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Stabilization of kaolin clay slurry with sodium silicate of different silicate moduli

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ABSTRACT

In the ceramic technological processes, the suspensions with high concentration of ceramic particles (> 60%) play a very important role because this let to obtain inter alia reasonable casting rates what is one of the most important steps during the ceramics manufacturing. The article shows the attempts to modify the rheological properties of concentrated ceramic slurries, based on kaolin KOC. Different alkali sodium silicate based stabilizers, i.e. sodium water glasses ((Na₂SiO₂)_nO) of silicate moduli in the range 1.74–3.25, were used for the research. The flow curves were analyzed and the technological parameters of slurries were described. Special attention was paid to the stabilization of slurries with the use of sodium water glasses of higher silicate moduli (> 2). It was found that the best results of the stabilization of the kaolin slurry can be obtained while using sodium water glass of silicate moduli 2–2.5. Sodium water glasses of the moduli smaller than 2 precipitated free silica in the suspension and increased the alkalinity of ceramic slurry while those larger than 2.5 created independent silicate micelles, co-existing with the dispersed kaolin grains. The mechanisms appearing during the stabilization of ceramic slurry with the use of sodium water glass were ion exchange and, the so called depleted stabilization.

1. Introduction

Ceramic slurries consist of inorganic components (clay minerals, quartz, feldspar), water and most frequently organic modified additives (plasticizers, fluidizers, antifoams, lubricants, etc.). Regardless the method of forming, the rheological properties of slurries are always a matter of great interest. These properties are often out of reach by normal mixing of ceramic mass with water. That is why it is an usual practice to add various modifiers to obtain the most beneficial rheological properties with the minimum use of water.

The polar liquids, mainly water, cause the dispersion of clay minerals grains. The polarity of water determines its physicochemical properties. The easiness of proton transportation from one water molecule to another and from one hydroxide ion to another allows, within a certain mass (volume) of water, the determined number of hydroxide and hydronium (oxonium) ions to be obtained. For its large number the balance state is established, and as a result, the ordered one. Among the charged grains or ions producing the electric field in the suspension, the ordered water molecules produce their own electric field, oriented oppositely. That is why the presence of water weakens significantly the

electrostatic interaction of ions or charged molecules in the suspension. What is more, the water dipoles take part in solvation (hydrophobic forces). In these conditions, the ceramic slurry becomes unstable and sediments easily. The addition of stabilizer results in a suspension not only with low viscosity but also high density (Horn, 1990; Iskece et al., 1999; Hamley, 2000; Cheng, 2003).

Due to their construction, the stabilizers used to modify the ceramic suspensions are divided into inorganic and organic. These in turn may be of natural, synthetic or artificial sources. They must also meet the following requirements: wettability of grains- by lowering the surface tension; breakage of aggregates and dissipation of the grains in a liquid phase- by means of the grain-stabilizer intermolecular interactions; reduction of viscosity and consolidation of dispersion- by changing the physicochemical interactions between the particles of the solid phase.

Depending on the type of the system (water suspension, non-water suspension), and the type of modifiers (organic, inorganic) four kinds of chemical stabilization can be listed:

- electrostatic- caused by the change of pH or ion exchange,
- polymeric (steric)- caused by the specific adsorption of organic

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- polymers (so called, spatial effect or antiflocculation effect),
- electro-spatial- caused by the specific adsorption of organic polymers with the functional groups capable of dissociating, or
- depleted- caused by the dispersion of other fractions.

The most effective mechanism of the suspension stabilization is the electro-spatial one connected with the activities of the organic macroparticles with the functional groups capable of dissociating. The organic polymer particles, the so called protective colloids, of big molecular weight, may undergo the multipoint adsorption- i.e. specific adsorption, and limit the access to the attractive van der Waals-London forces and in this way they may compensate the surface charge.

The stabilization (fluidization) of these can be done by:

- adsorption of the protective organic colloid on the surface of the grains from the solid phase and possible deactivation of the multivalent compensating cations, by creating the complex compounds;
- creating the so called potential tunnel around the functional groups of the adsorbed polymer (Bergaya and Lagaly, 2001; Dinger, 2002; Mpofu et al., 2003).

In the case of inorganic stabilizers the stabilization mechanism is the ion exchange. Reinforcement of negative charges on the grains surface results in the removal of the positive coagulation charges. In this process, Mg^{2+} , Ca^{2+} and Al^{3+} ions, characterized by a small ionic radius and high potential, are preferred. In the suspension, these cations are attracted to the negatively charged surface of grains, thereby reducing the intermolecular repulsive forces. If multivalent cations are combined with, for example, the silicate anion, they are immediately neutralized and removed to the medium, so that the viscosity of the suspension is getting lower (Otterstedt and Brandreth, 1998; Chi and Eggleton, 1999).

Izak et al., 2003 and Stempkowska et al., 2011 revealed that silicate fluidizers are not sensitive to overdosing in the suspension, unlike other inorganic stabilizers. That is why they are friendly in the use for application. This is characteristic for the organic fluidizers which work basing on specific adsorption and shielding of the van der Waals attractive forces. But there were no literature data about the fluidization mechanism of sodium water glasses of different silicate moduli, what could be very useful for the ceramic industry applications. Only articles about rheological properties of such slurries were found (Yildiz et al., 1998; Penner and Lagaly, 2001; Pacheco-Torgal et al., 2008; Penkavova et al., 2014). Because of this, the authors are trying to answer a question: How can the silicate modulus of the sodium water glass affect the mechanism of stabilization of the ceramic slurry? It is believed that these studies will help to understand the fluidization mechanism of sodium water glasses and will contribute to the development of knowledge about the structure and properties of sodium water glasses.

2. Materials and methods

2.1. Preparation of kaolin KOC slurries

The research was conducted with the use of concentrated kaolin KOC slurries which consisted of 60 wt% of kaolin KOC (Surmin-Kaolin, Poland; enriched in quartz and low in titanium and iron white-burned raw material, designed for the use in ceramic industry because of its stable rheological properties), 40 wt% of distilled water and sodium water glass $(Na_2SiO_2)_nO$ (Rudniki S.A. Chemical Plant, Poland) of different silicate moduli in the range of 1.74–3.25, which was added to the ceramic slurry in the amount of 0.1–0.5 wt% to the kaolin KOC dry mass. The sample was stirred for 5 min in such a way as not to aerate it. After obtaining a homogenous slurry, it was matured for 10 min and then again stirred before the measurement to destroy possible thixotropic structure.

To remove water from the kaolin and thereby to stabilize the clay

Table 1
Chemical analysis and mineralogical composition of kaolin KOC.

Chemical analysis [wt%]							
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O
51.60	34.20	0.49	0.47	0.08	0.13	0.71	0.32
Mineralogical content [wt%]							
Kaolinite		Mica		Quartz			
84.21		4.62		11.17			

mineral structure, kaolin KOC used for the study was calcined at 600 °C. Its chemical analysis and mineralogical composition is shown in Table 1. The sodium water glasses used in the study were filtered and its chemical analysis was performed with the use of the factory standards (Factory standard, 2016) (Table 2). Silicate moduli (M) were calculated on the basis of the following formula:

$$M = \frac{xSiO_2}{yNa_2O} \cdot 1.0323 \quad (1)$$

where: $xSiO_2$, yNa_2O - weight percentage content of silica and sodium oxide respectively; 1.0323- conversion factor from weight units to molar units.

The performed ²⁹Si resonance measurements (Bruker 300 MHz spectrometer, D₂O as a solvent) revealed that spatial structures of applied silicates were comparable with the literature data in the range of signal intensities (Harris et al., 1980; Harris and Knight, 1983; Ray and Plaisted, 1983; Svensson et al., 1986; Wijnen et al., 1990; Uchino et al., 1992; Bass and Turner, 1997; Schneider and Mastelaro, 2003). The signal intensity was calculated as the signal surface area by integration. For example, resonance spectrum of sodium water glass R-137 showed presence of some silicate polymer structures (Fig. 1).

2.2. Rheological measurements

The rheological measurements were conducted with the use of the rotary viscometer (Brookfield DV-III), equipped with a cylinder-and-spindle (R-29) measuring system. Flow curves were made for increasing and decreasing shear rates in the range of 2.5–50 s⁻¹ and measuring points related to the change of shear rate were collected every 30 s. Additionally, after each flow curve measurement, thixotropy was measured. It relied on stopping the rotation for 10 min, whereupon viscosity was measured at a constant shear rate of 5.6 s⁻¹ after the time of 2 s, 3 s, 4 s, 5 s, 10 s, 20 s and 30 s.

3. Results and discussion

3.1. Rheological characterization of kaolin KOC slurries modified with sodium water glasses

The results showed that slurries based on kaolin KOC and modified with sodium water glasses possess thixotropic properties, which was probably associated with the intermolecular interaction mechanism. They exhibited c flows both at increasing and decreasing shear rates. It can be assumed that decreasing apparent viscosity (Fig. 2) at the increasing shear rate was the result of the gradual destruction of the internal structures of the slurry and their arrangement along the flow direction. Disintegration of the internal structure at high shear rates was not immediate, reflecting the dynamic (non-rheostable) and reversible properties.

Increase the amount of fluidizer caused faster stabilization of the dispersion structure. Above the 0.3 wt% concentration of sodium water glasses with the silicate moduli in the range of 2.0–2.5 there was no visible improvement in stabilization of the ceramic slurry. Therefore, it can be concluded that the best fluidization properties were possessed by sodium water glasses with the silicate moduli in the range of 2.0–2.5

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