Influence of nepheline syenite and milling time on the rheological properties of a porcelain stoneware tile slip

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The rheological properties of porcelain stoneware tile slips were investigated using a rotational rheometer. The first step in the study was to evaluate the rheological behaviour of a reference slip at different particle size distributions to determine the optimum conditions at which to carry out the investigation of the influence of nepheline syenite in the mix. In the second step part of the K-feldspar in the reference mix was replaced with nepheline syenite such that the mix composition contained 10 % nepheline syenite. The flow curve, yield stress and thixotropy of the slips were evaluated at different milling times in order to study the effect of particle size on the rheological behaviour. The milling times for the reference mix and for the mix with nepheline syenite which resulted in the best rheological parameters were found.

Keywords: Porcelain Stoneware Tile Slip; Rheology; Yield Stress; Thixotropy; Nepheline Syenite

Influencia de nefelina sienita y del tiempo de molienda en las propiedades reológicas de una barbotina de porcelana gres

Se han investigado las propiedades reológicas de barbotinas de porcelana dura para pavimentos usando un reómetro rotacional. El primer paso del estudio fue evaluar el comportamiento reológico de una barbotina de referencia con diferentes distribuciones de tamaño de partícula con el fin de determinar las condiciones óptimas bajo las cuales estudiar la influencia de nefelina sienita en la mezcla. En la segunda etapa, parte del feldespato potásico de la mezcla de referencia se substituyó por nefelina sienita de forma que la composición de la mezcla tuviera un 10% de nefelina sienita. Se evaluaron las curvas de flujo, los puntos de fluidez y la tixotropía de las barbotinas tras diferentes tiempos de molienda con el fin de estudiar el efecto del tamaño de partícula en el comportamiento reológico. Se determinaron los tiempos de molienda en los que se alcanzaban los mejores parámetros reológicos para la mezcla de referencia y la de nefelina sienita.

Palabras clave: barbotinas de porcelana gres, reología, punto de fluidez, tixotropía, nefelina sienita.

1. INTRODUCTION

The rheological properties of the slips used in the manufacture of porcelain stoneware tile are of particular importance, especially in regard to the milling, mixing, pumping and spray drying processes (1,2). Many parameters affect the rheological properties of ceramic slips. Some of the most important parameters are the chemical and mineralogical properties of the raw materials, density of the slip, types and contents of deflocculants, pH and ions soluble in water, and particle size distribution (3,4,5).

Obtaining a better understanding of the rheology of porcelain stoneware tile slips is important in terms of being able to control the manufacturing process (6). The success of the firing process depends considerably on the type of fluxes and particle size distribution of the mix powders. Decreasing the particle size of a slip makes it possible to use a lower firing temperature, but also causes changes in the rheological properties of the slip. Indeed, the viscosity, yield stress and thixotropy of the slip increase with decreasing particle size. Therefore, it is necessary to optimize the particle size distribution of the slip solids so as to obtain the best possible rheological properties (7,8).

The most common appropriate models describing the variation in shear stress with shear rate for such complex systems as clay slips are summarized in Table I. There are

TABLE I: TYPICAL RHEOLOGICAL MODELS USED TO FIT THE SLIP BEHAVIOR

model		equation
linear	Newton	$\tau = \eta \dot{\gamma}$
	Bingham	$\tau = \tau_0 + \eta \dot{\gamma}$
non-linear	Casson	$\tau^m = \tau_0^m + \left(\eta_\infty \dot{\gamma} \right)^m$
	Ostwald – de-Waele	$\tau = \kappa \left(\dot{\gamma} \right)^n$
	Herschel - Bulkley	$\tau = \tau_0 + \kappa \left(\dot{\gamma} \right)^n$

τ = Stress, τ_0 = Yield stress, $\dot{\gamma}$ = Shear Rate, η =Viscosity, m and n = Fluidity Index, κ = Consistency Factor

linear models in which the stress is a linear function of the shear rate as well as non-linear models (9,10).

In this work an industrial porcelain stoneware tile mix was used as a reference mix and the rheological properties of this slip were investigated at different milling times and consequently at different particle size distributions. In a second step part of the work, potassium feldspar was replaced by an equal amount of nepheline syenite, such that the nepheline syenite content in the mix was 10 %. Using this mix containing nepheline syenite, slips were prepared at different milling times and the resulting rheological

properties were compared with those of the slip prepared from the reference mix.

The mineral nepheline syenite is a solid solution of the compounds $\text{Na}(\text{AlSi}_3\text{O}_8)$ and $\text{K}(\text{AlSi}_3\text{O}_8)$. It is one of feldspathoid at lowest Si content, used in the sanitaryware production, as it increases the whiteness of the products and in the sintering process of electrical porcelain and chinaware bodies (12, 13). Due to its greater fluxing activity in comparison with potassium feldspar, this feldspathoid is very appreciable in order to reduce the firing temperature and to increase the alkali level in glass phase. In this work the nepheline syenite is used in a porcelain stoneware tile slip by substituting the potassium feldspar to reduce the soaking time.

2. MATERIALS AND METHODS

A porcelain stoneware tile slip was prepared using industrial raw materials and a typical mix composition. In order to evaluate the effect of milling time and nepheline syenite as a flux, different samples were prepared at different milling times using both a reference mix (a typical industrial mix composition) and a mix in which part of the K-feldspar in the reference mix was replaced with nepheline syenite to give a mix with a 10 % nepheline syenite content. Some different concentrations of nepheline were rheologically tested and the 10% was chosen as the best amount. The mix compositions are reported in Table II. The chemical and mineralogical compositions of the raw materials used in the mixes are reported in Tables III and IV, respectively. Inductively coupled plasma optical emission spectrometry ICP-OES (Perkin Elmer Model 3200XL) was used for the chemical analyses and the mineralogical analyses were carried out using X-ray powder diffraction (Philips diffractometer Model PW 1927).

After obtaining slips, particle size distribution was performed by laser light diffraction (Malvern Mastersizer 2000) and slips were dried at 110°C and then milled in a laboratory milling equipment to obtain a particle size less than 125 μm . The powders obtained are wetted (about 6,4 kg water/ kg dry composition) and sieved at 800 μm to avoid agglomerates.

A series of test pieces in the shape of disks (40 mm diameter and 4 mm thick) were prepared by pressing at a forming pressure of 52 MPa. The test pieces were fired at 1260°C and different soaking times in an electrical gradient kiln (Ceramic Instrument Model 86V), in table V some sintering data are reported.

2.1 Rheological Measurements

The slips were prepared using a laboratory jar mill (about 2 l capacity) with three different milling times (8, 12 and 16 h). The water content in all the slips was 33 wt%.

The rheological measurements were carried out at 25 °C using a RS50 Haake rheometer (CS-CR) equipped with a plate-plate sensor. Before testing, all samples were subjected to pre-shearing at 1000 s^{-1} for 60 s with a rest for 180 s in order to have the same conditions for all the samples. The flow behaviour was obtained in the control shear rate mode, from 0 to 1000 s^{-1} in 180 s and from 1000 to 0 s^{-1} in 180 s, to evaluate the shear behaviour. The rheological model chosen to fit the experimental points was that of Casson's law (see table1).

TABLE II: COMPOSITION OF THE REFERENCE MIX (STD) AND THE MIX CONTAINING NEPHELINE SYENITE (C2)

Raw Materials	Mix Composition	
	(%)	
STD		C2
clay 1	9.92	9.92
clay 2	38.25	38.25
K-feldspar	15.49	5.49
Na-feldspar	35.37	35.37
nepheline syenite	0.00	10.00
deflocculant	0.96	0.96

TABLE III: CHEMICAL ANALYSIS OF THE RAW MATERIALS USED TO PREPARE THE MIXES

Oxide (%)	Raw Materials				
	clay 1	clay 2	K-feldspar	Na-feldspar	nepheline syenite
SiO_2	78.38	66.75	79.85	70.48	60.14
Al_2O_3	15.41	21.93	10.60	18.27	23.50
K_2O	0.31	1.33	4.38	0.57	5.00
Na_2O	0.16	0.22	3.64	9.07	10.40
CaO	0.06	0.33	0.41	0.74	0.40
MgO	0.05	0.52	0.14	0.10	0.03
ZrO_2	0.00	0.07	0.00	0.00	0.00
TiO_2	0.23	1.24	0.03	0.24	0.00
Fe_2O_3	0.12	0.99	0.45	0.13	0.09
SO_3	0.00	0.00	0.00	0.00	0.00
L.O.I.	5.41	6.62	0.50	0.38	0.55

TABLE IV: MINERALOGICAL ANALYSIS OF THE RAW MATERIALS USED TO PREPARE THE MIXES

Mineral	Raw Materials				
	clay 1	clay 2	K-feldspar	Na-feldspar	nepheline syenite
quartz	*	*	*	*	
illite		*			
kaolinite	*	*			
Na-feldspar	*	*	*	*	*
K-feldspar	*		*	*	*
Ca-feldspar	*	*	*	*	
nepheline					*

TABLE V: SINTERING PARAMETERS FOR THE REFERENCE MIX (STD) AND FOR THE NEPHELINE ADDED MIX

STD – 8h			C2 – 8h		
Soaking time (min)	Shrinkage (%)	Water absorption (%)	Soaking time (min)	Shrinkage (%)	Water absorption (%)
50	5.4	2.23	25	6.4	0.34
70	5.9	1.00	30	6.4	0.04
90	6.0	0.36	40	6.2	0.00
100	6.2	0.02	50	5.8	0.00

(C2) AT THE SAME MILLING TIME (8h) AND AT THE SAME TEMPERATURE (1260°C)

This model gave the best fit with the data for the reference sample. To have comparable data, the results for all the samples were fitted using this model. The yield stress was evaluated by determining the flow curve in the controlled shear stress mode, from 0.1 to 200 Pa for 180 s. The parameter of yield stress used in the Casson's model equation was the experimental one as it was determined directly. The yield stress is measured by evaluating the curve of deformation in function of the applied stress. The slope changing of this experimental curve represents the region of the yield stress. To find this region the experimental data of the curve were fitted by the power law equation:

$$y = a x^b \quad [1]$$

The yield stress value obtained is put in the Casson law so that the model is calculated on the control rate curve data by using the experimental value of yield stress.

As the time dependency is correlated with floc formation and breakdown during time under shear, it was evaluated by on-off cycles at a constant shear rate (shear rate 0 s^{-1} for 100-200-250 s and shear rate 50 s^{-1} for 100-150-200 s), in order to measure the build-up effects by the difference between $\tau_{\max}$ and τ_{eq} , where $\tau_{\max}$ and τ_{eq} are the maximum and equilibrium stress, respectively. These parameters represent the structural level of a slip: $\tau_{\max}$ is the first value of stress after the rest necessary to build up the gel structure and τ_{eq} is the value where the gel structure is completely destroyed. After this value the slip flows (10).

3. RESULTS AND DISCUSSION

3.1 Sintering results

The sintering results (see table V) confirm the good results of nepheline as flux agent. In this table it is possible to see that at the same conditions of temperature and milling time (8h) it is necessary a very lower soaking time in the case of C2 sample with nepheline than in the case of sample STD, to reach the same water absorption (0.00%). The soaking time to reach this absorption is 100min for the reference, 40-50min for the sample with nepheline. Only the presence of nepheline at the same particle size of reference can be helpful to reduce the soaking time. As it is possible to obtain slip with the nepheline at lower particle size than the reference with the same rheological behavior of the reference one, some experiments at finer particle size (milling time 12h and 16h) with nepheline are performing now as a reduction of soaking time is expected.

3.2 Rheological results

Reported in Table VI are the particle size distributions and the rheological properties of the slips after different milling times. As expected, decreasing particle size causes an increase in both the viscosity and yield stress of the slip because particle-particle contacts are more frequent. Between 12 and 16 h the rheological parameters did not change significantly for the slips containing nepheline syenite.

The effects of milling time on the rheological properties of the slips are shown in Figure 1 where the flow curves in the control rate mode are reported. In Figure 2 the slips with

TABLE VI: PARTICLE SIZE DISTRIBUTION AND RHEOLOGICAL PROPERTIES (AT 25°C) AFTER DIFFERENT MILLING TIMES OF THE SLIPS PREPARED FROM THE REFERENCE MIX (STD) AND THE MIX CONTAINING NEPHELINE SYENITE (C2).

Mix	Milling time (h)	Particle size (μm)		pH	Measured yield stress (γ/τ curve) (Pa)	Casson's parameter $m = 0.82$ η_s
		d50	d90			
STD	8	11.9	48.1	10.25	1.06	0.21
	16	8.5	28.0	10.10	2.72	0.33
C2	8	11.0	44.5	10.21	0.00	0.15
	12	9.6	36.9	10.35	0.65	0.21
	16	8.3	30.6	10.24	0.61	0.23

Figure1: Flow curves obtained in the control rate mode for the reference mix (STD).

Figure 2: Flow curves obtained in the control rate mode at different milling times for the mix containing nepheline syenite (C2) and the reference mix (STD).

nepheline at different milling time are reported. The viscosity of the slips increases with increasing milling time but the values are not higher than those for the reference slip. With the reference slip, Casson's equation gave the best fit for the flow curve data and thus this equation was also used for the slips prepared from the mix containing nepheline syenite. The slip parameters are reported in Table V where it can be seen that the viscosity increases with increasing milling time.

The most important differences are found at low values of the shear rate. A combination of the data obtained by

controlled shear rate and shear stress measurements is reported in Figure 3 to highlight the region at low shear rate. In this region the samples containing nepheline syenite show lower viscosity than the reference samples, although the milling time increases.

The yield stress is reported in Figure 4. The yield stress increases with increasing milling time. The parameter which is influenced most by the milling time is the time dependency, reported in Figures 5-6 where the build-up phenomena are reported in function of the time of measurements. So that it is possible to evaluate the thixotropic behaviour of the material during the time. Indeed, at 16h milling time the sample with nepheline syenite has the highest thixotropy even though the presence of nepheline syenite in the mix tends to reduce the time dependency. The increase in surface area due to the higher milling time causes an increase in sodium and potassium ions in the solution (11). These ions modify both the surface charge of the particles and the interactions between particles in the slip. At high values of milling time the slip becomes a colloidal system so that there is a greater tendency to create a gel like structure. The tendency to create a structure becomes more important when the particle size of the slip reaches this range with the consequent increase in thixotropy, yield stress and viscosity.

The milling time should also not exceed 12 h, a time at which the slip still shows no formation of structure, so that

the rheological parameters are better than in the case of the slip from the reference mix as the viscosity at low shear rate, yield stress and thixotropy all decreased. At high shear rate the flows curve of STD-8h and samples with nepheline (C2-12h and C2-16h) are similar, but at those values of shear rate the structure is completely destroyed. The presence of nepheline has also some advantages as it is possible to have finer particle size distributions without having an increasing of viscosity and a reduction of sintering time.

4. CONCLUSIONS

The addition of nepheline improves the sintering process of the porcelain stoneware as the soaking time was drastically reduced (about 50%) to obtain the water absorption zero and the same shrinkage of the reference. This result was obtained in about the same particle size distributions and at the same temperature of the reference sample (STD-8h).

The slips prepared with the mix containing nepheline syenite are found to have lower viscosity at low shear rate, lower yield stress and lower thixotropy than those of the slip of the reference mix. The thixotropy tends to increase by increasing the milling time.

The optimum milling time for the mix containing nepheline syenite is found to be 8 hours as in this condition

Figure 3: Combination curves of control rate and control stress data for the mix containing nepheline syenite (C2) and the reference mix (STD).

Figure 5: Experimental results of cycles at constant shear rate to determine the maximum and the equilibrium stress for the mix containing nepheline syenite (C2) and the reference mix (STD).

Figure 4: Control stress data to evaluate the yield stress for the mix containing nepheline syenite (C2).

Figure 6: thixotropic behaviour at different milling times for the mix containing nepheline syenite (C2) and the reference mix (STD).

the rheological parameters are better than in the case of the sample STD-8h and the soaking time to sinter the samples are drastically reduced.

Longer milling times have a negative influence on the thixotropic properties. This is probably due to the higher surface area of the particles which improves the reactions and the electrical interactions between particles.

The results obtained show that if the milling time of the slip prepared from the mix containing 10% nepheline syenite is not increased above 12 h, the resulting rheological properties are still good. This means that porcelain stoneware tile mixes containing nepheline syenite can be used to obtain slips with a finer particle size, thus making it possible to use a lower sintering temperature due to the presence of nepheline like flux and due to the presence of finer particles.

ACKNOWLEDGEMENTS

The authors wish to thank S. Degli Esposti and D. Naldi for their constructive contributions during the course of research.

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Recibido: 05.03.03

Aceptado: 21.04.03