RHEOLOGICAL BEHAVIOUR OF PORCELAIN TILE SLURRIES

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ABSTRACT

The Brazilian ceramic industry represents 1% of the national GIP, corresponding to 6 billion dollars revenue a year (2004). The abundance in natural raw materials, energy sources and machinery technology made the Brazilian industry evolves rapidly, being the fourth world producer. In the last five years, the production of Brazilian porcelain tiles (porcellanato) has grown considerably. As a result, the problems related to their fabrication process have also grown. As the porcelain tiles are produced via wet milling process in Brazil, their rheology has assumed as important role in quality control and productivity. In this way, this work deals with the study of the rheological behaviour of porcelain tile slurries produced via wet milling. The slurry deflocculation process was analyzed in terms of two types of deflocculants (sodium metasilicate against sodium silicate). As the porcelain paste is formed by clay minerals, the paste was mixed with water forming slurries (1,4g/cm^3). The rheological behaviour of the slurry was studied in function of the deflocculant used by means of viscosity analysis.

1. INTRODUCTION

The determination of the rheological characteristics such as viscosity and thixotropy of clay-water suspensions plays an important role in the application of clays[2]. These flow properties vary significantly due to the aggregation of clay particles under varying conditions of temperature and electrolytes. In many applications, especially in ceramic slurries, it becomes necessary to add certain additives, particularly deflocculants on the clay particles to adjust the flow behaviour [1,9].

Also, controlling the rheological properties of clay based slurries is often indispensable in industrial processes [9]. Liquidity at high solid contents is highly desired in many practical applications like ceramics processing by spray drying. Whereas the cations are responsible for coagulation of the negatively charged clay mineral particles, several multivalent anions counterbalance the coagulating power of the cations. It is well known that certain compounds have a pronounced liquefying effect on clay-water mixtures [3]. In ceramics engineering deflocculants like water glass, humic acids, polyanions and phosphates are common agents for increasing the weight of ceramic masses. Many liquefying agents are polymeric compounds but simple inorganic anions like orthophosphate and oligomeric phosphates such as sodium tripolyphosphate and even sodium silicates also cause pronounced liquefying, particularly with kaolin slurries [5]. The effect of silicates on the flow behaviour of ceramic pastes was reported in some papers [6,8].

Raw materials for technical applications are often mixtures of different clay minerals. The deflocculation of commercially used clays depends on the composition of the major phases [10]. An increasing amount of swelling clay minerals prevented liquefaction of clays by common additives. Many research works have been carried out on the rheological and colloidal properties of clay suspensions. These publications are concerned with the effects of factors such as concentration, pH [6], nature of exchangeable cations [5] and particle size [7], additives like salts [4,5], polymers and surfactants [4].

In the present study two types of sodium silicate are used to promote deflocculation of an industrial ceramic slurry. The study consists in the variation of the additive concentration and the analysis of the flow and viscosity behaviour of the slurries.

2. MATERIALS AND METHODS

Five minerals were used in this study: a clay, a potassic clay, an albite, a flux and a talc. Also, two types of sodium silicates were used: a metasilicate with SiO_2/Na_2O ratio 3:1 and a silicate with SiO_2/Na_2O ratio 2:1. The chemical analysis was determined by X-ray fluorescence (Philips PW2400, molten sample) and the phase (mineralogical) analysis by X-ray diffraction (Philips PW1830, CuKα, 0° to 75°, 0.05°/s, analysis with X'Pert HighScore software).

After chemical and phase characterization, the raw materials were dried, mixed and ground via wet milling in laboratory jar mills (300g, 30% wt water, 25min). The standard porcelain tile paste was composed by 30% flux, 34% potassic clay, 21% albite, 4% talc and 11% clay. After milling the density, residue and fluidity of the slurry were controlled according the standard procedure (1.6g/cm^3, 30s to 70s, 3.5% wt to 4.5% wt

325 Tyler mesh). The standard ceramic suspension (slurry) was used for the viscosity tests.

The viscosity tests were carried out with a rotational viscosimeter (Bohlin) with concentric cylinder geometry (DIN 53019, 20°C to 23°C). The velocity gradient used was 40s^{-1}, compatible with ceramic mixing processes. Each deflocculant was gradually added until the viscosity curve obtained became constant.

3. RESULTS AND DISCUSSION

The chemical and phase analysis of all raw materials are showed in table 1. Analyzing the results the flux is composed by clay minerals, feldspars and calcite. The potassic clay is formed by kaolinite and illite, a plastic raw material, and is contaminated with microcline. The albite mineral also contains illite in its composition. The talc contains some kaolin. Finally, the clay is formed by kaolinite and is contaminated by goethite and anatase.

Mineral	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI	Phases
Flux	52.1	25.7	0.2	0.7	8.5	0.7	1.3	3.0	8.0	Q, K, M, C, Ab, O
Potassic clay	67.5	21.2	0.2	0.7	0.0	0.1	3.2	0.2	6.6	Q, K, I, Mc
Albite	74.4	14.0	0.1	0.3	0.4	0.2	0.8	5.1	0.7	Q, I, Ab
Talc	66.5	2.6	0.2	1.1	0.3	23.2	0.1	0.2	4.9	Q, K, T
Clay	65.0	21.5	1.4	1.5	0.0	0.5	0.7	0.0	9.3	Q, K, M, G, A
Q is quartz, M is muscovite, K is kaolinite, G is goethite, T is talc, C is calcite, I is illite, A is anatase, Ab is albite, O is orthoclase, Mc is microcline										

Table 1. Chemical and phase (mineralogical) analysis of the raw materials (wt %)

Regarding the raw materials it is expected an influence of potassic clay and clay in the rheological behaviour of the slurries. Besides its amount in illite, the albite mineral apparently does not have a great influence on the rheology of the system. After preparation of the slurry with the indicated formulation, the fluidity of the system was determined for the sodium silicate and for the sodium metasilicate. The names 'sodium silicate' and 'sodium metasilicate' are used here as brand names.

Figure 1 shows the flow versus deflocculant concentration for both silicates. The starting point of both curves, 50s for silicate and 70s for metasilicate, indicates the approximately point where the slurries could flow out the mill. It is necessary a higher concentration of the silicate to initiate the suspension flow, but the suspension deflocculated with metasilicate became unstable at the minimum of the curve (25s) and the time necessary to flow became higher in comparison with the metasilicate, diminishing the suspension fluidity.

The suspension deflocculated with the silicate rapidly reached its minimum point of flow and maintained this minimum. The stability remained from 0.7% to 1.0% of silicate concentration and the time to flow was slightly smaller regarding the metasilicate time to flow. The minimum of the curve corresponds to the maximum dispersion of the particle aggregates, varying with the type of deflocculant and clay used present in the suspension. The best deflocculant is the one that reduces the suspension viscosity in a constant and smooth way.

Besides the results obtained the time to flow a suspension, although largely used in ceramic industries, is not sufficient to determine the rheological behaviour of a ceramic suspension. It is necessary to determine its viscosity using the rheological curves. Figure 2 shows the rheological behaviour of the studied suspension in function of the deflocculant addition.

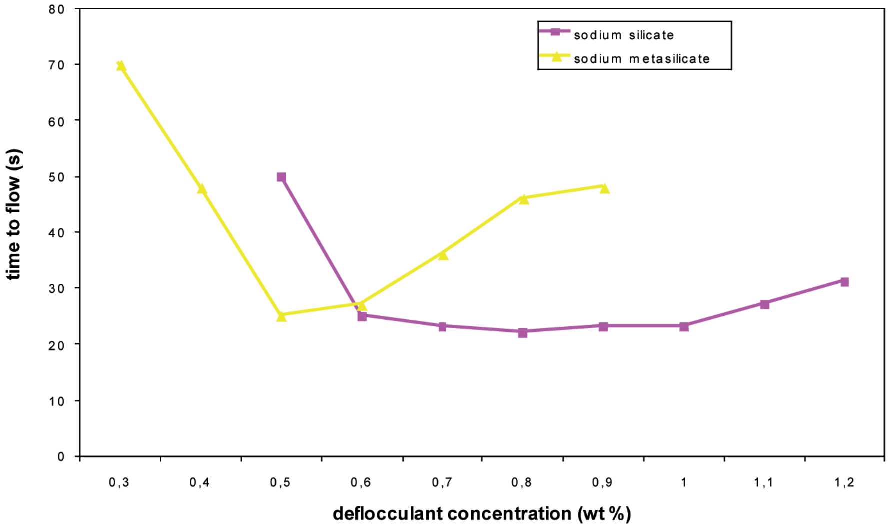

Figure 1. Flow curves for the ceramic suspension in function of the type of deflocculant used

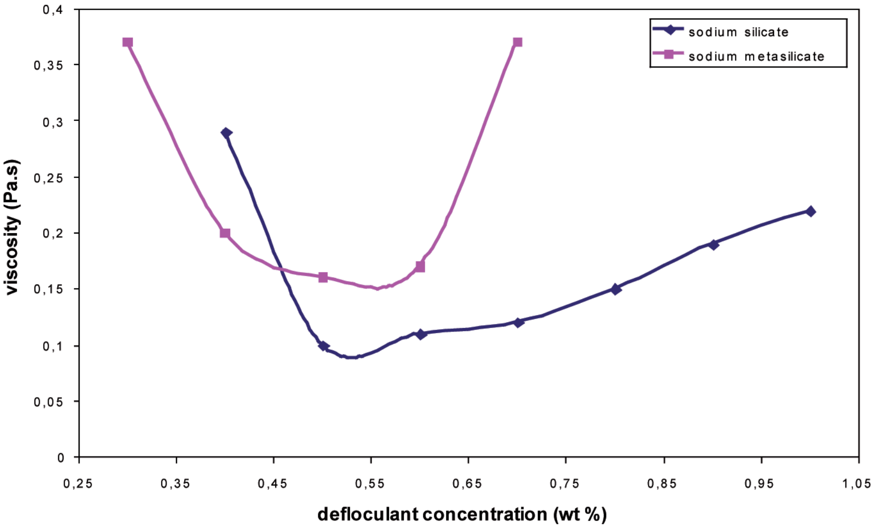

Figure 2. Viscosity curves for the ceramic suspension in function of the type of deflocculant used

The rheological curves confirm the results obtained from the flow curves. The viscosity curves show the suspension with the addition of metasilicate needs more deflocculant to flow. The suspension deflocculated with silicate shows a minimum at a small value of viscosity regarding the suspension deflocculated with metasilicate and the curve is more stable. The viscosity curve for the metasilicate additive is very unstable because it reduces and rises again abruptly in a reduced range of the deflocculant concentration (figure 2).

4. CONCLUSIONS

Analyzing the flow and viscosity curves the sodium silicate is the most effective deflocculant in the studied system. Besides the use of brand names it was not analyzed if the metasilicate used really is a metasilicate. The best results in flow and viscosity for the silicate are due its SiO_2/Na_2O ratio (2:1) regarding the metasilicate SiO_2/Na_2O ratio (3:1). The study, besides simple and easy to do, shows the importance of viscosity control in the ceramic industry. Variations of slurry viscosity are the major causes of variation in granule size and distribution after spray-drying. The viscosity control using flow time is simple, easy and fast to execute. Obviously by itself it is impossible to determine all rheological behaviour of a ceramic suspension, but the fluidity control using the Ford cups is an important control in the ceramic industry.

The rheological behaviour of ceramic suspensions is controlled not only by the type of deflocculant used in the process, but also by water hardness and pH and characteristics of the raw materials used (type, shape, particle size).

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