

## CORRELATION OF VISCOSITY OF UN-FLOCCULATED AND FLOCCULATED KAOLIN SLURRIES WITH TEMPERATURE

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**ABSTRACT:** The effect of temperature on the flow curves of both un-flocculated and flocculated kaolin slurries at 40% by mass concentration over the temperature range of 21°C and 89°C has been studied previously (Zengeni et al., 2019). A co-axial cylinder viscometer was used to make flow curve measurements over the shear rate range of 10 to 300 s<sup>-1</sup>. These data have been re-analysed using the power law model and the effect of Brownian motion on determining the rheological behaviour assessed. The slurry relative viscosity has been found to correlate well with a dimensionless quantity, the Colloid number.

**KEY WORDS:** Kaolin, slurry, viscosity, Brownian motion, temperature

### NOTATION

a, d	Particle size (m)
C	Colloid number (-)
N	Flow behaviour index in power law model (-)
k <sub>B</sub>	Boltzmann's constant (J/K)
K	Consistency coefficient in power law model (Pa s <sup>n</sup> )
Re <sub>p</sub>	Particle Reynolds number
t <sub>r</sub>	Relative time (-)
T	Absolute temperature (K)
v	Solid volume fraction (-)
v <sub>m</sub>	Maximum solids volume fraction
$\dot{\gamma}$	Shear rate (s <sup>-1</sup> )
$\eta_0$	Liquid viscosity (Pa s)
$\eta_r$	Relative viscosity (-)
$\eta_s$	Slurry viscosity (Pa s)
$\rho_r$	Relative density (-)
$\tau$	Shear stress (Pa)
$\tau_r$	Reduced shear stress (-)

## 1. INTRODUCTION

It is often believed that when the flow curve of a mineral slurry is measured as a function of temperature and the flow curve is represented by the Bingham Plastic model, the plastic viscosity in the model decreases with increasing temperature at the same rate as the viscosity of the suspending liquid (water with some dissolved salts) decreases. The yield stress parameter in the model is assumed to remain largely constant. This has been assumed for many years by the major turnkey engineering companies involved in long distance slurry pipeline design and construction (Thomas, 2019). A decrease in the slurry dynamic viscosity with temperature, the shear stress divided by the shear rate at a given shear rate, often occurs, particularly when most or all particles are greater than about 1 to 2  $\mu\text{m}$  in size, and therefore when there is little or no effect on slurry viscosity arising from particle Brownian motion.

However, when the slurry contains a significant proportion of particles below 1 to 2  $\mu\text{m}$ , Brownian motion effects can cause an increase in slurry viscosity with increasing temperature at a given shear rate and solids concentration, as demonstrated by several experimental studies. The effect of temperature on slurry viscosity levels can have an impact on parameters such as pipe deposition velocity, laminar-turbulent transition velocity and pipeline friction pressure gradients.

## 2. LITERATURE REVIEW

### 2.1. STUDIES ON EFFECT OF TEMPERATURE ON SLURRY VISCOSITY

There appears to be limited research into the effect of temperature on the rheological properties of non-Newtonian mineral slurries. Understanding the influence of temperature on slurry viscosity is of relevance for the mining industry for instance, where slurries are pumped at elevated temperatures. For example, autoclave circuits for mineral extraction are operated at temperatures of the order of 200°C (and elevated pressure) and the tailings from this process are pumped at temperatures of the order of 70°C (Zengeni et al., 2019).

Mosa et al. (2007) studied the effect of slurry temperature, slurry pH and particle degradation on rheology and pressure drop of coal-water slurries containing particles up to 250  $\mu\text{m}$  and found that slurry viscosity and the degree of shear-thinning property sharply decrease with increasing slurry temperature. This can be accounted for by the decrease in the water viscosity, with an increase in temperature. They suggest that the reduced viscosity with shear rate can be explained by assuming that the loosely packed particle aggregates are broken up by shear forces, thereby releasing trapped water and subsequently reducing the effective volume solids concentration. Senapati et al. (2009) investigated the rheological behaviour of limestone-water slurry samples at different solids volume concentrations, particle size distributions and slurry temperatures. The relative viscosity of the slurry (the ratio of slurry viscosity to the suspending liquid viscosity) was found to decrease with increasing temperature in the temperature range studied (30 to 50°C). Two limestone samples were used, both having a size varying between 2  $\mu\text{m}$  and 200  $\mu\text{m}$ , and one having a  $d_{50}$  of 26  $\mu\text{m}$  while the other 53  $\mu\text{m}$ , and therefore little or no effect of particle Brownian motion would be expected to occur.

Some experimental studies have shown that slurry viscosities can increase with increasing temperature. The rheological behaviour of Wyoming Na-bentonite in water dispersions was investigated by Vryzas et al. (2017) over the temperature range 25°C to 80°C. The particle size ranged from 0.6 µm to 200 µm, with a  $d_{50}$  of 36 µm, and therefore some effects from particle Brownian motion on slurry viscosity may be expected. The experimental results indicated an increase in shear stresses at lower shear rates with temperature, while the effect was less significant at higher shear rates up to 170 s<sup>-1</sup>. The yield stress parameter in the Herschel-Bulkley model increased linearly with temperature by almost three-fold, while the consistency coefficient decreased with temperature by almost five-fold, and the flow behavior index increased, tending towards a Newtonian value of one. Yong et al. (2018) measured the flow curves of freshly-thickened copper tailings that contained cement, covering a range of temperatures from 2°C to 60°C. The particle size of the copper tailings ranged from 0.3 µm to almost 200 µm, with a  $d_{50}$  of 60 µm, and 5% of the distribution below 2 µm. The results from this study showed an increase in the shear stress and apparent viscosity of the samples as the temperature was raised, indicating that even a relatively small fraction of < 2 µm can have a significant impact. However, it is unclear whether the viscosity increase is due to the chemical reaction arising from cement addition.

These four studies suggest that sometimes viscosity decreases with temperature at a given shear rate and solids concentration, and sometimes increases. The latter behaviour would appear, in part, to be related to the influence of particle Brownian motion effects when there is a significant proportion of particles less than a few microns.

## 2.2. BROWNIAN MOTION AND DIMENSIONAL ANALYSIS

Zengeni et al. (2019) stated that the trend of an increasing slurry viscosity with an increase in sample temperature was not expected. This is because a general reduction in viscosity with increasing temperature was considered more likely to occur and that it would be reasonable to assume that the slurry viscous properties will scale with temperature in line with the viscosity of water. If only hydrodynamic effects occur under shear this would be the case and many equations have been published relating slurry relative viscosity,  $\eta_r$ , to the solids volume fraction,  $v$ , the maximum particle packing fraction,  $v_m$ , and the intrinsic viscosity,  $[\eta]$ , which is a function of particle morphology. Typically,  $[\eta]$ , is 2.5 for spheres and can take values up to about 3 or more for angular particles. An example of such an equation is the Krieger and Dougherty expression (1959):

$$\eta_r = \frac{\eta_s}{\eta_o} = \left[ \frac{1}{1-v/v_m} \right]^{2.5v_m} \quad (1)$$

This equation can predict the slurry relative viscosity quite well over a wide range of solids volume fractions, provided none of the particles are affected by particle surface forces and by Brownian motion, in other words that the minimum particle size is larger than about 2 µm. Eqn (1) shows that as the slurry temperature is varied, so the water viscosity varies, and the equation predicts that the slurry viscosity will vary by the same amount, provided the solids volume fraction, particle size distribution and particle shape remain constant.

However, in addition to purely hydrodynamic forces a further influence on the determination of slurry viscosity is the Brownian motion of the finer particles, typically below about 2  $\mu\text{m}$ , which can lead to shear-thinning flow behaviour. Both translational and rotational Brownian motion occur but it is the former that is more usually important and that causes the collision between adjacent particles. This then leads to an additional energy dissipation source as manifested through an increase in slurry viscosity with increasing temperature. Krieger (1963) and then later Chaffey (1977) in the development of their ideas on the major factors determining slurry viscosity levels recognised the importance of Brownian motion. To explain shear-thinning flow behaviour (followed sometimes by shear-thickening) with increasing shear rate, at least two processes need to be invoked in addition to viscous hydrodynamic effects. These processes may relate to Brownian motion, inertia, particle deformability or interactions due to van der Waals, electrostatic or steric forces. Dimensional analysis shows which processes are most important for a given particle size and shear rate.

Krieger (1963) appears to be the first to have published a simple dimensional analysis of the fundamental variables affecting slurry rheology, although one of the dimensionless groups, which he presented and named the Colloid number, had appeared previously in an earlier theoretical work. Krieger was concerned essentially with establishing the importance of Brownian motion in the rheology of fine particle slurries where surface force effects are minimised, and hence the number of variables he considered was nine in total. These nine variables lead to six dimensionless groups and thus he concluded that the relative viscosity of a slurry containing rigid spheres can be written as

$$\eta_r = \frac{\eta_s}{\eta_o} = f(v, C, t_r, \rho_r, Re_p) \quad (2)$$

where  $t_r$  is a relative time,  $\rho_r$  is a relative density and  $Re_p$  is a particle Reynolds number. If steady flow is assumed, the particles are effectively neutrally-buoyant (essentially the case when they are very fine because gravitational settling rates are so low), and laminar flow occurs, then relative viscosity is a function of two dimensionless groups - the solids volume fraction,  $v$ , and a Colloid number,  $C$ :

$$\eta_r = f(v, C) \quad (3)$$

where the dimensionless Colloid number includes Boltzmann's constant,  $k_B$ , and the absolute temperature,  $T$ , and is given by

$$C = \frac{\eta_o \dot{\gamma} d^3}{k_B T} \quad (4)$$

and  $d$  is a representative particle size from the whole particle size distribution. A typical plot of  $\eta_r$  versus  $C$ , at a constant solids concentration,  $v$ , is shown in Figure 1.

Under isothermal conditions, the plot represents the shear-thinning flow behaviour to be expected for a monodispersed slurry, or, alternatively, the effect of variation in particle size,  $d$ , on suspension viscosity at a constant shear rate. Woods and Krieger (1970) and Papir and Krieger (1970) used another dimensionless quantity as an alternative to the

Colloid number and which includes the Brownian motion effect called a reduced shear stress,  $\tau_r$ , given by

$$\tau_r = \frac{\tau d^3}{k_B T} \tag{5}$$

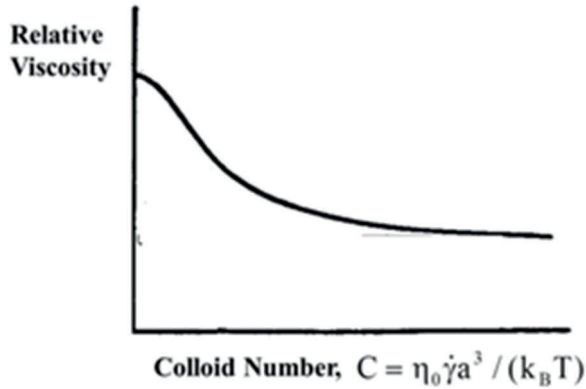


Figure 1 Typical plot of relative viscosity v. Colloid number for a mono-sized slurry

### 3. ZENGENI ET AL. KAOLIN SLURRY FLOW CURVE DATA

#### 3.1. UN-FLOCCULATED AND FLOCCULATED KAOLIN SLURRIES

Zengeni et al. (2019) sourced kaolin clay from Serina Trading in Cape Town for their flow curve measurements. Figure 2 gives the kaolin particle size distribution (PSD), measured using laser diffraction. Approximately 15% of the distribution is less than 2  $\mu\text{m}$  and so this fraction can be affected by Brownian motion and therefore have a substantial influence on the rheological properties of the kaolin slurry.

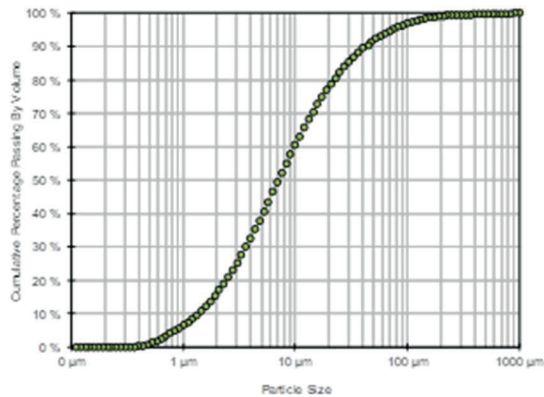


Figure 2 Kaolin clay measured particle size distribution

The investigation into the effect of temperature on the slurry flow curves was carried out using two samples of kaolin clay slurry (referred to as “un-flocculated” and “flocculated”), with the difference between the two being the method of preparation. The un-flocculated sample was prepared by mixing dry kaolin clay with potable water with an agitator until it was well-mixed. The pH and conductivity of the make-up water at 16 °C were 9.8 and 96 mS/m respectively. The flocculated sample was prepared from a dilute kaolin slurry (prepared with potable water as described above) and fed to a bench top 100 mm diameter dynamic thickening apparatus where a polymer flocculant (Magnafloc 5250) was dosed to encourage the formation of flocs. The settled flocculated (“thickened”) kaolin slurry was withdrawn from the thickener underflow, with the thickener being operated in continuous steady-state mode, until sufficient flocculated sample had been collected. The thickener underflow sample was at a solids concentration of 46% by mass. The sample at 46% by mass was diluted using potable water to a target concentration of 40%. The slurry pH and conductivity of the samples were recorded.

Additional rheological data using flocculated kaolin slurries having concentrations of 36% and 49% by mass were also obtained by Nekhavhambe (2019) as part of the same study but were not included in the Zengini et al. (2019) paper.

### 3.2. RHEOLOGICAL MEASUREMENTS

An Anton Paar Rheolab QC rotational viscometer with temperature control jacket was used, where the bob rotates and the cup is stationary. The CC35/HR measuring system was used and the dimensions are as follows: bob radius = 17.5 mm, cup radius = 21.0 mm, gap width = 3.5 mm, and bob cone angle of 120°. For each viscometer test (for a specific temperature), 60 ml of slurry sample was transferred into the viscometer cup with a syringe. The rotational viscometer torque and rotational speed were recorded over a shear rate range of 10 to 300 s<sup>-1</sup>. The corrected torque and rotational speed were converted to wall shear stress and shear rate respectively according to ISO 3219 standard procedures. To calculate the corrected torque, the torque measured for the conical part of the bob immersed in the slurry was deducted from the torque measurement. The sample average temperatures are summarised in Table 1.

Table 1

Summary of rheological tests

Slurry Sample	Parameter	Test				
		Test 1	Test 2	Test 3	Test 4	Test 5
Un-flocculated 40% by mass	Temp., °C	21.1	43.1	60.4	79.9	89.0
	pH	8.6	8.4	8.2	8.0	7.9
	Conductivity, mS/m	106	120	131	143	149
Flocculated 40% by mass	Temp., °C	22.5	36.7	55.7	77.6	85.0
	pH	8.1	8.1	8.2	8.2	8.2
	Conductivity, mS/m	123	132	143	156	161

### 3.3. MEASURED FLOW CURVES

The flow curves for the 40% by mass un-flocculated kaolin slurries are presented in Figure 3 at five temperatures from 21.1 to 89.0°C. There is a clear and consistent temperature dependency. Increasing slurry temperature results in an upward shift in the flow curve, whose general shape and slope remain approximately constant, but there is a noticeable and approximately uniform increase in shear stress across the shear rate range used.

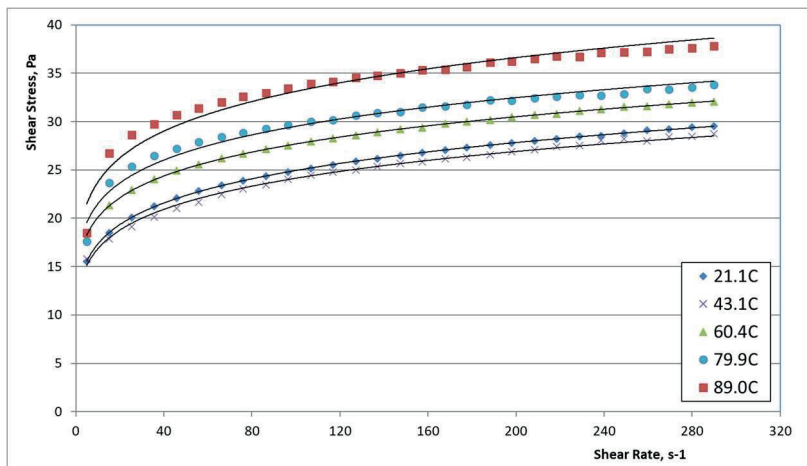


Figure 3 Flow curves for un-flocculated kaolin at 40% by mass

Zengini et al. (2019) used the Herschel Bulkley flow model to fit their data. However, the simpler power law model also represents the data reasonably well:

$$\tau = K\dot{\gamma}^n \quad (6)$$

Table 2 gives the estimates of the K and n parameters in the power law model, together with the associated R-squared value. While the flow behaviour index remains largely

constant, the consistency coefficient increases essentially monotonically, as is often the case with this and other slurry systems.

Table 2  
Estimated power law flow model parameters for un-flocculated slurry samples

Temp., °C	Consistency Coefficient, K, Pa.s <sup>n</sup>	Flow Behaviour Index, n	R <sup>2</sup> Value
21.1	12.1	0.158	0.9998
43.1	11.8	0.156	0.9954
60.4	14.6	0.139	0.9997
79.9	15.7	0.138	0.9746
89.0	17.0	0.145	0.9556

The flow curves for the 40% by mass flocculated slurries are presented in Figure 4 for five temperatures from 22.5 to 85.0°C.

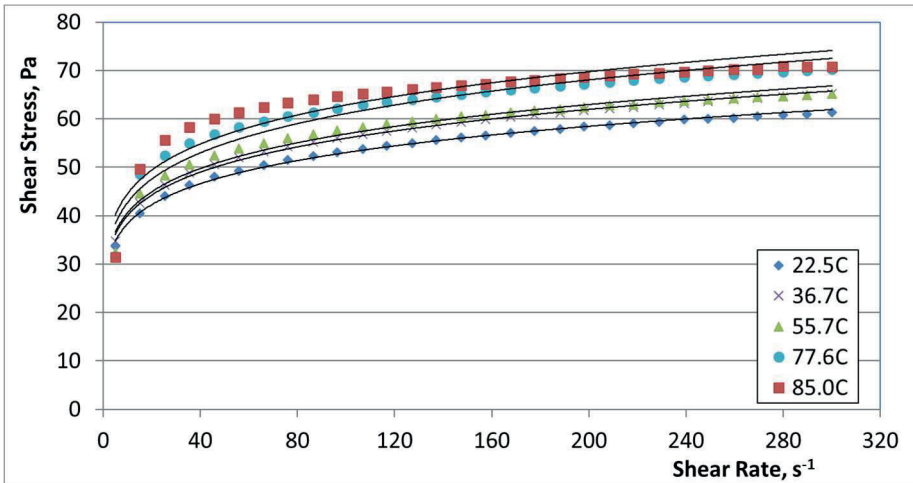


Figure 4 Flow curves for flocculated kaolin at 40% by mass

Table 3 gives the estimates of the K and n parameters in the power law model, together with the associated R-squared values for these flocculated slurry data. The K and n-values at 22.5°C of 27.7 Pa.s<sup>n</sup> and 0.141 respectively are similar to interpolated values obtained from data at room temperature by Heywood and Richardson (1978) of approximately 23 Pa.s<sup>n</sup> and 0.146 during pipe flow measurements using flocculated kaolin slurry at a concentration of 40% by mass flowing in a 42mm ID pipe. In this earlier study, a shear rate range of 30 to 1000 s<sup>-1</sup> was applied using a finer kaolin with a d<sub>50</sub> of 2.2 µm compared with 7 µm in this study.



Table 3  
Estimated power law flow model parameters for flocculated slurry samples

Temperature, °C	Consistency Coefficient, K, Pa.s <sup>n</sup>	Flow Behaviour Index, n	R <sup>2</sup> Value
22.5	27.7	0.141	0.9965
36.7	28.6	0.146	0.9964
55.7	29.0	0.147	0.9664
77.6	29.8	0.156	0.9367
85.0	31.6	0.150	0.8822

Figure 5 shows how the consistency coefficient, K, increases with temperature for both the un-flocculated and flocculated kaolin slurries, while the flow behaviour index remains largely constant at between about 0.138 and 0.159. There appears to be an approximately linear relationship between the consistency coefficient and temperature in both cases. As expected, the K-values are significantly larger for the flocculated kaolin compared with the un-flocculated slurries.

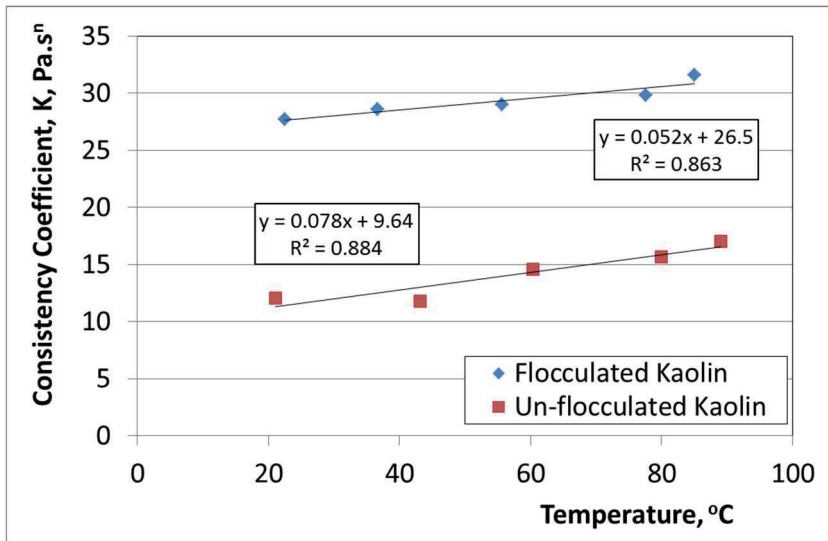


Figure 5 Consistency coefficient, K, as a function of temperature

#### 4. CORRELATION OF RELATIVE VISCOSITY WITH COLLOID NUMBER

##### 4.1. CORRELATION OF RELATIVE VISCOSITY FOR UN-FLOCCULATED SLURRIES

The relative viscosity data are plotted in Figure 6 for the five temperatures as a function of the Colloid number defined in Eqn (4). An arbitrary particle size,  $d$ , of 1  $\mu\text{m}$  has been

used to calculate the Colloid number. The data from five temperatures are brought together well and essentially superpose. A power law fit has been added to the figure for the 60.4°C data which gives an excellent fit ( $R^2 = 1$ ) with the following relationship:

$$\eta_r = 4360C^{-0.86} \tag{7}$$

Figure 6 shows that temperature is still a parameter. This is probably because the kaolin particle size distribution contains a significant proportion of particle sizes that are not greatly affected by Brownian motion and the flow curves are also determined by a combination of hydrodynamic, mechanical and particle surface forces.

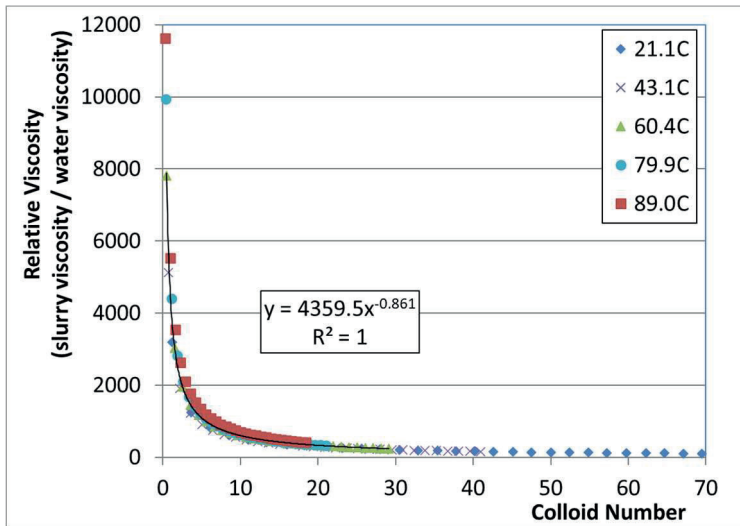


Figure 6 Relative viscosity as function of Colloid number for un-flocculated slurries

Figure 7 shows all the relative viscosity data on a logarithmic basis and demonstrates the power law relationship with a straight line for each of the five temperatures.

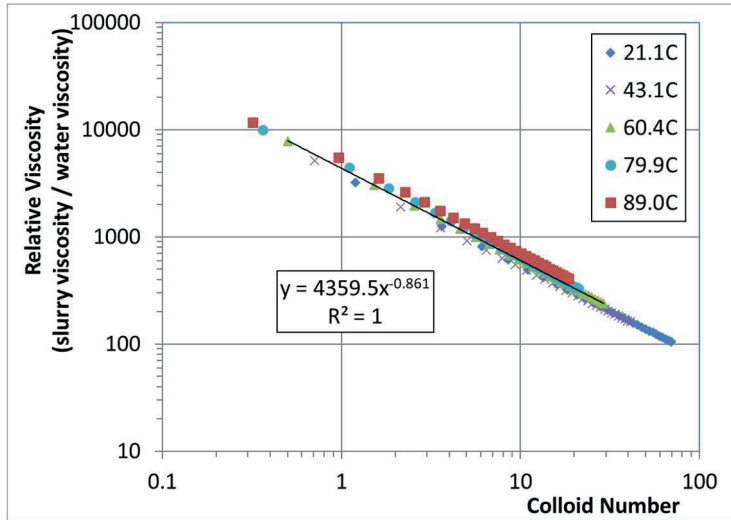


Figure 7 Relative viscosity as function of Colloid number using log co-ordinates for un-flocculated slurries

#### 4.2. CORRELATION OF REDUCED VISCOSITY FOR FLOCCULATED KAOLIN SLURRIES

The relative viscosity data for the flocculated slurries are plotted for the five temperatures from 22.5 to 85°C as a function of the Colloid number in Figure 8 using the same arbitrary particle size of 1  $\mu\text{m}$  to calculate the Colloid number. A power law fit has been added to the figure for the 55.7°C data, which again gives an excellent fit:

$$\eta_r = 8830C^{-0.85} \quad (8)$$

Figure 8 shows, as in the case of the un-flocculated slurries, that temperature is still a parameter because of the little or no effect of Brownian motion on the coarser particles in the particle size distribution.

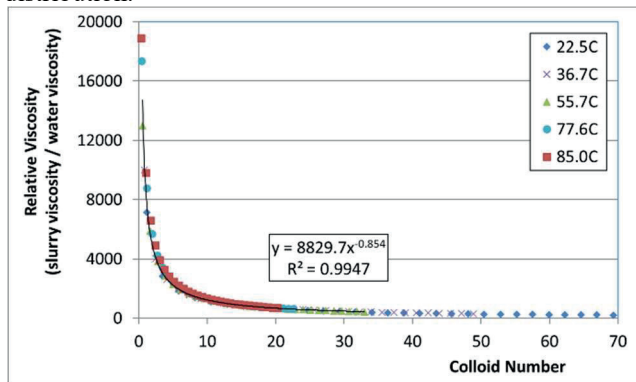


Figure 8 Relative viscosity as function of Colloid number for flocculated slurries

Figure 9 shows all the relative viscosity data on a logarithmic basis and demonstrates the power law relationship with a straight line for each of the five temperatures.

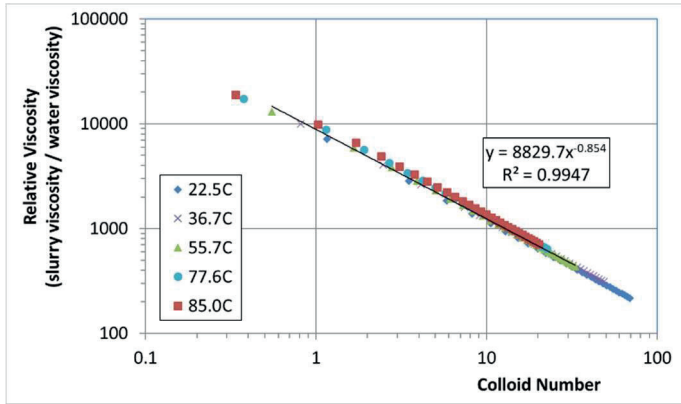


Figure 9 Relative viscosity as function of Colloid number using log co-ordinates for flocculated slurries

## 5. DISCUSSION AND CONCLUSIONS

This paper has presented slurry flow curve data for one concentration (40% by mass) of kaolin solids in both un-flocculated and flocculated states at five temperatures to determine the effect of temperature on the flow curves. The data previously obtained by Zengeni et al. (2019) have been re-analysed using the power law model and the consistency coefficient in the model was found to increase with increasing temperature while the flow behaviour index stays essentially constant at between 0.138 and 0.159 for all test conditions.

The increase in slurry viscosity at a given shear rate with temperature was originally unexpected (Zengeni et al., 2019), but the kaolin particle size distribution suggests that a significant proportion of the fine solids ( $< 2 \mu\text{m}$ ) would be affected by Brownian motion and this would become increasingly important as the temperature was raised. In view of this, the flow curve data were further analysed in terms of the relative slurry viscosity (the ratio of slurry viscosity to the water viscosity at a given shear rate and temperature) and a Colloid number, a dimensionless quantity that takes account of Brownian motion influences on the flow curve.

It was found that over five temperatures both the un-flocculated and flocculated kaolin slurry data could be brought together using the Colloid number, although there is still a temperature influence in this correlation method. It is likely that the use of a finer kaolin PSD would result in less of a temperature effect on the correlation. Further investigation of the effect of Brownian motion on slurry viscosity could include the measurement of the flow curves of slurries containing two or more well-defined PSD's at the same total solids concentration. In the first case, one PSD could be used where all particles are less than 1 to 2  $\mu\text{m}$ , and in the second case a PSD could be used where all particles are sufficiently large such that no Brownian motion effects are to be expected.

Using the intermediate temperature used for the un-flocculated kaolin of 60.4°C a power law fit between the reduced slurry viscosity and the Colloid number was possible with an index on the Colloid number of -0.86. A similar exercise was performed for the intermediate temperature of 57.7°C for the flocculated slurry and a similar index of -0.85 was found. The ratio of the constants in the two correlations of 4360 to 8830 for the un-flocculated and flocculated slurries respectively at

the two temperatures of 60.4°C and 57.7°C suggest that on average the viscosities of the flocculated slurries were slightly more than twice those of the un-flocculated slurries.

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#### REFERENCES

1. Chaffey, C.E., 1977. Mechanisms and equations for shear-thinning, thickening in dispersions. *Colloid and Polymer Science* 255(7), 691-698.
2. Heywood, N.I., Richardson, J.F., 1978. Rheological behaviour of flocculated and dispersed kaolin suspensions in pipe flow. *Transactions of Society of Rheology* 22(6), 599-613.
3. Krieger, I.M., 1963. A dimensional approach to colloid rheology. *Transactions of Society of Rheology* 7, 101-109.
4. Krieger, I.M., Dougherty, T.J., 1959. A mechanism for non-Newtonian flow in suspensions of rigid spheres. *Transactions of Society of Rheology*, 3(1), 137-152.
5. Mosa, E.S., Saleh, A.M., Taha, A.T., El-Molla, A.M., 2007. A Study on the effect of slurry temperature, slurry pH and particle degradation on rheology and pressure drop of coal water slurries. *Journal of Engineering Sciences, Assiut University*, 35(5), 1297-1311.
6. Nekhavhambe, D., 2019. Personal communication, 25th November
7. Papir, Y.S., Krieger, I.M., 1970. Rheological studies on dispersions of uniform colloidal spheres: II. Dispersions in nonaqueous media. *Journal of Colloid and Interface Science*, 34(1), 126-130.
8. Senapati, P.K, Panda, D, Parida, A., 2009. Predicting viscosity of limestone-water slurry. *Journal of Minerals and Materials Characterisation and Engineering*, 8(3), 203-211.
9. Thomas, A.D. 2019. Personal communication, 13th November.
10. Woods, M.E., Krieger, I M., 1970. Rheological studies on dispersions of uniform colloidal spheres I. Aqueous dispersions in steady shear flow. *Journal of Colloids and Interface Science*, 34(1), 91-99.
11. Vryzas Z., Kelessidis C.V., Nalbantian L., Zaspali, V., Gerogiorgis. D.I., Wubulikasimu, Y., 2017. Effect of temperature on the rheological properties of neat aqueous Wyoming sodium bentonite dispersions. *Applied Clay Science*, 136, pp. 26-36.
12. Yong, W, Aixiang, W., Zhuen, R., Hongjiang, W., Yiming, W., Fei, J., 2018. Temperature effects on rheological properties of fresh thickened copper tailings that contain cement, *Hindawi Journal of Chemistry*, Article ID 5082636.
13. Zengeni, B., Nekhavhambe, D., Goosen, P., 2019. Sensitivity of non-Newtonian slurry viscous properties to temperature. Proc. 19th Transport and Sedimentation (T&S) Conference, Cape Town, South Africa, 24-27 September, 285 – 292.

