

## A new rheological model for the flow curve of porcelain stoneware slips containing nepheline syenite

A. Salem<sup>a\*</sup>, S.H. Jazayeri<sup>b</sup>, E. Rastelli<sup>c</sup> and G. Timellini<sup>c</sup>

<sup>a</sup>Mineral Processing Research Center, Chemical Engineering Department, Sahand University of Technology, Tabriz, Iran

<sup>b</sup>Chemical Engineering Department, Iran University of Science and Technology, Tehran, Iran

<sup>c</sup>Centro Ceramico Bologna, Via Martelli 26, 40138 Bologna, Italy

Rheological properties of commercial porcelain stoneware slip and compositions modified by nepheline syenite were studied at different milling times. Firstly, the investigation was focused on the effects of the content of nepheline syenite and the particle size distribution on the rheological properties. For this purpose, flow curve data and yield stresses were obtained for the porcelain stoneware slips using a rotational rheometer. It was found that the viscosity and yield stress of porcelain stoneware compositions significantly depend on the above parameters and a minimum viscosity is achieved when 10 wt.% nepheline syenite is added to the mix. The optimum milling time was determined for the modified composition which resulted in the best rheological properties. Finally, a new rheological model was developed for these types of slips using an hyperbolic function. The new model satisfactorily correlates the shear stress to the shear rate for the slips at different milling times. The results showed that the proposed model predicts the behavior of the flow curves, yield stress and infinite viscosity for the porcelain stoneware slips both with and without the yield stress.

**Key words:** Porcelain stoneware slip, Rheology, Flow curve, Yield stress, Nepheline syenite.

### Introduction

According to the literature the main parts of porcelain stoneware tile manufacturing technology are: milling, mixing, spray drying, pressing and firing [1]. The milling and spray drying process is the most extensive with regard to the rheological properties. The experiments performed by Jazayeri *et al.* with an industrial spray dryer showed that the physical characteristics of ceramic slips were significantly affected the efficiency of this equipment [2]. A porcelain stoneware composition is a mix of natural materials which contains mainly kaolinite, illite, quartz and fluxing agents such as sodium and potassium feldspars. Sanchez *et al.* studied a wide range of porcelain stoneware components containing proportions of kaolin, quartz, potassium and sodium feldspars to evaluate the effect of each raw material individually [3]. They concluded that the nature of feldspar used in the starting composition did not affect the proportion of dissolving quartz or mullite. Nepheline syenite is another fluxing agent that has been used in ceramic product compositions such as electrical porcelain, sanitary ware and china table ware due to it reducing the firing temperature [4]. Nepheline syenite is actually a mix of about 55 wt.% albite, 25 wt.% potassium feldspar and

only about 20 wt.% nepheline [5]. Compared to pure feldspar, the advantages coming from the use of nepheline syenite are: (i) the content of sodium and potassium oxides is higher than 14 wt.%. (ii) the melting point is generally lower than sodium and potassium feldspars which always contains another phase such as quartz which shifts the melting point to higher temperatures [6]. The kinetic investigation carried out by Salem *et al.* about non-isothermal shrinkage of porcelain stoneware bodies using dilatometric analysis clearly showed that the presence of 5 wt.% nepheline syenite in the starting composition can accelerate the sintering rate remarkably [7].

On the basis of the observed behavior between shear rate and shear stress, the fluids are classified to Newtonian and non-Newtonian systems [8]. According to a rheological text, Newtonian slips are defined as those exhibiting a direct proportionality relationship between shear stress and shear rate, whereas for non-Newtonian slips, the relationship between shear stress and shear rate is not linear [9].

The behavior of porcelain stoneware slip is affected remarkably by its composition. Rastelli *et al.* studied the rheological properties of a porcelain stoneware slip to find the suitable amount of alternative clay that can be used to substitute partially in a porcelain stoneware composition without negatively affecting the rheology of the slip [10]. They reported that although the presence of magnesium causes rheological problems but an optimum content of clay containing magnesium was found without significantly changing its viscosity, yield stress and thixotropy. Ceramic

\*Corresponding author:  
Tel : +98 412 345 9159  
Fax: +98 412 344 4355  
E-mail: salem@sut.ac.ir

slips are generally non-Newtonian systems with a variation in viscosity. To classify the behavior of ceramic slips Gutierrez *et al.* reconsidered the plastic and pseudoplastic behavior and presented methods that can be used in determining the flow curve and yield stress [9]. The authors reported different rheological models to mathematically describe the flow curve behavior.

It is quite useful to characterize the rheological behavior of ceramic slips at different shear rates. In the ceramic suspensions, a structural interpretation of the flow is interesting because, useful information can be obtained on the degree of aggregation of a dispersed phase and its modification induced by changes of shear flow conditions. The structure of concentrated suspensions undergo modifications under shear variations connected both with kinetics of particles and break down of aggregates [11]. Albertazzi and Rastelli reported a method for evaluating of thixotropy and yield stress of industrial ceramic slips using a torque-type rheometer [12]. They investigated the thixotropy of slips by performing rheological tests in an "on-off" cycle and constant shear rate.

The yield stress is the lowest value of stress necessary to move the suspension [8]. The viscosity as well as yield stress depends on the suspension structure, so it is important to evaluate them which are directly correlated with structural formation. The yield stress is another reason for the presence of a structure in suspension. Rheological characterization becomes so essential in quality control of industrial products in order to obtain a homogeneous and stable suspension to have densified products after firing. Walker and Reed studied the effect of rheological properties (viscosity and yield stress) of alumina slurries on the quality of spray dried granules [13]. They showed that the morphology of granules is effectively influenced by the rheological properties of the slurry.

Most equations which describe the relationship between the shear stress and shear rate are empirical. There are linear models in which the shear stress is a linear function of shear rate as well as non-linear models. The power law equation is the most used empirical model for slips without a yield stress [14]. The Herschel-Bulkley equation exhibits a yield stress in addition to the power law term. This model which is of a power law type depends on three parameters as follows:

$$\tau = \tau_0 + k\dot{\gamma}^n \tag{1}$$

where  $\tau_0$  is the yield stress of the slip and  $k$  and  $n$  are constants of the model. Another empirical model showing approximately Newtonian behavior at a higher shear rate is Casson's equation:

$$\tau^n = \tau_0^n + (\eta_\infty \dot{\gamma})^n \tag{2}$$

where  $\eta_\infty$  is the viscosity at a high shear rate in which all of the suspension structure was destroyed. Besides these famous models, there are many other empirical formulae which describe the flow curve behavior for limited range [15].

In this study, a set of experimental characterizations of porcelain stoneware slips has been carried out in order to examine the relationships between the content of nepheline syenite and the rheological characteristics of slips at different milling times. For this purpose, a new rheological model was developed and fitted for all the data sets. The objective of the new rheological model was to evaluate its applicability for slips with or without a yield stress.

### New Rheological Model

A new model, representing the flow curve behavior of porcelain stoneware slips, was derived with a view to obtaining an expression, relating the shear stress to shear rate. The mathematical equation which relates the original coordinates for the hyperbolic shape shown in Fig. 1 has the following form:

$$\frac{x^2}{A^2} - \frac{y^2}{B^2} = 1 \tag{3}$$

where  $A$  and  $B$  are the constants of the hyperbolic equation. The relationship between  $A$  and  $B$  can be described by:

$$\lambda = \frac{C}{A} \quad A^2 + B^2 = C^2 \tag{4}$$

where  $\lambda$  is a constant ratio. By transforming the axes to  $x'$  and  $y'$ , we can consider the following relation between the new and old coordinates:

$$x' = x - C \quad y' = y \tag{5}$$

By substituting equation (5) into the hyperbolic model, Eq. (3), the following relationship can be found between  $x'$  and  $y'$ :

$$\left(\frac{x' + \lambda \cdot A}{A}\right)^2 - \left(\frac{y'}{B}\right)^2 = 1 \tag{6}$$

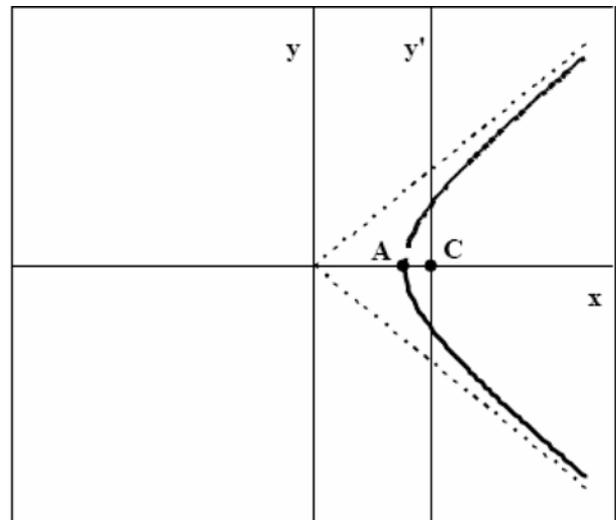


Fig. 1. The hyperbolic function used in the rheological modeling.

Consider  $x' = \dot{\gamma}$  and  $y' = \tau$  therefore, the following equation was obtained to relate the shear stress to shear rate:

$$\left(\frac{\dot{\gamma} + \lambda \cdot A}{A}\right)^2 - \left(\frac{\tau}{B}\right)^2 = 1 \quad (7)$$

The generalized model to cover all range of power can be represented as:

$$\left(\frac{\dot{\gamma} + \lambda \cdot A}{A}\right)^m - \left(\frac{\tau}{B}\right)^m = 1 \quad (8)$$

and

$$\tau = B \left[ \left( \frac{\dot{\gamma} + \lambda \cdot A}{A} \right)^m - 1 \right]^{\frac{1}{m}} \quad (9)$$

where  $m$  is a power constant of the general equation. The new model which depends on four parameters  $A$ ,  $B$ ,  $\lambda$  and  $m$  can be used to match the flow curve data by nonlinear regression techniques. By substituting  $\dot{\gamma} \rightarrow 0$  the value of the yield stress is obtained as follows:

$$\tau_0 = B(\lambda^m - 1)^{\frac{1}{m}} \quad (10)$$

It is interesting to note that the value of  $B \neq 0$  in all cases that  $\tau > \tau_0$ . The value of the yield stress will be equal to zero when the value of  $\lambda$  is considered equal to 1. Many useful relations are included in the above model as special cases. It can be reduced to a Bingham model when  $m = 1$ . The resulting equation is:

$$\tau = \frac{B}{A} \dot{\gamma} + B(\lambda - 1) \quad (11)$$

It can be also used to describe Newtonian behavior as following equation, when  $m = 1$  and  $\lambda = 1$ :

$$\tau = \frac{B}{A} \dot{\gamma} \quad (12)$$

The model contains the index  $m$  which allows covering a wide range of operating conditions. It is possible to calculate the values of the viscosity as a function of the shear stress using equation (9) and according to the following functions:

$$\frac{1}{A} \left( \frac{\dot{\gamma} + \lambda \cdot A}{A} \right)^{m-1} - \frac{1}{B} \left( \frac{\tau}{B} \right)^{m-1} \frac{d\tau}{d\dot{\gamma}} = 0 \quad (13)$$

$$\eta = \frac{d\tau}{d\dot{\gamma}} \quad (14)$$

$$\eta = \frac{B}{A} \left[ \left( \frac{B}{\tau} \right)^m + 1 \right]^{\frac{m-1}{m}} \quad (15)$$

Equation (15) shows that the value of the viscosity

**Table 1.** The composition of the reference mix

materials	clays		feldspars		deflocculant
	Clay 1	Clay 2	Feldspar 1	Feldspar 2	
weighy Percentage	9.92	38.25	15.49	35.38	0.96

reaches a constant value when  $\tau \rightarrow \infty$ . The value of the viscosity at a high shear rate or shear stress (infinite viscosity,  $\eta_\infty$ ) in which all of the slip structure was destroyed, can be obtained from the following ratio:

$$\eta_\infty = \frac{B}{A} \quad (16)$$

## Materials and Methods

An industrial porcelain stoneware composition was used as reference mix (Table 1). Also, three modified porcelain stoneware compositions were prepared by replacing 5.0, 10.0 and 15.5 wt.% nepheline syenite with K- feldspar in the reference mix. The chemical and mineralogical analyses were performed on raw materials to characterize the effect of nepheline syenite because rheological properties are strongly influenced by chemical and diffractometric aspects. Chemical analysis was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES model 3200 XL Perkin Elmer). The mineralogical compositions of the raw materials were determined by Rietveld method [16-17]. The data collection was carried out using a Philips PW 1710 instrument. The chemical and mineralogical analyses are reported in Tables 2 and 3 where the porcelain stoneware compositions are compared.

In order to evaluate the effect of the addition of nepheline syenite on the rheological properties, both the reference body mix and modified composition slips were prepared by dispersing the raw materials in distilled water, 67 wt.% solid and 0.96wt.% deflocculant, and finally milled for 8, 12 and 16 hours in a ceramic jar mill. Romagnoli and Andreola presented an interesting systematic approach to obtain the optimum mixing ratio of deflocculants for slips containing clay minerals [18]. The particle size distributions of slips were determined by laser light diffraction (Malvern Mastersizer 2000).

To understand the effects of the content of nepheline syenite and milling time on the rheological properties of suspensions, the flow curves and yield stress tests were performed immediately using a rotational rheometer (Haake R550) to evaluate the structural differences in porcelain stoneware slips. Before the measurements all the slips were subjected to pre-shearing at  $1000 \text{ s}^{-1}$  for 60 s with a rest time of 180 s in order to have the same conditions for all the slips. The rheological characterizations performed were: (i) a flow curve in control shear rate mode, from 0 to  $1000 \text{ s}^{-1}$  for 180 s, to evaluate the shear behavior and viscosity. As a wet milling process is the most common ceramic grinding process, a low viscosity is important because it allows draining the

**Table 2.** The chemical analysis of the raw materials and porcelain stoneware compositions

oxides (%)	raw materials					compositions			
	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline syenite	STD	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
SiO <sub>2</sub>	78.38	66.75	72.35	70.11	60.14	70.07	69.47	68.87	68.13
Al <sub>2</sub> O <sub>3</sub>	15.41	21.63	13.50	17.82	23.50	18.39	18.89	19.37	19.96
K <sub>2</sub> O	0.31	1.33	6.58	0.59	0.59	1.78	1.71	1.63	1.54
Na <sub>2</sub> O	0.16	0.22	0.21	8.97	5.00	3.34	3.85	4.36	4.93
CaO	0.06	0.33	2.53	1.32	10.40	1.00	0.89	0.79	0.67
MgO	0.05	0.52	0.17	0.19	0.40	0.30	0.29	0.29	0.28
ZrO <sub>2</sub>	0.00	0.07	0.00	0.00	0.03	0.03	0.03	0.03	0.03
TiO <sub>2</sub>	0.23	1.24	0.00	0.06	0.00	0.52	0.52	0.52	0.52
Fe <sub>2</sub> O <sub>3</sub>	0.12	0.99	1.02	0.30	0.00	0.66	0.61	0.57	0.52
SO <sub>3</sub>	0.00	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00
L.O.I	5.41	6.62	3.60	0.64	0.55	3.89	3.74	3.59	3.41

**Table 3.** The mineralogical analysis of the raw materials and porcelain stoneware compositions

minerals (%)	raw materials					compositions			
	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline syenite	STD	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
quartz	60.0	38.0	38.0	13.0	0.0	31.3	29.4	27.4	25.3
kaolinite	39.0	40.0	0.0	0.0	0.0	19.4	19.4	19.4	19.4
illite	0.0	13.0	6.0	0.0	0.0	6.0	5.7	5.4	5.0
smectite	0.0	2.0	0.0	0.0	0.0	0.8	0.8	0.8	0.8
albite	0.0	2.0	2.0	76.0	56.0	28.2	30.9	33.6	36.7
orthoclase	0.0	0.0	39.0	4.0	22.0	7.5	6.7	5.8	4.9
anorthite	0.0	2.0	12.0	6.0	0.0	4.8	4.2	3.6	2.9
nepheline	0.0	0.0	0.0	0.0	22.0	0.0	1.1	2.2	3.4
impurity	1.0	3.0	3.0	1.0	0.0	2.1	1.9	1.8	1.6

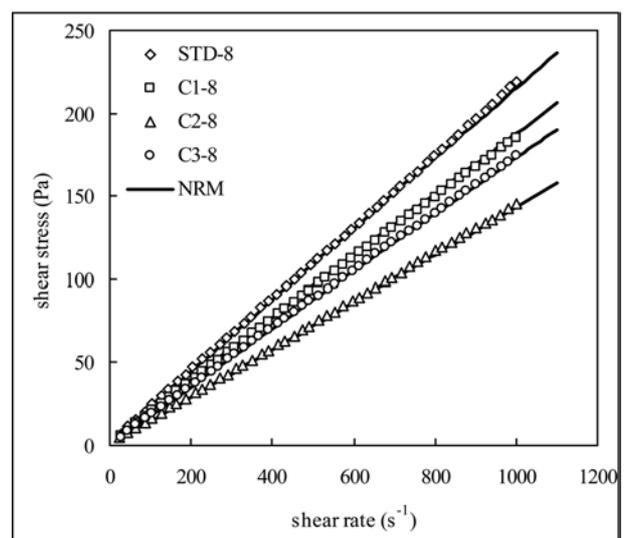
slip from the drum ball mill, easily. (ii) The yield stress was evaluated by performing a flow curve in control shear stress mode, 0.1-200 Pa for 300 s. In this case it is possible to obtain an experimental value of the yield stress. The yield stress was measured by evaluating the deformation curve as a function of the applied shear stress. The slope change of this experimental curve represents the yield stress. To find this region the experimental data were fitted by a power law equation as follows:

$$\gamma = a\tau^b \quad (17)$$

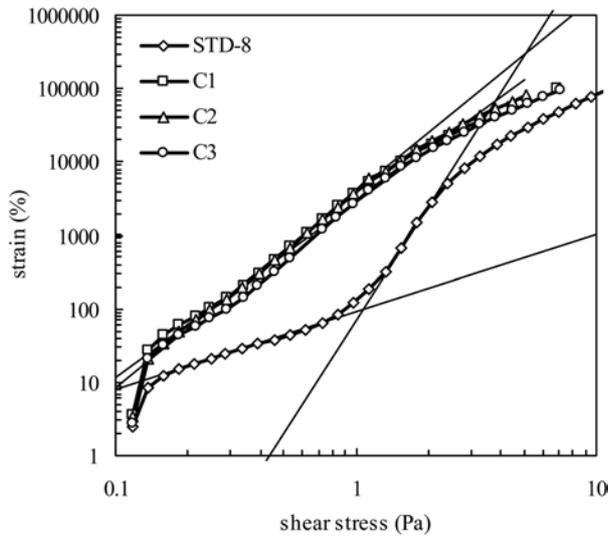
(iii) The new rheological model (NRM) was fitted for each set of experimental data to calculate the rheological parameters.

## Results and Discussion

Nepheline syenite decreases the viscosity at low and high shear rates as is shown in Fig. 2. The yield stress, Fig. 3, decreases in the presence of nepheline syenite and the best concentration seems to be 10 wt.% as the shear behavior becomes Newtonian and the yield stress

**Fig. 2.** The flow curves of reference and modified porcelain stoneware slips milled for 8 hours.

reaches zero as reported in Table 4 where the rheological properties are presented. In particular, the slip containing



**Fig. 3.** The yield stress of reference and modified porcelain stoneware slips milled for 8 hours.

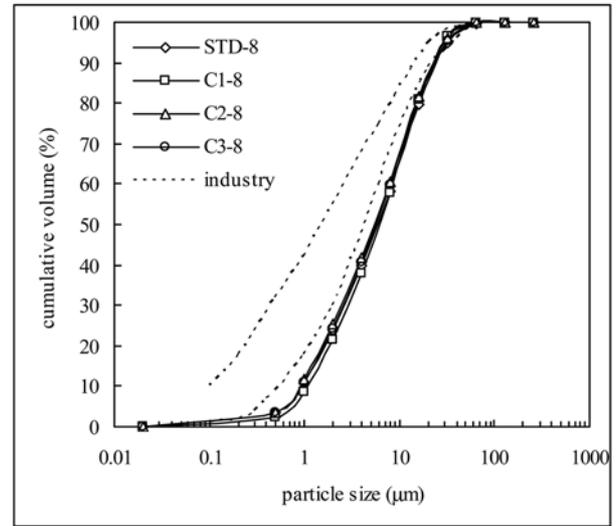
**Table 4.** The best rheological model for porcelain stoneware slip at 25 °C

composition	milling time (h)	particle size distribution ( $\mu\text{m}$ )		
		$d_{90}$	$d_{50}$	$d_{10}$
STD	8	48.14	11.93	1.89
	16	28.01	8.51	1.87
$C_1$	8	44.8	12.5	2.2
	8	44.48	10.98	1.79
$C_2$	12	36.94	9.55	1.68
	16	30.57	8.27	1.63
$C_3$	8	46.4	11.4	1.9

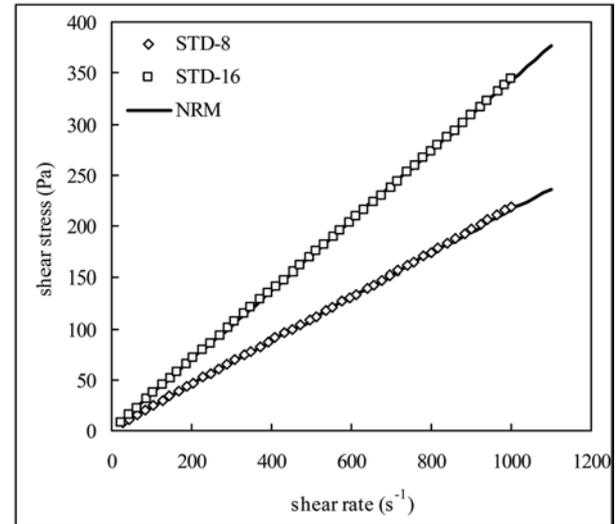
10 wt.% nepheline syenite exhibits the best rheological behavior, a low viscosity and yield stress. It seems that 10 wt.% is the best concentration of nepheline syenite in order to have a good rheological stabilization. The improvement of the rheological properties by the addition of nepheline syenite is probably due to an increment in the amount of alkali ions. By substituting nepheline syenite into the porcelain stoneware composition, the content of calcium decreases and the sodium content increases. Calcium in particular tends to destabilize the suspensions by increasing the forces of attraction and consequently it increases the yield stress and viscosity [19].

The particle size distributions, Fig. 4, are very close to those of industrial bodies, confirming that the presence of nepheline syenite does not significantly affect the grindability of porcelain stoneware composition. According to Table 4 data the particle size of modified compositions is less than that for the reference mix. This phenomena is due to a decrease in the viscosity at a low shear rate.

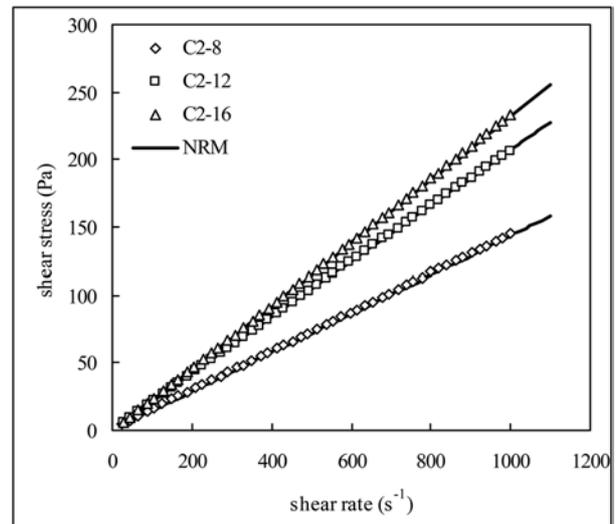
As reported in Table 4, the particle size of STD and  $C_2$  compositions decrease as the milling time rises. The effects of milling time on the flow curves of slips are shown in Figs. 5 and 6. As expected, decreasing the



**Fig. 4.** Particle size distribution of porcelain stoneware slips milled for 8 hours.



**Fig. 5.** The flow curves of STD slips prepared at different milling times.



**Fig. 6.** The flow curves of  $C_2$  slips prepared at different milling times.

particle size causes an increase in both viscosity and yield stress (Figs. 7 and 8) of slips because particle-particle contacts are more frequent. Between 12 and 16 hours the rheological behavior did not change significantly for the slip containing 10 wt.% nepheline syenite. The viscosity of the C<sub>2</sub> slip increases with an increase in the milling time but the values are not higher than those for the reference composition.

The most important differences were found at lower shear rates. A combination of data obtained by controlled shear rate and shear stress measurements are reported in Figs. 9, 10 and 11 to highlight the region at low shear rate. It is clear that the viscosity is very sensitive to the shear stress for these types of slips especially at low shear stress, reaching a constant value at a high shear stress. In this region the samples containing nepheline syenite show a lower viscosity than the reference sample, although the

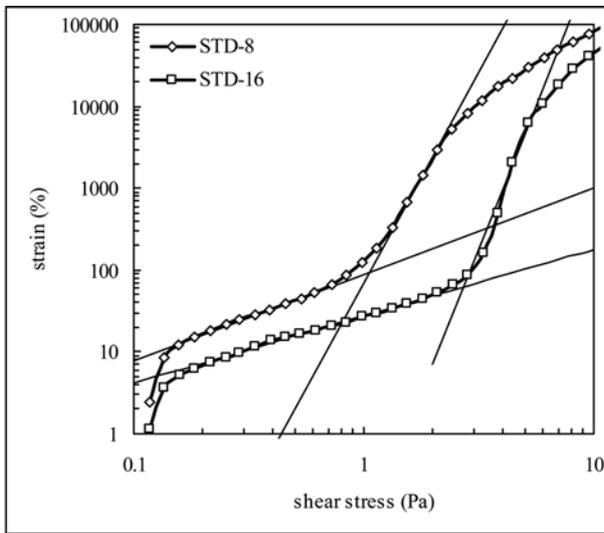


Fig. 7. Control stress data to evaluate the yield stress of the STD slip prepared at different milling times.

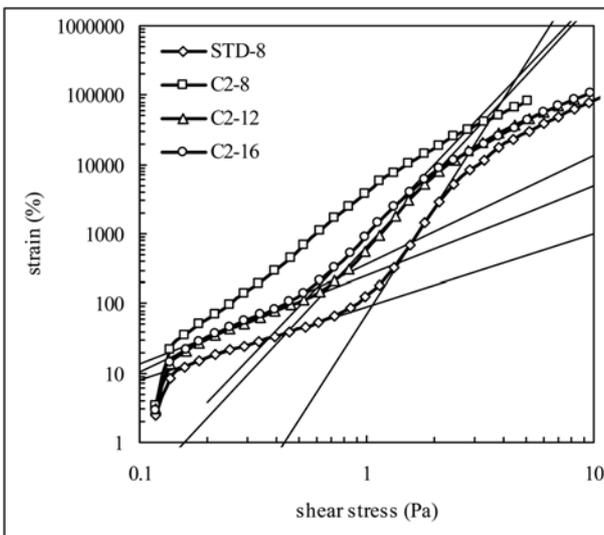


Fig. 8. Control stress data to evaluate the yield stress of the C<sub>2</sub> slip prepared at different milling times.

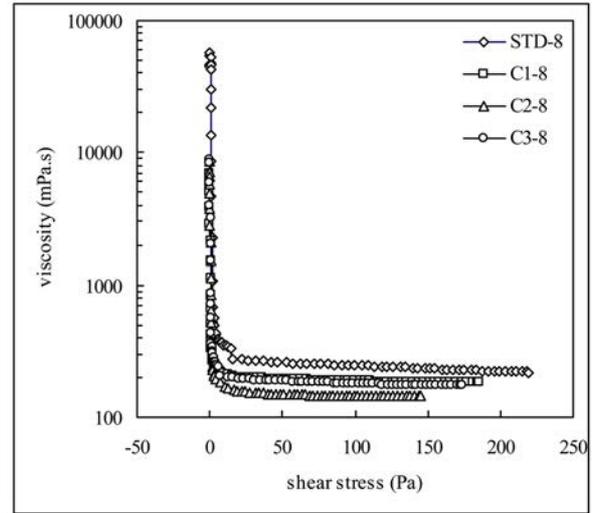


Fig. 9. The variation of viscosity with shear stress for porcelain stoneware slips.

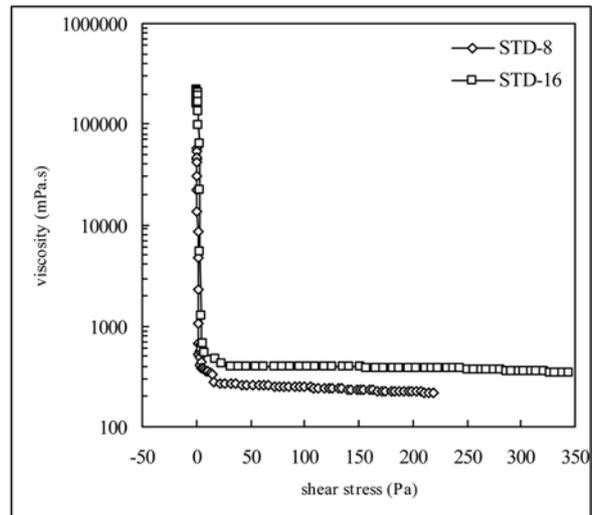


Fig. 10. The variation of viscosity with shear stress for the STD slip prepared at different milling times.

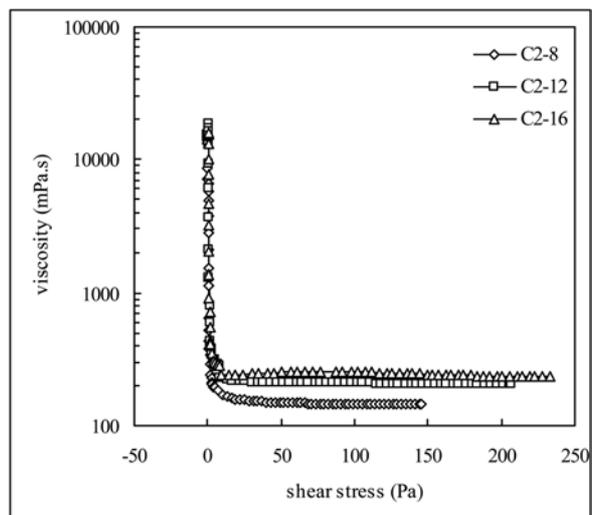


Fig. 11. The variation of viscosity with shear stress for the C<sub>2</sub> slip prepared at different milling times.

milling time increases. The milling time should also not exceed 12 hours, a time at which the slip still shows a low structural formation therefore, the rheological behavior is better than that for reference mix slip because both the viscosity and yield stress decrease. The presence of nepheline syenite also has some advantages. It is possible to have finer particle size distributions without having an increase in viscosity and yield stress.

The experimental data obtained for a variety of porcelain stoneware slips containing different contents of nepheline syenite were used to evaluate the new rheological model (NRM). All of the rheological data were curve fitted to the proposed model, Eq. (9), which describes the relationship between the shear stress and shear rate for porcelain stoneware slips. The parameters A, B,  $\lambda$ , m and  $\tau_0$  were estimated from the experimental data using non linear regression analysis (Matlab software version 7.3). The behavior of the proposed rheological model is shown in Figs. 2, 5 and 6 for different porcelain stoneware compositions at different milling times. The model in its general form provides a finite equation for the prediction of the shear stress as function of shear rate for all porcelain stoneware slips with and without a yield stress. For these porcelain stoneware slips it was found that the values of the parameters A and B increase with an increase in the content of nepheline syenite, reaching a maximum value (Table 5). The optimum rheological properties were obtained with 10 wt.% nepheline syenite used in the porcelain stoneware composition. It is interesting to note that the values of yield stress obtained by the new rheological

model are very close to those obtained experimentally according to data in Table 6.

The data in Table 6 give a comparison between the predicted and experimental viscosity of porcelain stoneware slips at high shear rates. It is clear that the infinitive viscosities are near to the values predicted by the proposed rheological model.

## Conclusions

Porcelain stoneware slips were prepared to study the effects of nepheline syenite and milling time on rheological properties. The shear stress-shear rate data, viscosity and yield stress were determined using a rotational rheometer. A new rheological model was presented and the results are summarized below.

It was found that the value of the viscosity and yield stress of porcelain stoneware slips containing nepheline syenite are significantly lower than the slips prepared without it. Both the viscosity and yield stress depend greatly on the milling time compared to the reference slip. A low viscosity and yield stress were obtained when 10 wt.% nepheline syenite was added to the body composition even at higher milling times.

A new rheological model was proposed to fit the shear stress-shear rate data for porcelain stoneware slips with or without yield stress. The proposed model shows a correlation of the flow curve data for a variety of porcelain stoneware slips. The model predicted the values of the yield stress near to those values obtained experimentally. The validity

**Table 5.** The parameters of the new rheological model

composition	milling time (h)	A (s <sup>-1</sup> )	B (Pa)	$\lambda-1$	m	R <sup>2*</sup>
STD	8	5055	1045.5	$9.5 \times 10^{-4}$	1.013	0.999
	16	14450	5219.9	$6.0 \times 10^{-4}$	0.9835	0.999
C <sub>1</sub>	8	31150	5148.6	$7.2 \times 10^{-5}$	1.029	1.000
	8	139400	19980.0	0.0	1.000	1.000
C <sub>2</sub>	12	8228	1646.0	$3.8 \times 10^{-4}$	1.016	1.000
	16	5297	1291.2	$5.5 \times 10^{-4}$	1.010	1.000
C <sub>3</sub>	8	65090	10390.0	0.0	0.9807	1.000

\*R<sup>2</sup>: least square regression coefficient

**Table 6.** The experimental and calculated values of the yield stress and infinitive viscosity values for porcelain stoneware slips prepared at different milling times

composition	milling time (h)	$\tau_{0,exp.}$ (Pa)	$\tau_{0,cal.}$ (Pa)	$\eta_{\infty,exp.}$ (mPa.s)	$\eta_{\infty,cal.}$ (mPa.s)
STD	8	1.06	1.10	219	207
	16	2.72	2.72	344	361
C <sub>1</sub>	8	0.33	0.50	185	165
	8	0.00	0.00	145	143
C <sub>2</sub>	12	0.65	0.68	206	200
	16	0.61	0.60	233	244
C <sub>3</sub>	8	0.00	0.00	174	160

of the model to describe the values of infinitive viscosity was substantiated. The model can also be used for slips that are prepared with other materials.

### **Acknowledgments**

We would like to thank Iranian Industries and Mines Ministry for supporting this investigation. We would also like to thank Mr. S. Degli Esposti and Mr. D. Naldi for their contributions during research.

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