

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

**Investigation of Ethanol as a Feasible Tracer in  
the Experimental Investigation of a Non-  
Newtonian Fluid Undergoing Pulse Jet Mixing**

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**Principal Investigators:**

Maximiliano Edrei (DOE Fellow Student)  
Florida International University

Chris Guenther, Mentor  
National Energy Technology Laboratory

Balaji Gopalan, Mentor  
WVURC

**Florida International University Program Director:**

Leonel Lagos Ph.D., PMP®

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**Applied Research Center**  
FLORIDA INTERNATIONAL UNIVERSITY

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## ABSTRACT

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The research performed provides analytical work to support the investigation of the use of pulse jet mixing (PJM) vessels at the Hanford Site Waste Treatment Facility (WTP). Currently, the experimental group at the National Energy Technology Laboratory (NETL) Morgantown site is transitioning their focus from studying Newtonian fluid undergoing the PJM process to a non-Newtonian Bingham plastic type fluid. Previously, conductivity probes at different locations were used to determine the mixing state of the tank as the mixing process took place. Due to the nature of the non-Newtonian fluid, this method is no longer viable and a new procedure must be established. Insertion of ethanol into the top of the tanks while non-Newtonian fluid is undergoing pulse jet mixing was investigated and established as a viable method for determining the mixed state of the PJM tank. This method was then tested by applying it to the quantification of mixing states at different locations of a bench-scale mixing vessel to gain insight into the effects of sparging in the mixing of a Bingham plastic type fluid. Similarities in the effects of sparging in mixing vessels between Newtonian and non-Newtonian fluids were observed.

In addition to this research work, the non-Newtonian fluid was prepared at the NETL facility. Literature recommends that the non-Newtonian fluid (a kaolin clay mixture) be sheared through a pump for two hours and allowed to sit for three days to reach stable rheological properties. This recommendation was tested and evaluated. The data collected showed that shearing has a critical role in the yield stress of the fluid. The data also suggested that the viscosity did not reach stable values after the prescribed three days.

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# 1. INTRODUCTION

Currently, there are 53 million gallons of high level waste (HLW) being stored inside tanks located at the Hanford Site. The Department of Energy’s (DOE) main objective is to immobilize the waste in order to prevent contamination to the environment. The planned solution for this objective is to have the radioactive waste undergo separation and vitrification, which converts the waste into glass for permanent storage. The waste needs to have particular rheological properties before it goes through this process, including density, viscosity, porosity, etc. The density of HLW is not homogeneous. The HLW separates into multiple layers, referred to as the salt cake, the supernate, and the sludge due to density differences. This leads to the need to properly mix the HLW inside the storage tanks prior to treatment.

Pulse jet mixing (PJM) is the method that was chosen by DOE to mix the HLW slurry before the vitrification process. This method involves sucking a portion of the waste from the tank into a pressurized vessel and then injecting it back into the tank in order to mix the waste using the pressurized jets. This process is repeated over a number of cycles. The main reason for choosing PJMs for this task is that there are no mechanical moving parts and the process can be operated remotely with minimal interference required by the workers [1].

At NETL’s Morgantown site, testing of the PJM process with non-Newtonian fluid is in the initiation stage. A mixture of kaolin clay, Bentonite, and water is the composition of the non-Newtonian fluid of choice for testing. The kaolin clay mixture is identified as a Bingham plastic type fluid. Bingham plastic type fluids are characterized by possessing a yield stress. This rheological behavior is shown by the diagram below:

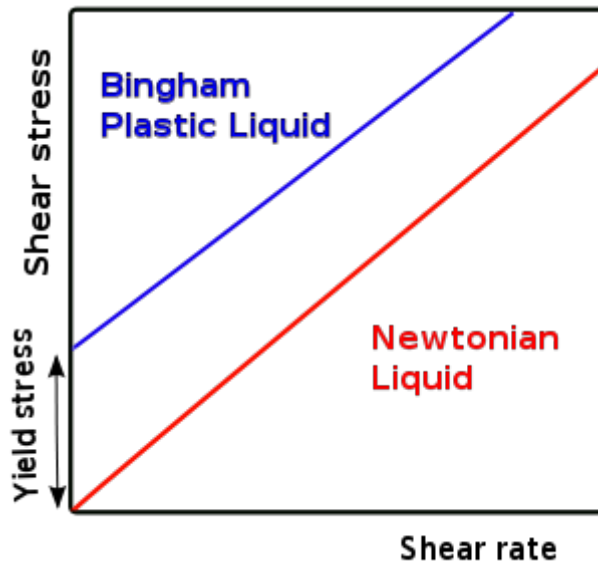


Figure 1. Bingham plastic comparison. (Ref: [https://en.wikipedia.org/wiki/Bingham\\_plastic](https://en.wikipedia.org/wiki/Bingham_plastic))

As Figure 1 depicts, the shear stress vs. shear rate behavior of Bingham plastics and Newtonian liquids are both linear. The difference lies in that Bingham plastics require that they experience

an initial shear stress for them to behave as liquids. This fluid will behave as a solid under any stress under a critical value. This is referred to as the yield stress.

In addition, the kaolin clay mixture's viscosity and yield stress are very sensitive to the addition of sodium; therefore, the conductivity probes used during the Newtonian mixing phase are not appropriate for this application. This is because the addition of sodium as a tracer would result in varied viscosities and yield stresses in the tanks as a function of sodium concentration. A new tracer and method for ascertaining the mixture state of the tank during the PJM testing process is necessary.

Alcohols are substances which do not have any sodium content and are therefore a possible tracer by which to indicate the mixing state of the tank. The main focus for this research is to therefore establish a consistent and reliable procedure by which to quantify the concentration of alcohol in a specific sample of non-Newtonian fluid. Ethanol is readily available at the facility and is therefore the alcohol of choice.

## 2. EXECUTIVE SUMMARY

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This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2016, a DOE Fellow intern Maximiliano Edrei spent 10 weeks doing a summer internship at the National Energy Technology Laboratory in Morgantown under the supervision and guidance of the Director of Computational Science & Engineering Division, Chris Guenther. The intern's project was initiated on June 4, 2016, and continued through August 12, 2016 with the objective of verifying the feasibility of using ethanol as a tracer during the mixing of a non-Newtonian fluid undergoing the PJM process.



### 3. RESEARCH DESCRIPTION

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To investigate the feasibility of using ethanol as a tracer, a small bench-scale mixing vessel was created in which the mixing states were then evaluated using ethanol. Prior to the development of this bench-scale test, a method for determining the concentration of ethanol in the kaolin clay mixture was developed.

The instrument chosen to characterize the concentration of ethanol was a gas chromatograph machine (GC). The Autosystem XL GC uses the variation of interaction strengths between compounds and a stationary phase to separate the original solution into its individual components. The original solution is vaporized and is then forced through a column coated by a liquid stationary phase. The vapors are forced by an inert gas, helium in this case. At the end of the long column is a detector which signals when a molecule has reached it. The stronger the interaction between a vaporized compound and the stationary coating in the tube, the longer it will take for that particular compound to reach the detector. In this manner, the original sample mixture is separated. [2]

Based on the intensity of the detector signal, it is possible to calculate the concentration. This is accomplished by running the GC with a standard solution of known concentration and calculating the area under the peak. The following equation can then be applied:

$$\frac{C_{\text{standard}}}{\text{Peak Area}_{\text{Standard}}} = \frac{C_{\text{sample}}}{\text{Peak Area}_{\text{Sample}}}$$

**Equation 1. Concentration peak area relationship.**

This entails that the signal intensity is always the same for a given concentration of a compound. All that is required is to ascertain the intensity value and the behavior of the signal peaks as concentrations increase by evaluating peaks of known concentrations referred to in this study as standards. Once this calibration procedure is carried out for ethanol, one can calculate the concentration of an unknown sample.

This method of quantifying concentrations of ethanol requires that the kaolin and bentonite be removed from the water and ethanol. This is because bentonite and kaolin have high molecular weights which can accumulate within the GC column, eventually rendering it inoperable. Having the non-Newtonian fluid undergo centrifugal separation for a certain amount of time will suffice in the separation of the clay and ethanol-water mixture. Once a method for determining the concentration of ethanol in a sample of kaolin clay mixture was established, a bench-scale mixing vessel was designed.

The automatic mixing mechanism available at this scale within the lab is a magnetic stirrer. Therefore, this is the mixing mechanism used in this experiment. The first requirement of this mixing vessel experiment was that there be a method to obtain kaolin clay mixture samples consistently in the same location at varying heights of the vessel. The second requirement was that there be no visible movement of the kaolin clay near the top of the vessel in order to emulate mixing in which the yield stress is not reached in certain portions of the tank. In this manner, the

advantages of using spargers as a secondary mixing mechanism on non-Newtonian fluids were investigated.

In order to begin to develop the bench-scale mixing test, a mixing container was chosen. A cylindrical-shaped vessel was selected in order to stay as consistent as possible with the field-scale tank PJM process. The inner diameter of the vessel is 6.5 inches, which was chosen to be within the length scale order of the 3-inch rotating magnet. The corresponding height of this cylinder is 8 inches.

Before sampling heights of the vessel were chosen, a corresponding fill height and rotations per minute (RPM) that do not produce movement (vortices) at the top of the vessel needed to be established. The following visual investigation was carried out in order to obtain a suitable fill height and corresponding RPMs.

**Table 1. Appropriate RPM Investigation**

<b>h= 3.25 inches</b>	
<b>RPM</b>	<b>Visible movement on top</b>
300	1-inch D vortex
260	.5 -inch vortex
240	Minute circulation movement
200	No visible movement

To begin the investigation, a fill height for non-Newtonian fluid in the vessel was chosen to be a constant of 3.25 inches. At 300 RPMs a clear vortex was observed at the top of the vessel caused by the magnetic stirrer. The RPMs were lowered until movement ceased at the top of the bench-scale vessel, signifying that the yield stress had not been reached in that region. An RPM of 200 at a height of 3.25 inches was chosen on this basis.

Once the fill height and RPMs were established, the sampling heights from which to consistently obtain samples were chosen.

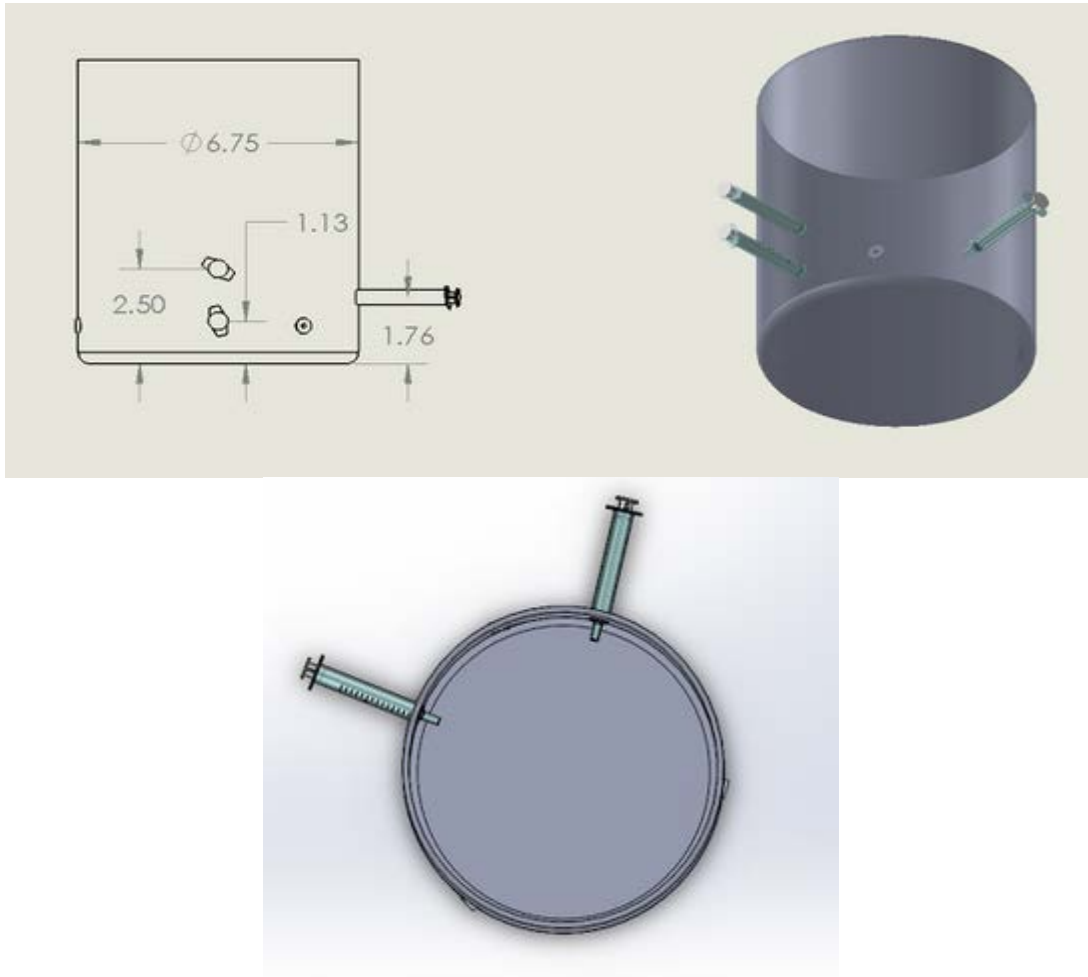
**Table 2. Sampling Positions**

<b>Sampler name</b>	<b>Position based on percentage of height</b>
Sampling #1	35%
Sampling #2	50 %
Sampling #3	75%

Three regions are of interest in this experiment. A bottom sampling position (#1) is desired in order to ascertain when the tracer has reached the bottom of the vessel. A middle sampling height (#2) is inserted in order to observe any time delays in mixing between the bottom and middle sampler. The top sampler (#3) is intended to be near the stagnant zone. These locations are expected to represent the most significant mixing scales within the experiment.

To obtain samples in a consistent manner, holes were drilled at the sampling locations. Large plastic syringes were installed through these holes in order to house smaller syringes which could

be easily retracted and replaced without leaving a significant hole in the transition process from which the thick fluid could escape. A model of this bench-scale mixing vessel is shown below:



**Figure 2. Bench-scale illustration (dimensions in inches).**

Finally, the last aspect of the experiment is the sparger system. The spargers promote mixing by introducing bubbles which push fluid towards the top of the vessel. For this reason, they are introduced near the bottom of the vessel, approximately at 30 percent of the height. The spargers were affixed to the vessel in a similar manner to that of the samplers. Three holes were drilled equidistant from each other about the circumference of the cylinder. The air outlets were sealed into these entrances. In order to keep track of the amount of air bubbles being introduced to the vessel, flow meters were attached right before the outlets of the spargers. The target airflow for the spargers were calculated using a ratio which indicates fully mixed conditions in the Newtonian PJM process:

$$\text{Approximate Mixing Time} = \frac{\text{Fille Volume}}{\text{SLPM}}$$

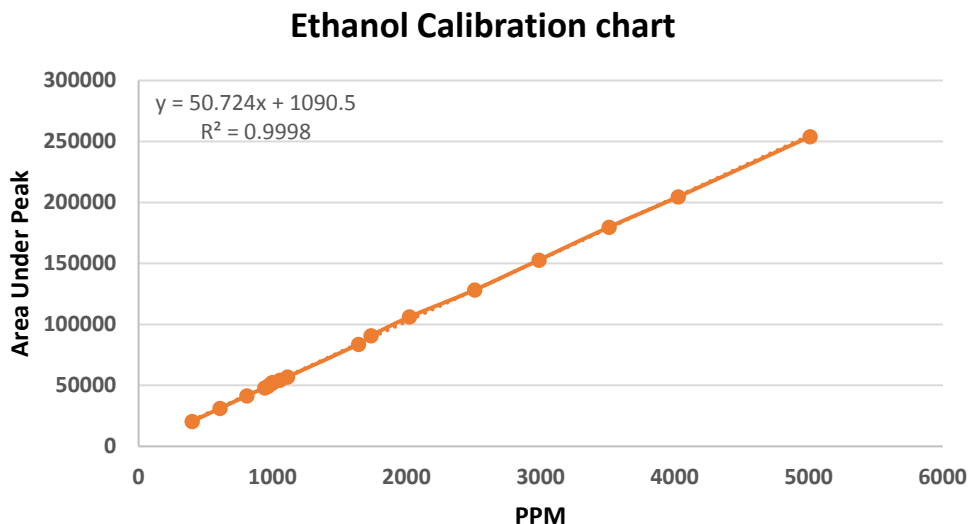
**Equation 2. Sparger based mixing time approximation.**

Using this equation, given that the fill volume is approximate 1.9 liters and a desired mixing time of 20 minutes, the air flow rate was calculated to be about 90 liters per second.

## 4. RESULTS AND ANALYSIS

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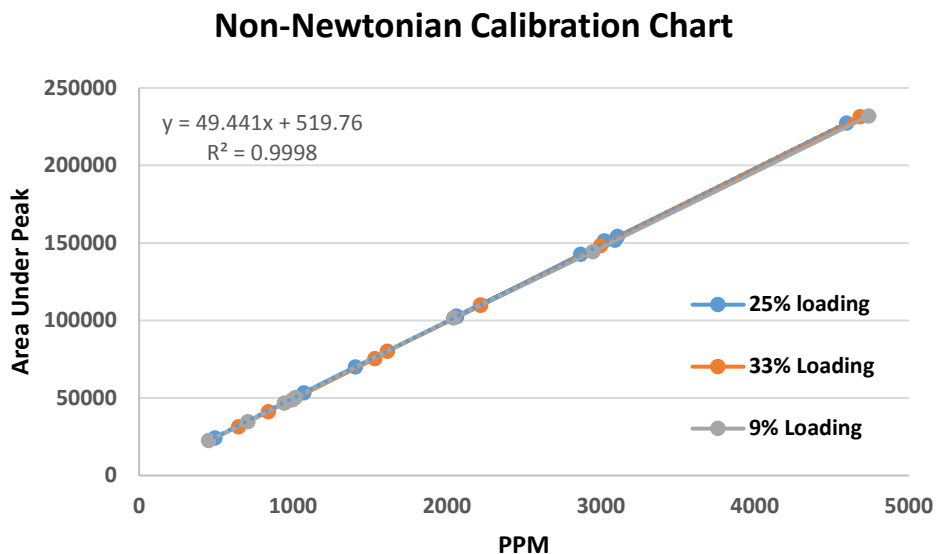
Varying concentrations of ethanol were prepared and sent through the GC. The GC quantifies the signal strength by the area underneath the curve created by the graphed signal. The area created by each concentration standard was logged, resulting in the following graph:



**Figure 3. Standard calibration chart.**

Concentration standards of 400 ppm to 5000 ppm were tested. It was observed that there exists a positive linear relationship between the signal strength produced by the GC and the concentration of ethanol. The slope of this line could be used to ascertain concentrations of unknown ethanol samples. The average discrepancy of the instantaneous slope of each data point is 0.6 area/ppm. This is near a one-percent error, which is acceptable for its intended application.

Following this study, a similar procedure was followed to verify that the results are not affected when separating the water-ethanol mixture from the kaolin clay. Ethanol was introduced to the non-Newtonian fluid at varying concentrations, then centrifuged to obtain a clear water-ethanol mixture and ran through the GC. The experiments that will be taking place at NETL will use non-Newtonian fluid at different concentrations of kaolin clay; therefore, this procedure was repeated at different clay loadings.



**Figure 4. Non-Newtonian calibration chart.**

It was observed that the same linear relationship between signal strength and concentration held true. A peculiar difference observed is the average slope of the line decreased. This decrease in instantaneous slope stayed generally the same for varying clay loadings. This could be attributed to ethanol evaporation throughout the separation process or ethanol being absorbed by the clay.

Once the ethanol concentration calibration charts were developed, the mixing experiment was performed. The first test was conducted without the utilization of spargers. Using the magnetic stirrer as the sole mixing mechanism, ethanol was poured into the top of the vessel in a quantity such that the fully mixed condition of the fluid would have 500 ppm of ethanol. The following data points were obtained under such conditions:

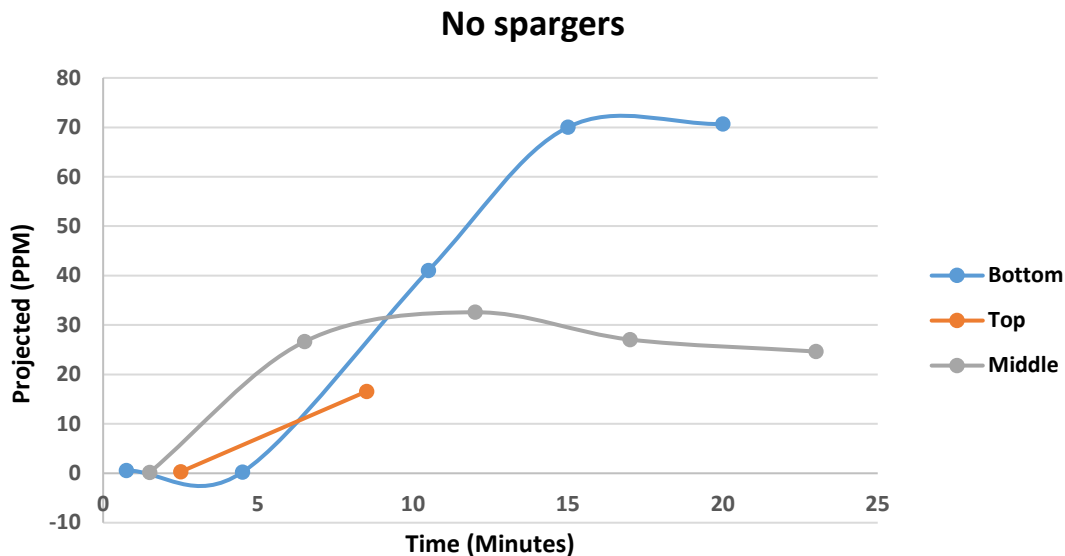


Figure 5. Mixing vessel data without spargers.

It was observed that mixing was taking place in a slow manner, when compared to the 20-minute target. The bottom of the tank seemed to be mixing at the fastest rate. It is possible that, despite the absence of visible moving structures at the top of the vessel, ethanol could still be travelling to the bottom of the tank through the eddy created by the magnetic stirrer. The same experiment was then performed with the use of spargers at 90 ccm/min:

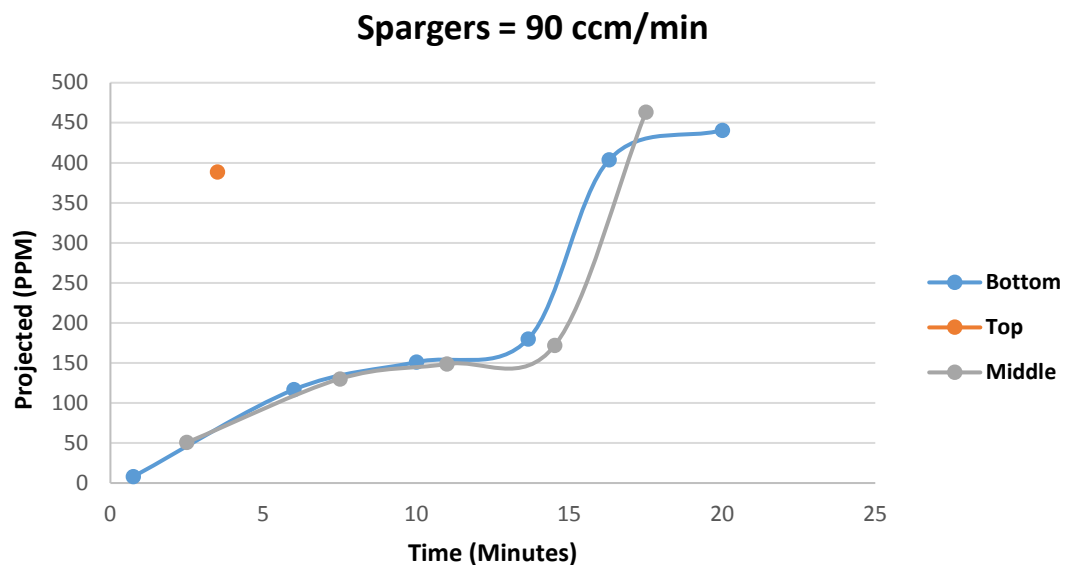


Figure 6. Mixing vessel data with spargers set to 90 ccm/min.

The fully mixed conditions of this process should yield 460 ppm in accordance with the amount of ethanol inserted at the top. The first result to notice is that the vessel was fully mixed at around 20 minutes. The top probe reflected a nearly fully mixed condition at the very beginning

of the mixing process. These are indications of the spargers' ability to increase the mixing rate. It was also noticed that both the middle and bottom probe follow each other closely. The same behavior was observed in the Newtonian phase of the PJM experiments, showing that the mixing mechanisms by which spargers operate are similar in Newtonian fluids as they are in Bingham plastics. There was also an appearance of an inflection point, after which a higher mixing rate was observed. This inflection can possibly be a phenomena attributed to non-Newtonian fluids undergoing sparging.

A final experiment using this mixing vessel was conducted with the spargers set to 60 ccm/min. The following data resulted:

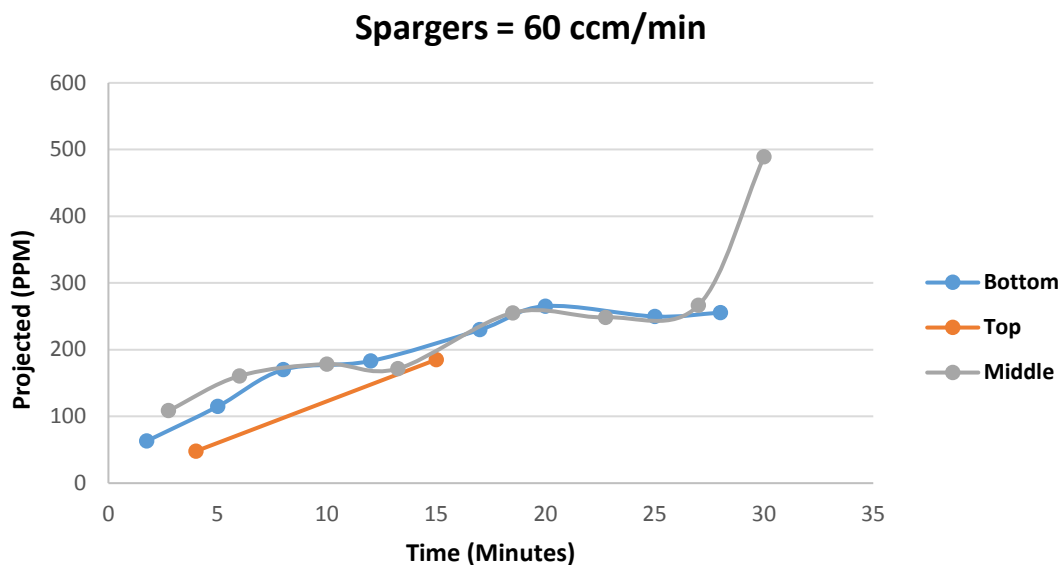


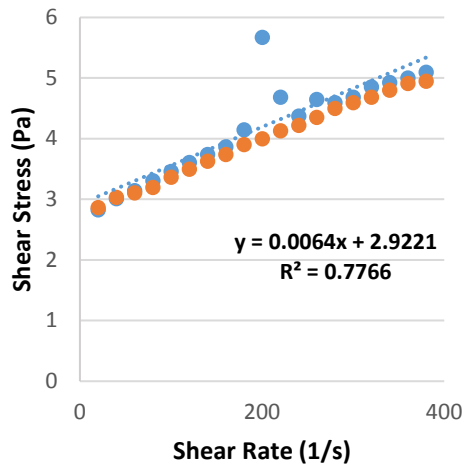
Figure 7. Mixing vessel data with spargers set to 60 ccm/min.

With the sparger flow rate reduced by 33 percent, the new projected time to reach a fully mixed state was approximately 30 minutes. The amount of ethanol used theoretically should yield 510 ppm. At 30 minutes, the middle probe showed a fully mixed state, again verifying the mixing time equation. A difference observed when using a lower sparger flow rate is the top probe. The top probe exhibited the same mixing behavior as that of the case without spargers. The close agreement between the bottom and middle probes was still observed. An inflection followed by a sharp increase in mixing rate was still observed, but much later in the mixing process.

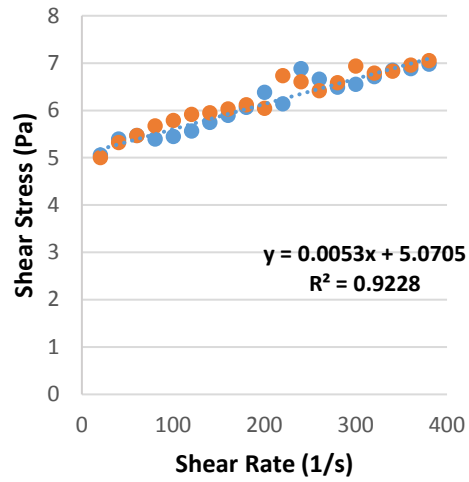
### Rheological Analysis of Kaolin Clay Mixture

Another task that was undertaken was the analysis of a non-Newtonian fluid made at the NETL facility. Literature recommends that the non-Newtonian fluid, a kaolin clay mixture, be sheared with a pump for 2 hours and allowed to sit for 3 days in order to reach a steady viscosity and yield stress. In order to validate this recommendation, a study was conducted to see how the kaolin clay mixture's rheology is affected by shearing time and time left sitting after shearing. This was accomplished by taking samples of the sheared kaolin clay mixture at 30, 60, 90, and 120 minutes of shearing and obtaining stress strain curves of each sample every 24 hours. The

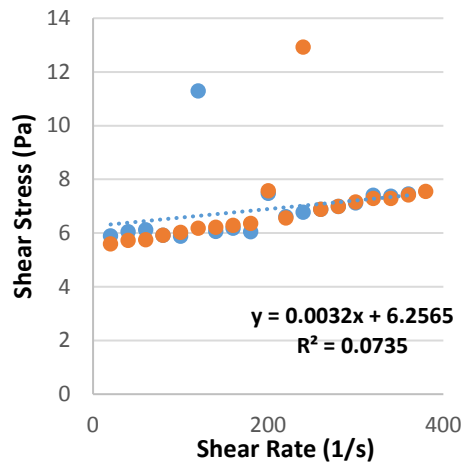
following data shows the stress vs. strain relationship of each sample at the initial (0 hours left sitting) time:



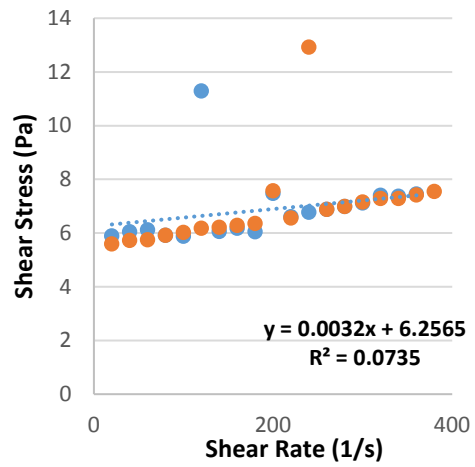
(a)



(b)

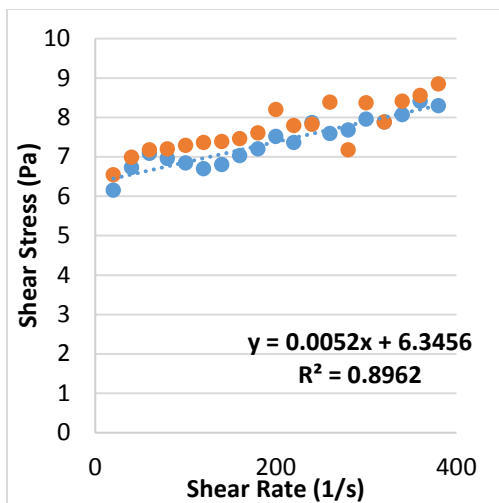


(c)



(d)





(e)

Figure 8. Initial shear stress vs. shear rate for varying amounts of pump shearing time (a) no shearing time (b) 30 mins, (c) 60 mins, (d) 90 mins, and (e) 120 mins.

From Figure 8, it can be concluded that the stress strain relationship is linear, confirming it behaves as a Bingham plastic. Each sample was run twice; one analysis is represented by blue while the other is represented by red. Although there is some scatter in the data, a consistent line was observed with an average discrepancy of 2%.

The offset of the line equation of each graph is the yield stress of the fluid while the slope of this line is the viscosity. The following graphs portray the trends of viscosity and yield stress as a function of pump shearing time:

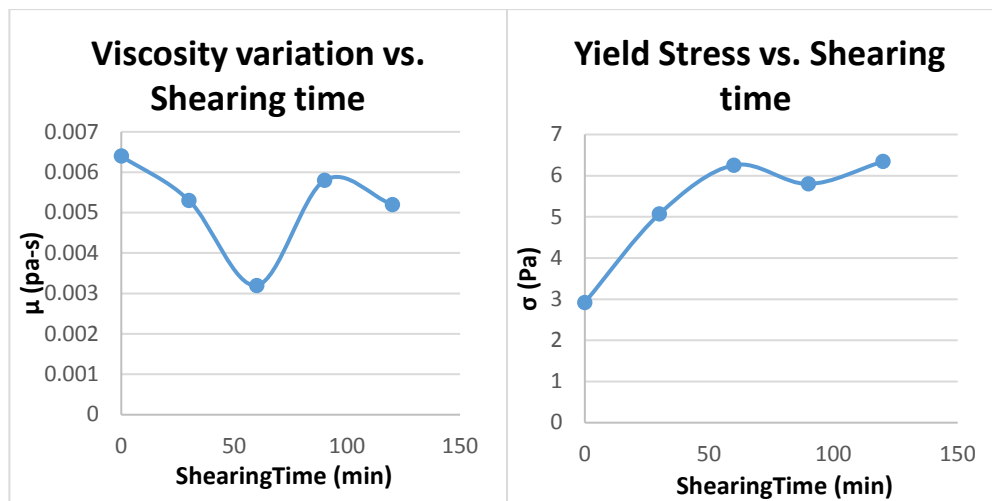


Figure 9. Viscosity and yield stress study for zero sitting time for (a) viscosity and (b) yield stress.

It is observed from Figure 9 (b) that the yield stress increases with increasing pump shearing time. The rate of yield stress increase with respect to shearing time decreases to almost zero after 2 hours. This suggests that the shear stress will no longer increase if the non-Newtonian fluid were sheared for longer durations.

From Figure 9 (a), it is observed that the viscosity varies by as much as 3 cP as a function of shearing time. No discernable trend can be asserted in regards to the viscosity fluctuations as a function of shearing time from the data collected. This same analysis was repeated for 24, 48, and 72 hours sitting time. In order to get another perspective, the shear stress and yield stress was also plotted vs. time left sitting:

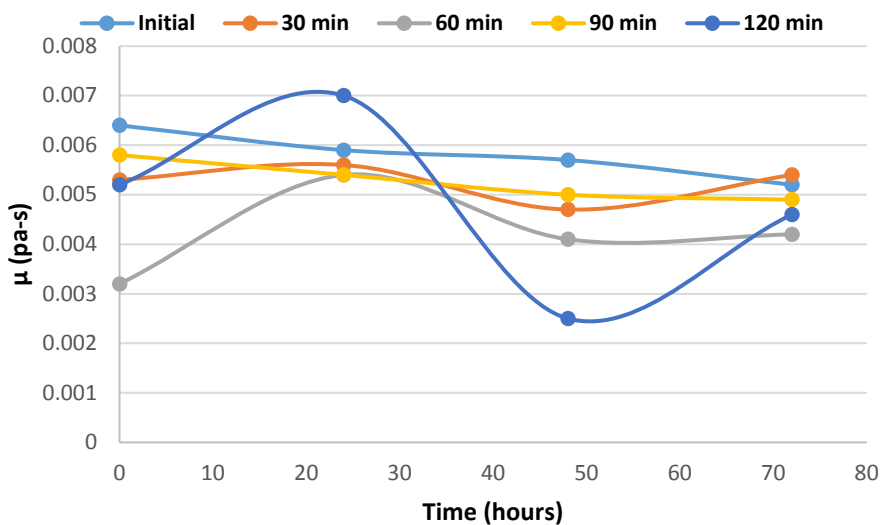


Figure 10. Viscosity variations vs. time left sitting.

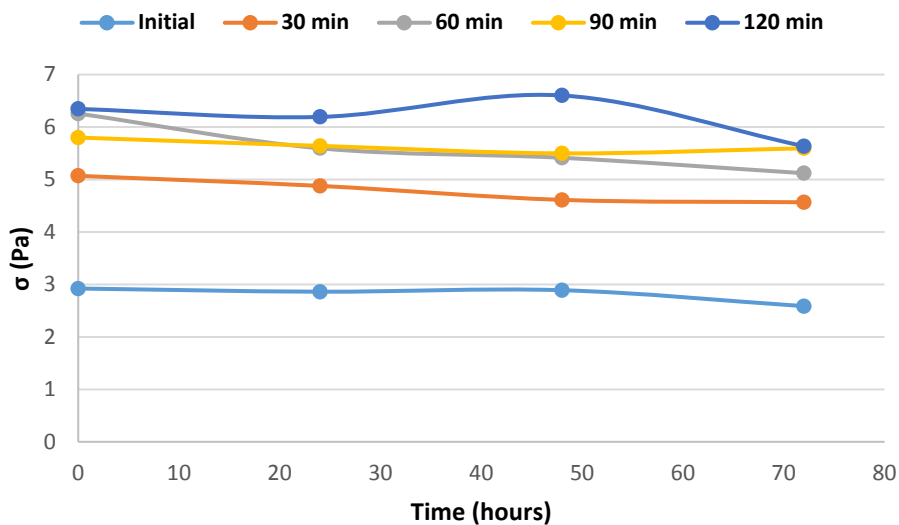


Figure 11. Yield stress variation vs. time left sitting.

It was observed that the viscosity changed by at most an average of 1.5 cP throughout the three days left sitting. With exception to that of the 120 min sheared sample, which changed by 4 cp. High variations were observed on the 120 min sheared sample, which increased by 34% on the first day, decreased 64% on the second, and increased 85% on the last day left sitting. It should be mentioned that this kind of variations in viscosities may be absolute ones, which are a

byproduct of the instrumental error or natural viscosity variations of a complex fluid. If this is the case then these variances can be considered negligible at higher viscosities. Another aspect to notice is that after three days, the viscosities of the different samples seem to be converging. If this is not a coincidence, then this would signify the onset of viscosity stabilization for the non-Newtonian samples.

The yield stress, on the other hand, maintained relatively stable values with an average variance of 10%, mostly independent of the time left sitting. This signifies that the yield stress is mostly affected by shearing time as opposed to sitting time.

This data suggests that further viscosity measurements as a function of sitting time need to be conducted in order to ascertain the general viscosity stability of the non-Newtonian fluid. Further yield stress measurements as a function of shearing time should also be conducted in order to understand when the yield stress reaches a steady value. These analyses will ensure that the basic rheology of the non-Newtonian fluid is understood while it is undergoing the pulse jet mixing process.

## 5. CONCLUSION

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In the experimental investigation of a Bingham plastic undergoing the PJM process, ethanol as a tracer was shown to be a viable option for the quantification of mixing. This was achieved by developing calibration curves from the response signals of the GC for both standards and non-Newtonian samples. A bench-scale mixing vessel was then created in order to validate the quantification of the mixing method in addition to gaining insight into the effects of sparging of non-Newtonian fluid.

The equation for estimating mixing times as a function of sparging flow rate developed from observations of Newtonian fluid undergoing the PJM process were shown to be valid for use with a Bingham plastic. The independence of height with respect to the mixing rate was suggested by the data collected, as is also the case with a Newtonian fluid undergoing the PJM process.

Finally, the claim in existing literature that the non-Newtonian fluid is required to be sheared for 2 hours and left sitting for three days to reach steady rheological properties was investigated. Results show that the viscosity varied at most by 4 cP, which could be attributed to instrumental or natural viscosity variances of the complex fluid. The data does suggest that the viscosity may be capable of becoming stable after a longer sitting time. More extensive viscosity data should be collected in order to confidently ascertain trends. The yield stress, however, clearly increased with increased shearing time and is largely independent of the sitting time according to the data collected.

## 6. REFERENCES

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[2] "Gas Chromatography." *Gas Chromatography*. Sheffield Hallam University, n.d. Web. 07 Sept. 2016.