Effects of Water-to-Cement Ratios and Metakaolin on the Rheological Properties of Cement Grouts Using Vipulanandan Rheological Model

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Abstract
In this study cement (Portland Cement Type 1) grouts were prepared with water-to-cement ratios of 0.6 and 1.0 without and with clay content of 10%. The test results showed that all the cement grouts tested were shear thinning fluids representing non-Newtonian fluids. The rheological constitutive relationships for the cement grouts were predicted using the new Vipulanandan rheological model (2014) and compared with the Herschel-Bulkley (HB) model (1926) that has been used for decades. Based on the root mean square error (RMSE) of the predictions of the experimental results, Vipulanandan rheological model predicted the measured shear stress at various shear strain rates for the grouts better than the HB model. The yield stresses predicted by the Vipulanandan Model was higher than the HB model. The new Vipulanandan rheological model also has a limit on the shear stress tolerance for the cement grouts were as the HB model does not have a limit. Based on the Vipulanandan rheological model the maximum shear stresses produced by the grouts with w/c ratios of 0.6 and 1.0 without clay was 58 Pa and 33 Pa respectively. With the addition of 10% clay to the cement grouts it increased the maximum shear stresses to over 100% for the w/c ratios investigated.

1. Introduction
Cement grouts are used in multiple applications including stabilizing the soils, repairing various damaged infrastructures, installing wells, leaking pipes and solidification of contaminated soils (Yeon et al. 1997;Stille et al. 2010; Taehee et al. 2013; Vipulanandan et al. 2014 and 2017; Vipulanandan 2021). In all these applications cement grouts have to be injected at varying pressures to flow through complex macro and microstructures and hence the cement grouts rheological properties become very important. One of the major variables for the cement grout is the water-to-cement ratio. Also for some applications cement grouts are modified by adding clay, which will also impact the rheological properties of the cement grouts. In the area of structural construction, cement grouts are used in the ducts of the post tensioned beams and the long-term performance of the beams are very much depended on the durability of the injected grouts to bond the concrete to the post-tensioned steel reinforcements and to transfer the loads. Cement grouts are used in cementing the oil, gas and water wells and the wells are expected to be productive for decades (Heinold et al. 2002; Vipulanandan et al. 2017 and 2018). Also cement grouts are used for repairing these wells and also in CO_2 sequestration wells.

Cement grouts are used in repairing beams, pipelines and underground storage facilities in-situ and the successful operations very much depends on the durability and long-term strength of the cement grouts (Vipulanandan 2021). Cement grouts are used in also stabilizing the soils to strength them for multiple applications. Hence there is an increasing interest in understanding and quantifying not only the variation of strength with curing time but also the long-term stress-strain behavior of the cement grouts. For grouting applications modifiers such as various types of clays (metakaolin, bentonite) ashes, silica fume and cement kiln dust have been used. Modifiers with reactive minerals with the cement grout changes the hardening process and the flow properties of cementitious grouts (Vipulanandan et al. 2014; Celik et al. 2015;

Mohammed 2017). The metakaolin (clay (MK)) has been used as cement replacement material up to 30% leading to microstructure modification, protecting against aggressive action of organic acids and diffusion of harmful ions which can lead to degradation of the cement matrix (Vipulanandan et al. 2017 and 2018). Also to reduce the impact on the environment, clays have been used to partially replace the cementitious materials (Vipulanandan 2021). The amount of water added to the cement grouts gives it the ability to be pumped into porous soils and fractured concrete. In general the groutability increases with the addition of water but it results in decrease in the strength and longer setting times. Hence, the long-term durability of the grouts with higher water-to-cement ratio must be investigated.

In order describe the behavior of various types of fluids such as grouts and drilling fluids, Power law and Herschel-Bulkley have been used for decades and the flow properties have been estimated based on these models (Celik et al. 2015; Afolabi et al. 2017 and 2019; Tchameniet al. 2019). The Herschel-Bulkley model that was developed in 1926 has been used to predict the shear-thinning and shear-thickenning behaviors of various types slurries. The new Vipulanandan rheological model that was developed in year 2014 for all types of fluids (shear thining, shear thickening and Newtonian) has been used to characterize shear thinning behavior of drilling muds and oil well cement slurries (Afolabi et al. 2017 and 2019 and 2017; Tchameniet al. 2019; Mohammed, 2017; Vipulanandan et al. 2014 and 2017). In addition, the new Vipulanandan rheological relationship for shear thinning fluids limits the magnitude of the shear stress tolerance of drilling mud but all the other relationships predicted infinite shear stress tolerance for the drilling mud (Vipulanandan et al. 2014; Mohammed 2017; Afolabi et al. 2019 and Tchameniet al. 2019) have clearly stated that of the several rheological models that were investigated to predict the rheological properties of nano-modified bentonite drilling muds, the new Vipulanandan rheological model better predicted the test results.

2. Objectives

The focus was to test and quantify the addition of meta kaoline (MK) clay and water-to-cement ratio on the rheological properties of the cement grouts. The specific focus of the study are as follows:

i. Quantify the rheological properties of cement grouts modified with clay (MK) and water-to-cement (w/c) ratios.

ii. Model the rheological properties of cement grouts with and without clay and also verify the models.

MODELS

Constitutive Models for Fluids

The cement grouts showed that the rate of increase in the shear stress (τ) decreased with the increase in shear strain rate ($\dot{\gamma}$) (tangent viscosity), representing a shear thinning fluid. It is important to satisfy the observed test results with the constitutive model. Some of the observed conditions for cement slurries are as follows (Vipulanandan et al. 2014, 2015b):

Yield shear stress $\tau = \tau_o$ when the shear stain rate is zero.

The tangential viscosity is $\frac{d\tau}{d\dot{\gamma}} > 0$ (1)

Also the rate of change of tangential viscosity is $\frac{d^2\tau}{d\dot{\gamma}^2} < 0$ (2)

At the strain rate of infinity (very large shear stain rate) the ultimate shear stress $\tau = \tau_{max}$ (3)

Herschel-Bulkley (HB) model (1926)

The HB constitutive model (Eqn. 4) has three parameters and it is as follows (Vipulanandan et al. 2014, 2017):

$$\tau = \tau_{o1} + r * (\dot{\gamma})^m \tag{4}$$

The material parameters are τ_{o1}, r and m representing the yield stress and two fluid material parameters respectively. When the applied shear stress will be greater than the yield stress the fluid starts to flows. Hence, the HB model must satisfy the conditions in Eqns. (1), (2) and (3).
The tangent viscosity will be as follows (Vipulanandan et al. 2014, 2017):

$$\frac{d\tau}{d\dot{\gamma}} = r * m * \dot{\gamma}^{(m-1)} > 0 \Rightarrow r * m > 0 \tag{5}$$

The rate of change of tangent viscosity is as follows (Vipulanandan et al. 2014):

$$\frac{d^2\tau}{d\dot{\gamma}^2} = r * m(m-1) * \dot{\gamma}^{(m-2)} \Rightarrow \mathrm{r} * \mathrm{m} * (\mathrm{m}-1) < 0 \tag{6}$$

The conditions in Eqn. (1) and Eqn. (2) will be satisfied only when 0< m < 1 and r> 0.

Also from the Eqn. (4) , at a shear strain rate of infinity the ultimate shear stress will be infinity and no shear thinning fluid will have infinity shear stress capacity. Hence, HB model does not satisfy the upper limit condition for the ultimate shear stress limit.

Vipulanandan rheological model (2014)

The performance of Vipulanandan Rheological Model predictions have been verified researchers around the world (Afolabi et al. 2017 and 2019; Mohammed, 2017; Tchameniet al. 2019). The constitutive model is represented as follows (Vipulanandan et al. 2014, 2017):

$$\tau - \tau_{o2} = \frac{\dot{\gamma}}{A + B * \dot{\gamma}} \tag{7}$$

Where the model parameters are τ_{o2}: yield stress (Pa); A $(\text{Pa. s})^{-1}$ and B $(\text{Pa})^{-1}$. So the tangential viscosity and rate of change of tangential viscosity for shear thinning fluids will be represented as follows (Vipulanandan et al. 2014, 2015b):

$$\frac{d\tau}{d\dot{\gamma}} = \frac{(A + B\dot{\gamma}) - \dot{\gamma} * B}{(C + B\dot{\gamma})^2} = \frac{A}{(A + B\dot{\gamma})^2} > 0 \Rightarrow A > 0$$

$$\frac{d^2\tau}{d\dot{\gamma}^2} = \frac{-2AB}{(A + B\dot{\gamma})^3} < 0 \Rightarrow B > 0$$

Also when the shear stain rate reaches infinite the ultimate shear strength

$$\tau_{\max} = \frac{1}{B} + \tau_{o2} \tag{8}$$

Hence, the Eqn. (7) has a limit to the fluid shear stress tolerance representing the ultimate shear strength of the fluid.

3. MATERIALSAND METHODS

Cement grout

Portland cement (Type 1) (ASTM C 150 -16) was used in preparing the grouts.

Clay (MK)

Commercially available metakaolin clay was used in this study. Different percentages of the metakaolin up to 10% (by the weight of dry cement) was added to cement.

Rheological test

The cement grouts with and without clay (MK)) were tested using a rheometer with varying speed. The speed accuracy of this device was 0.001 rpm. A standard solution with a viscosity of 100 cP was used to calibrate the instrument. All the rheological tests were performed after 10 minutes of mixing of the cement grouts. For all the tests, at least three samples were tested for each condition.

4. RESULTS AND DISCUSSION

Clay (MK)

In Fig.1 the grain size distribution of the metakaolin, using the hydrometer method (ASTM D 422-07) is compared to the cement. The d_{50} of 1.9 μm, over 10 times finer than the cement. The coefficient of uniformity (C_u) for the clay was 3.68.

Rheological properties

Cement grouts investigated in this study with 10% clay (MK) contents showed different rheological properties. All the tested grouts showed non-Newtonian shear thinning behavior as shown in Fig. 2.

Adding water to the grout reduced the apparent viscosity (secant viscosity) of the cement grouts. The apparent viscosity of the cement grouts with w/c ratio of 0.6 and 1.0 without clay (MK) at a shear strain rate of 170 s^{-1} (100 rpm, at room temperature) were 18 cP and 11 cP respectively as summarized in Table 1. Adding of ten percentage of clay (MK) to the cement grout increased the apparent viscosity with w/c ratio of 0.6 and 1 at a shear strain rate of 170 $s^{-1}$from 18 cP to 61 cP and from 11 cP to 41 cP respectively as summarized in Table 1.

The constitutive relationships for cement grouts with various w/c ratios and with different clay (MK) content are shown in Fig. 2. Reducing the water-to-cement ratio increased the shear stress at the same shear strain rates, which indicates lower flow properties of the cement grout with decreased w/c ratio. Also adding clay (MK)) the increased yield stress and the apparent viscosity at the same shear strain rates and w/c ratio as shown in Fig. 2.

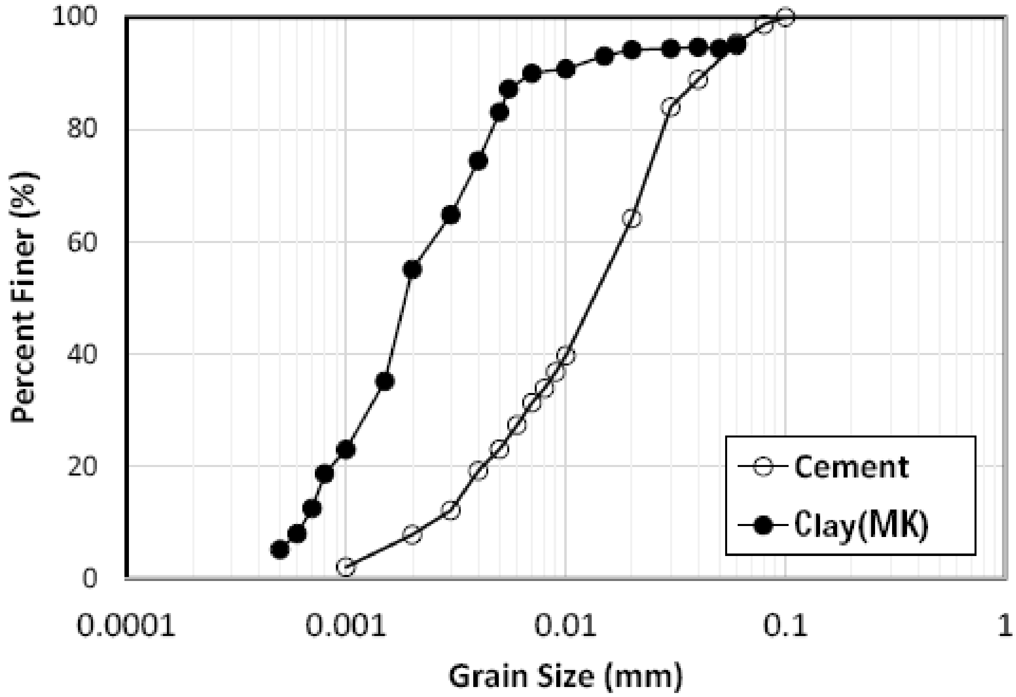

Figure 1. Particle size distribution of the cement and clay

Constitutive models for rheological properties

The behavior of cement grouts with varying clay (MK) and various water-to-cement ratios were predicted using the Vipulanandan rheological relationship and compared with the Herschel- Bulkley relationship as shown in Fig. 2.

Herschel-Bulkley model (1926)

Water-to-cement of 0.6

The behavior of cement grouts (w/c ratio of 0.6) at different percentages of clay (MK) were modeled using the HB model (Eqn. (4)) up to a shear strain rate of 1024 s^{-1}(600 rpm). The coefficients of determination (R^2) were varied between 0.98 and 0.99 (Table 1). The root mean square of error (RMSE) for cement grout slurry at 0% and 10% of clay (MK) was 2.58 Pa and 4.75 Pa respectively (Table 2). The addition of 10% clay (MK) to the cement grout with w/c ratio of 0.6 increased the yield stress (τ_{o1}) from 3.2 Pa to 10.2 Pa, a 219% increase(Table 2). The model parameter k for the cement grout with w/c ratio of 0.6 at 0% and 10% of clay (MK) was 9.64 Pa.s^n and 52.10 Pa.s^n respectively (Table 1). The model parameter m for the cement grout slurry with w/c ratio of 0.6 with 0% and 10% of clay (MK) was 0.267 Pa.s^n and 0.179 Pa.s^n respectively (Table 1).

Water-to-cement ratio of 1.0

The behavior of cement grout with w/c ratio of 1.0 with different percentages of clay (MK) were modeled using the HB model (Eqn. (4)). The R^2 varied between 0.97 and 0.99 (Table 2). The RMSE for cement grout modified with 0% and 10% of clay (MK) was 0.92 Pa and 4.25 Pa respectively (Table 2). The yield stress (τ_{o1}) for the cement grout with 0% clay (MK) was 1.8 Pa and increased to 6.7 Pa with increasing the clay (MK) to 10%, a 272% increase, and the trend was similar to what was observed with w/c ratio of 0.6. The model parameter k for the cement grout with w/c ratio of 1.0 at 0% and 10% of clay (MK) was 1.08 Pa.s^n and 11.3 Pa.s^n respectively(Table 2). The model parameter m for the cement grout with w/c ratio of 1.0 with 0% and 10% of clay (MK) was 0.463 Pa.s^n and 0.275 Pa.s^n respectively (Table

1).

Vipulanandan rheological model (2014)

Water-to-cement of 0.6

The performance of the cement grout with w/c ratio of 0.6 with different percentages of clay (MK) were modeled using the Vipulanandan rheological model (Eqn. (7)). The R^2varied between 0.97 and 0.99 (Table 2). The RMSE for the cement grout modified with 0% and 10% of clay (MK) was 1.12 Pa and 4.49 Pa respectively (Table 2). The yield stress (τ_{o2}) for the cement grout with 0% clay (MK) was 3.6 Pa and increased to 10.6 Pa with increasing the clay (MK) content to 10%, a 194% increase(Table 2). The model parameter A for the cement grout with 0% and 10% of clay (MK) was 2.635 Pa.$s^{-1}$and 0.495Pa.s^{-1} respectively, a 81% reduction. The model parameter B for the cement grout with 0% and 10% clay (MK) was 0.018 Pa $^{-1}$ and 0.007 Pa^{-1} respectively, a 61% reduction (Table 2).

Water-to-cement ratio of 1.0

The performance of the cement grout slurry with w/c ratio of 1.0 at different percentages of clay (MK) with w/c ratio of 1.0 was modeled using the Vipulanandan rheological model (Eqn. (7)). The coefficients of determination (R^2) were varied between 0.98 and 0.99 (Table 2). The root mean square of error (RMSE) for the cement grout modified with 0% and 10% of clay (MK) was 1.09 Pa and 3.16 Pa respectively (Table 2). The yield stress (τ_{o2}) for the cement grout slurry with 0% of clay (MK) was 1.8 Pa and increased to 6.6 Pa with the increase in the clay (MK) to 10%, a 267% increase as shown in Fig. 5 and also summarized in Table 2. The A parameter of the model for the cement grout slurry with 0% and 10% of clay (MK) was 8.49 Pa.s^{-1} and 0.85 Pa.s^{-1} respectively, a 90% reduction. The B parameter of the model for the cement grout slurry with 0% and 10% of clay (MK) was 0.032 Pa $^{-1}$ and 0.014 Pa^{-1} respectively, a 56% reduction (Table 2).

Table 1. Herschel-Bulkley rheological model parameter for cement grout modified with clay (MK)

		Herschel-Bulkley Model (1926)					
w/c	Clay Content (%)	τ_{o1} (Pa)	r (Pa.s^n)	m	RMSE (Pa)	R^2	Apparent Viscosity (cP), at 170 s^{-1}
0.6	0	3.2 ± 2.3	9.64 ±0.08	0.267 ±0.03	2.58	0.98	18 ±3
	3	4.4± 1.9	14.06 ±0.06	0.254 ±0.06	2.30	0.99	25 ± 2.5
	5	7.4 ± 3.2	21.40 ±0.07	0.238 ±0.03	2.33	0.99	42 ±3
	10	10.2 ±3	52.10 ±0.06	0.179 ±0.02	4.75	0.99	61 ± 2
1	0	1.8 ±3.3	1.08 ±0.09	0.463 ±0.04	0.92	0.99	11± 3
	3	3.2 ±2.5	5.25 ±0.1	0.314 ±0.01	1.20	0.99	18 ± 2
	5	5.1 ±+2	9.02 ±0.05	0.288 ±0.02	3.93	0.97	29 ± 3
	10	6.7± 3	11.30 ±0.06	0.275 ±0.03	4.25	0.97	41 ±3

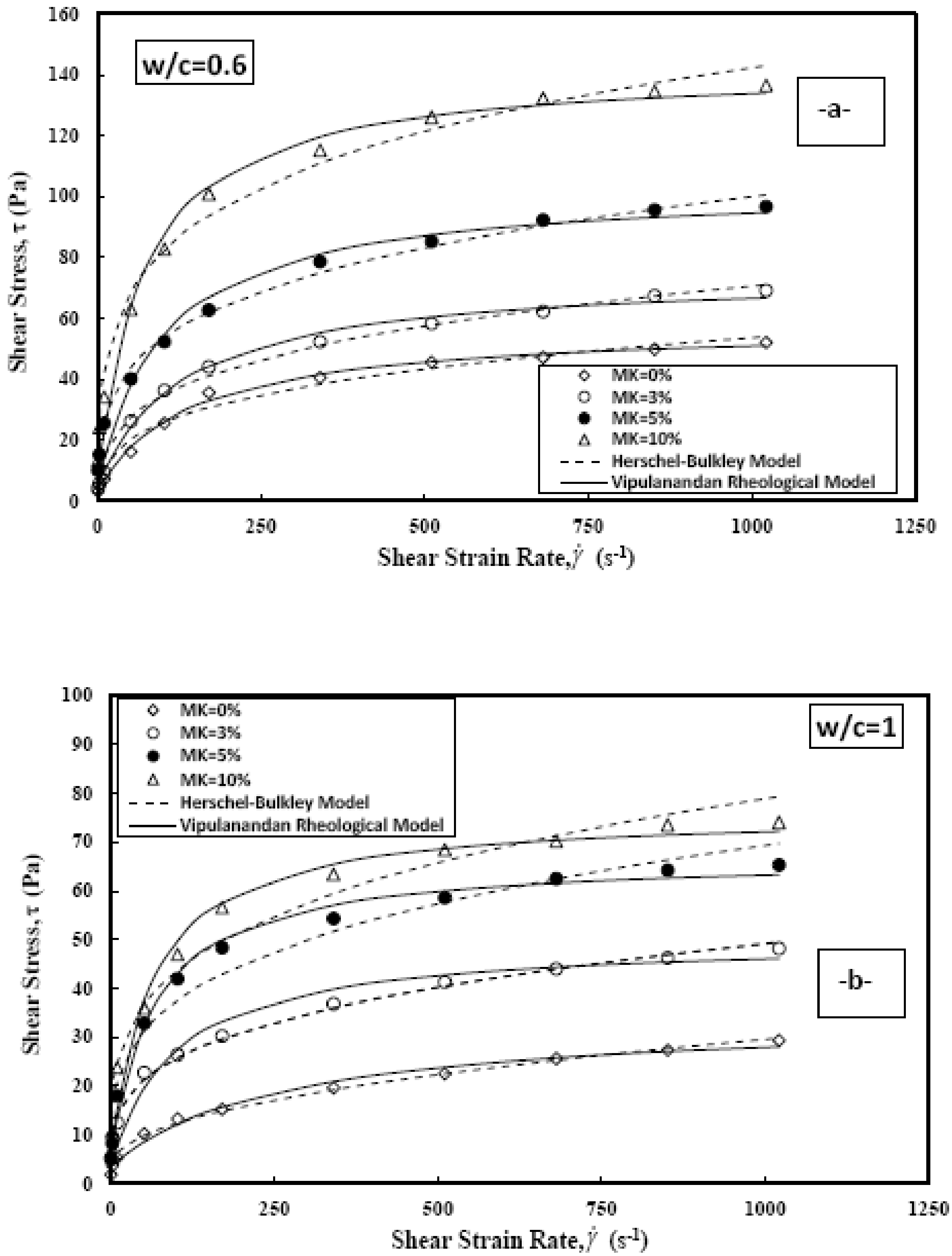

Figure 2. Measured and Predicted Shear Stress and Shear Strain Relationship for the Grouts with Clay (a) w/c ratio of 0.6 and (b) w/c ratio of 1.0.

Table 2. Vipulanandan rheological model parameter for cement grout modified with clay (MK)

		Vipulanandan Rheological Model (2014)					
w/c	Clay Content (%)	τ_{o2} (Pa)	A (Pa.s^{-1})	B (Pa)$^{-1}$	τ_{max} (Pa)	RMSE (Pa)	R^2
0.6	0	3.6 ± 2.1	2.635 ±0.2	0.018 ±0.001	58	1.12	0.99
	3	4.7 ±0.5	1.879 ±0.2	0.014±0.002	75	1.64	0.99
	5	7.7 ±1.6	1.01 ±0.1	0.010 ±0.002	107	2.01	0.97
	10	10.6 ±2.5	0.495 ±0.2	0.007 ±0.002	148	4.49	0.98
1	0	1.8 ±2	8.49 ±0.3	0.032 ±0.002	33	1.09	0.99
	3	3.5 ±2.2	2.089 ±0.2	0.021 ±0.003	50	1.22	0.98
	5	5.2 ±2	1.036 ±0.1	0.016 ±0.002	67	2.00	0.99
	10	6.6 ±1.8	0.85±0.2	0.014 ±0.001	78	3.16	0.98

Yield Shear Stress (τ_{o2})

Based on the rheological model prediction of the test results, Vipulanandan Rheological Model was used to determine the yield stresses for grout mixes. Reducing the water-to-cement ratio increased the yield shear stress, which indicates lower flow properties of the cement grout with decreased w/c ratio as shown in Fig. 3. Increasing the w/c ratio 0.6 to 1.0 reduced the yield stress from 3.6 Pa to 1.8 Pa, 50% reduction. Also adding clay (MK) it increased yield stress as shown in Fig. 3. With w/c ratio of 0.6, adding 10% clay increased the yield stress from 3.6 Pa to 10.6 Pa, almost 3 times increase. With the w/c ratio of 1.0, addition of 10% clay increase the yield stress from 1.8 Pa to 6.6 Pa, 3.5 times increase.

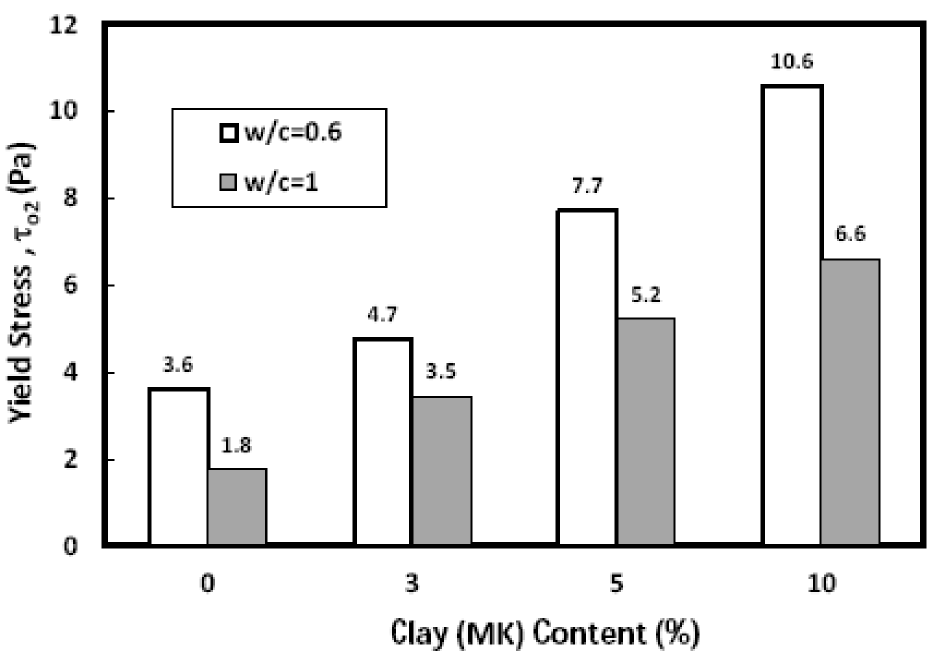

Figure 3. Variation of yield stress with varying water contents and clay contents predicted with Vipulanandan rheological model

Maximum Shear Strength ($\tau_{max.}$)

Based on the Vipulanandan rheological model there is a limit on the maxium shear stress ($\tau_{max.}$) for the cement grouts at the relatively high rate of shear strains. The τ_{max} for the cement grout slurries with w/c ratio of 0.6 and 1 at 0% and 10% of clay (MK) were 58 Pa, 148 Pa and 33 Pa, 78 Pa respectively as shown in Fig. 4 and also summarized in Table 2. The addition of 10% of clay (MK) to the cement grouts increased the ultimate shear strength by 160% and 144% for w/c ratio of 0.6 and 1 respectively (Table 2).

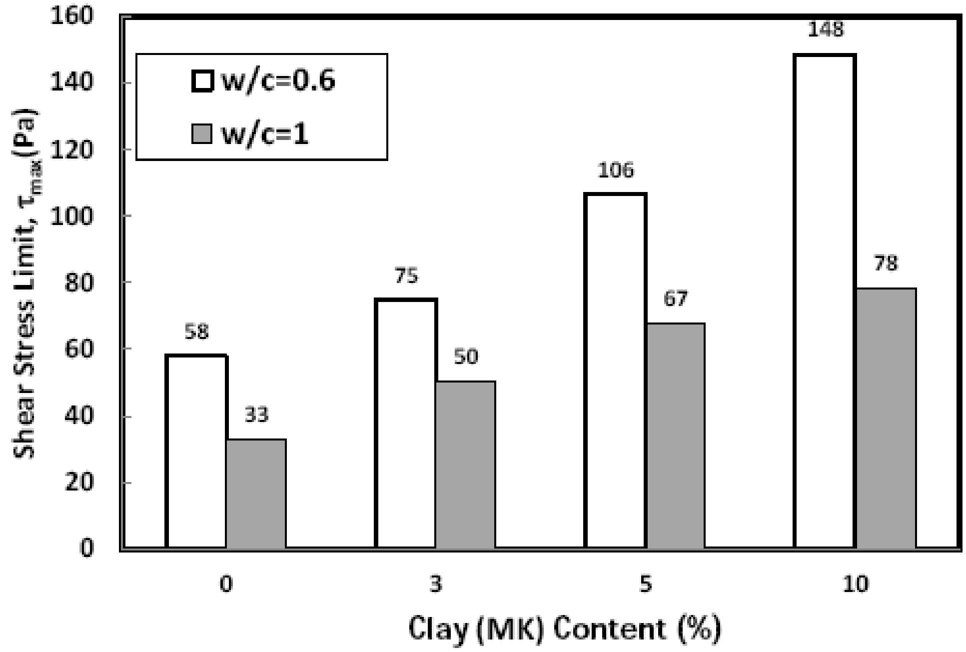

Figure 4. Variation of maximum shear stress tolerance for the cement grouts with different w/c ratios and clay contents predicted by the Vipulanandan Rheological Model

5. CONCLUSIONS

Based on the experimental and analytical modeling of the rheological properties of cement grouts with w/c ratios of 0.6 and 1.0 and modified with up to 10% clay (MK) following conclusions are advanced:

1) The rheological tests showed that the cement grouts with and without up to 10% clay additive had a shear thinning behavior.
2) Vipulanandan rheological model was used to predict shear stress- shear strain rate relationship and the rheological model predicted the test results very well compared to the Herschel-Bulkley model based on root-mean square error.
3) The yield stress and maximum shear stress limit reduced with the increase in the water-to-cement ratio while adding the clay (MK) increased these two properties. These two properties were quantified with the Vipulanandan rheological model.

6. ACKNOWLEDGEMENT

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