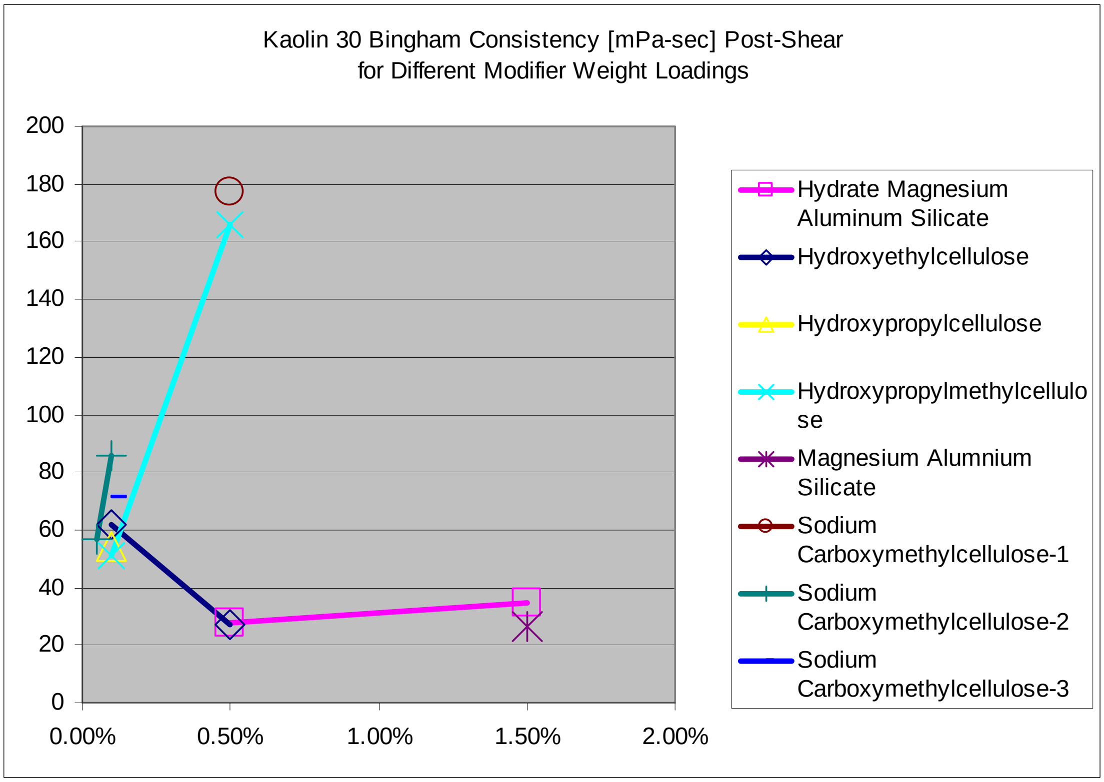

Figure 4. Kaolin 30 Bingham Consistency [mPa-sec] Post-Shearing after 24 Hours

Flow Curve Measurement of Thick Materials (> 150 Pa)

In order to measure the flow properties of these thick slurries having a Bingham Plastic yield stress greater than 150 Pa, the method for measuring flow curves had to be refined. The primary method used to measure the clay slurry prior to adding the modifiers was using concentric geometry. Some limited testing indicated that a cone and plate type of technique might be useful but also indicated that the samples are time dependent with respect to the amount of time between loading the sample on to the plate and starting the measurement. When the sample is placed on the plate and the cone is lowered into measuring position, the slurry is extruded between the gap between the cone and plate, applying a shear to the material. More research needs to be performed to refine the flow curve methods for these thick materials.

The shapes of the flow curves did not tend to match a standard flow curve response except during the decreasing shear portion of the curve. Even during the decreasing shear, the shear stress results from the measurement were impacted by the time between the sample loading and the application of shear.

Given the condition that repeatable results via flow curve measurements may not be obtained, a 3rd phase of testing was performed with another set of test mixtures developed to examine in more detail the addition of magnesium aluminum silicate with and without sodium carboxymethylcellulose. In this phase of testing, 2-4 wt% magnesium aluminum silicate by itself and combined with 0.03-0.05 wt% sodium carboxymethylcellulose were investigated. The test matrix is shown in Table 3. The experiments were to be used to determine if the combination of the vane yield stress and the Bingham Plastic properties could be achieved without substantial additional testing.

Table 3. Organic/inorganic Rheology Modifier Study Phase 3

Primary Modifier		Secondary Modifier		24 hr Vane Yield Stress [Pa] After Blending is Completed	Bingham Plastic Properties after shearing	
Type	Wt% Added	Type	Wt% Added		Yield Stress [Pa]	Plastic Viscosity [mPa-sec]
Magnesium Aluminum Silicate	2.0%	---	0	162	62	36
	2.5%	---	0	200	76	39
	3.0%	---	0	225	92	44
	3.5%	---	0	269	110	51
	4.0%	---	0	321	119	55
	2.0%	Sodium Carboxymethyl-cellulose-2	0.05%	275	82	80
	3.0%	Sodium Carboxymethyl-cellulose-2	0.05%	376	122	120
	2.0%	Sodium Carboxymethyl-cellulose-2	0.03%	176	57	77
	3.0%	Sodium Carboxymethyl-cellulose-2	0.03%	245	90	89

The results from the 3rd phase of testing showed that the vane yield stress could be reached but the Bingham Plastic properties were still 3 times too high. Surface fits to the data are shown graphically in Figure 5 and Figure 6 where red represents low yield stresses or consistencies while violet represents high values. Figure 5 shows that small additions of cellulose cause the Bingham plastic yield stress to increase much more rapidly than with smectite addition. Figure 6 shows that the Bingham plastic consistency also increases much more with respect to the cellulose than the smectite. By dropping the organic modifier, the Bingham Plastic shear stress would approach the target but then the vane yield stress would be too low. The problem with the organic modifier was that the material began to show the same elastic behavior as that in the 1st phase of testing. However, the smectite modifiers did show predictable rheological behavior but did not produce the vane yield stress required. Based on these findings it was concluded that the vane yield stress and Bingham Plastic properties could not be achieved with smectite and an organic modifier, given the time constraints. At this time the customer decided that the secondary objective for the post shear properties was not as critical as the initial yield stress. The focus was shifted to finding a modifier that could provide a significant high yield stress (600 Pa) in just 24 hours. At this point the decision was made to use Laponite® as the rheological modifier due to availability.

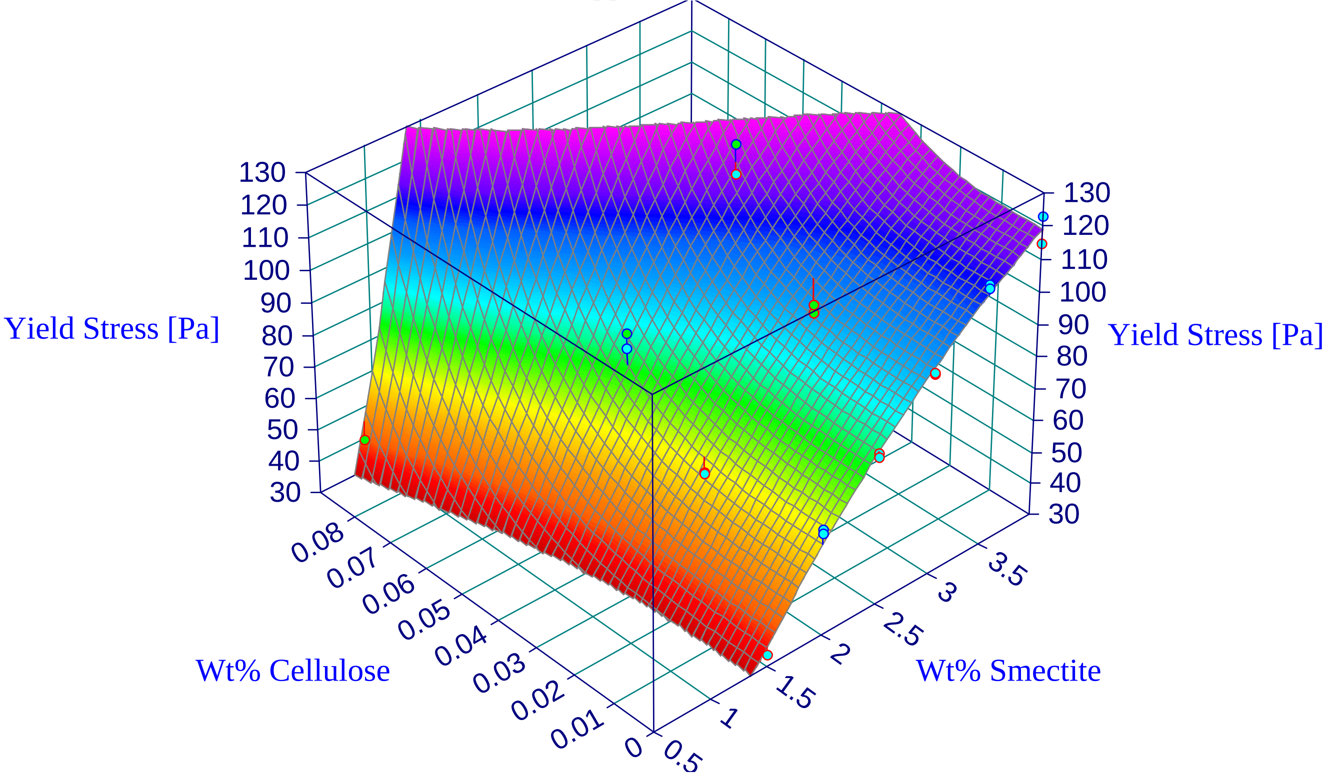

Figure 5. Bingham Yield Stress after shearing as function of wt% cellulose and wt% smectite

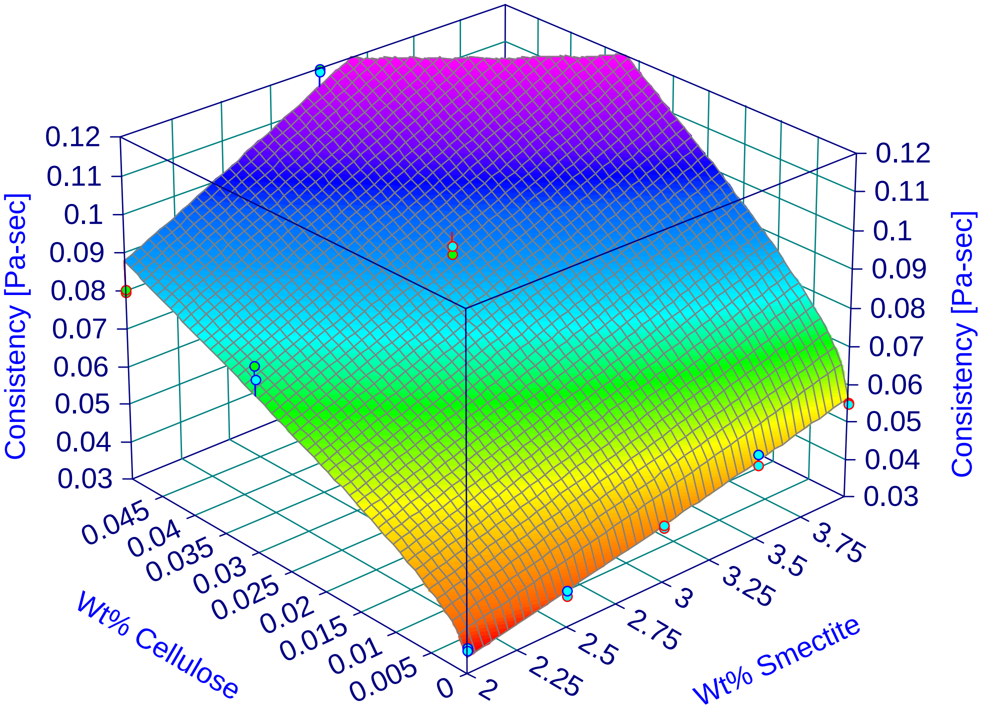

Figure 6. Bingham Consistency after shearing as function of wt% cellulose and wt% smectite

LAPONITE MODIFIER STUDY

Samples were prepared to evaluate the impact of laponite when blended with the clay slurry. The testing covered between 0 to 4 wt% laponite. The results shown in Table 4 indicate that a vane yield stress of 300 Pa is possible, were the vane measurements were obtained after 22 hours. The vane yield stresses are show graphically in Figure 7.

Table 4. Yield Stresses of Kaolin-Laponite Mixes

Wt % Added Laponite	22 hr Vane Yield Stress [Pa] After Blending is Completed	Wt % Added Laponite	22 hr Vane Yield Stress [Pa] After Blending is Completed
0.0	50.7	2.4	476
0.0	51.3	2.4	479
0.5	44.5	2.4	374
0.5	45.3	2.6	356
1.0	93.0	2.6	376
1.0	90.8	2.8	623
1.5	135	2.8	634
1.5	134	2.8	572
2.0	275	3.0	704
2.0	307	3.0	691
2.0	317	3.0	564
2.2	257	4.0	1070
2.2	269	4.0	1056
2.2	272	--	--

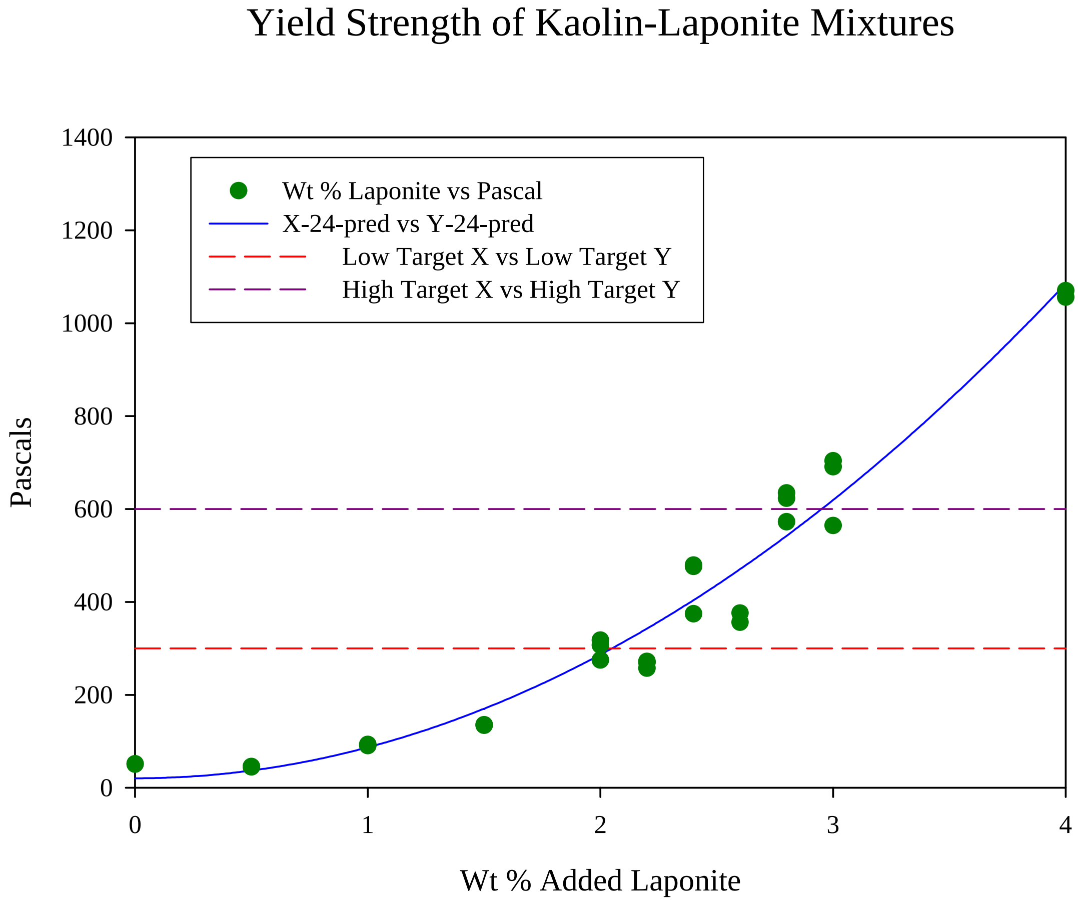

Figure 7. Yield Strength of Kaolin-Laponite Mixtures

Based on the clay slurry - Laponite mixtures, 1.9 weight percent additional Laponite mixed with the clay slurry would provide a vane yield stress of 300 Pa within 24 hours of mixing. The density of the clay-Laponite slurry was 1.172 g/mL. To produce a mixture with a vane yield stress of 600 Pa, the blend would require 3 weight percent Laponite.

Based on the recommendations, the clay slurry used for the PJM testing was blended with 3 wt% laponite and a sample pulled for analysis. After 24 hours, the vane yield stresses were measured and shown in Table 5. The target of 600 Pascal was reached. The variation observed is typical of many of the high yield stress materials tested in this report.

Table 5. 24 Hour Vane Yield Stresses for Kaolin-Laponite Material

Sample	Average Yield Stress [Pa]
1	610
2	605
3	579
Overall Average	598

CONCLUSIONS

These experiments showed that the rheological properties of the clay slurry (Kaolin/Bentonite) could be significantly modified by adding small quantities of inorganic and organic modifiers. The addition of organic modifiers like hydroxyethylcellulose, hydroxypropylmethylcellulose, and hydroxypropylcellulose at a target 0.50 wt% increased the vane yield stress from 51 Pa up to 311 - 724 Pa. The Bingham Plastic yield stress ranged between 21 to 101 Pa and the plastic viscosity between 24 to 166 mPa-sec. The inorganic modifiers had a much smaller impact on the clay slurry. An 0.50 wt% addition of the inorganic semectites modifiers (magnesium aluminum silicate and hydrate magnesium aluminum silicate), only increased the vane yield stress to 36-46 Pa. The problem with using the organic modifiers was that the material began to show elastic behavior. This elastic behavior gave the material very unpredictable flow curve behavior during the initial up flow measurement. To try to combine the best of both the organic and inorganic modifiers, 10-to-1 combinations of the smectites to organic modifiers were examined. Initially it appeared possible to combine the smectites with the organic modifiers to produce a material with the targeted rheological properties. However, testing revealed that the vane yield stress could be obtained, but the Bingham Plastic parameters were still 3 times too high. The organic modifiers were further reduced to a few hundredths of a percent, showing that the Bingham Plastic parameter could be approached, but the vane yield stress was then too low. The organic and inorganic rheology modifiers tested were determined unacceptable. Laponite® (synthetic lithium aluminum silicate) was also tested. The Laponite® increased the yield stress of the Kaolin clay mixture while still producing a slurry that had suitable shear thinning properties. Laponite® additions generated mixtures with yield stresses as high as 1500 Pa. These findings led to the decision to use Laponite® as the rheological modifier. Ultimately, an addition of 3.0 wt% Laponite® to the clay slurry produced a 600 Pa vane yield stress material with sufficient shear thinning properties that met the needs of the Pulse Jets pilot work.

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