

Improvement of the deflocculating power of polyacrylates in ceramic slips by small additions of quaternary ammonium salts

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Abstract

In this work, we examine the effect of small additions of cationic quaternary ammonium salts (QAS) of different molecular weight on the rheology of an industrial ceramic suspension deflocculated with sodium polyacrylate and sodium metasilicate. The observed shear thinning behaviors obey the typical power law of fluid rheology. In order to characterize the rheological behavior of these slurries, three new parameters are introduced: a low shear rate consistency index and two transient viscosities, distant from the equilibrium, after increasing and decreasing the shear rates. These parameters vary with polyacrylate molecular weight and on additions of small quantities of QAS, which we found to be useful for decreasing the slurry viscosity.

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1. Introduction

Controlling the rheological behavior of slurries in industrial ceramic processes plays an important role in the quality of the final product. The rheology of slurries depends directly on the aggregation level of solid particles [1]. An accurate characterization of rheology can lead to increased control and reduce the costs of ceramic production. The solid content should be as high as possible and the viscosity low enough to assure easy handling throughout the industrial process. Appropriate control of rheology permits an increase in the solid content and consequently lowers drying costs. Industrial ceramic slurries are complex aqueous suspensions of powdered minerals with appropriate inorganic and organic additives as dispersants [2]. The rheology of slurries can be complex and several phenomena may be observed such as yield stress, shear thinning and thixotropy [3].

The electrical surface charges on ceramic particles induce amongst them electrostatic repulsion and, as a consequence, dispersion in water [4]. The addition of dispersants regulates these electrostatic forces. These dispersants may be adsorbed onto surface particles modifying the surface charge and the thickness of the electric double layer [5]. The particles thus repel one another, dispersing and increasing the stability of the slurry [6–10]. High electrostatic repulsion between solid particles facilitates dispersion and particle stability [11]. Polymeric dispersants can also alter the interaction between particles through steric repulsion [12]. The addition of these molecules changes the mechanism of particle aggregation and the colloidal properties of the slurry [13,14]. In summary, the stabilization of slurry relies on the high dispersion of ceramic particles, which occurs when the electrostatic and steric repulsions are stronger than the van der Waals attractions [15–17].

Shear thinning involves the break down of the network of suspended particles, which forms the internal structure of the slurry, resulting in smaller flow units, and decreased viscosity. According to the Derjaguin–Landau–Verwey–

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Overbeek (DLVO) theory for colloidal suspensions, the stabilization of the suspension is due to interparticle repulsion forces that counteract van der Waals attraction. These forces depend on steric interactions and particle concentration.

For many years, industrial slurries have been treated using inorganic dispersants such as sodium polyphosphates and sodium metasilicate. Adsorption of sodium polyphosphates has been studied by several authors [18,19]. Some inorganic molecules have a strong tendency to interact electrostatically with the surface ions of ceramic particles increasing the thickness of the electrical double layer and thus the repulsion between particles. Polyphosphates have the ability to adsorb onto clay particle surfaces via electrostatic and/or chemisorption mechanisms, forming a bond between the surface metal ions and the oxygen atoms of polyphosphate [20]. In highly concentrated ceramic slurry tripolyphosphate performs better than diphosphate and hexametaphosphate [21]. Recently, organic polyelectrolytes (i.e., polymers) have also been introduced to the ceramic industry as powerful deflocculating agents. These water-soluble polymers permit better control of deflocculation and could potentially substitute polyphosphates [22]. Generally, these polymers contain carboxylic groups with polyacrylates being the most widely used in the ceramic industry.

In this study, we examine the influence of small additions of quaternary ammonium salts (QAS) of different molecular weight on the rheology of an industrial slurry deflocculated with sodium polyacrylate and sodium metasilicate. Cationic molecules (i.e., QAS) and anionic polymers (i.e., sodium polyacrylate) are able to interact with clay particles since the different charge distribution between the edges (positive charge) and the faces (negative charge).

2. Experimental

2.1. Materials and sample preparation

The analyzed slurry was a typical ceramic suspension used in the manufacture of white porcelain tiles, made with a mixture of 45 wt.% of feldspar, 15 wt.% of plastic clay (Hymod KC, from Imerys) and 40 wt.% of kaolin. The chemical compositions of these raw materials are shown in Table 1. In the preparation of samples, industrial conditions were reproduced in smaller scale. The mixture was powdered by grinding in a wet ball mill until no significant residue was found on 325 Mesh (Tyler). The final product had a specific surface area of 13.4 m²/g and an average particle size of 2.1 μm. The components used to make the slurry dispersants were (1) sodium metasilicate, (2) sodium polyacrylates (Rohm and Haas) with molecular weights 2000, 10,000 and 70,000 g/mol (PA-2, PA-10 and PA-70, respectively), and (3) a series of alkyltrimethylammonium salts with alkyl chain lengths in the range of 10 to 18 carbon atoms:

Table 1

Chemical compositions for the raw materials used in the ceramic suspension

	Feldspar	Plastic clay	Kaolin
%SiO ₂	74.4	54.2	52.7
%Al ₂ O ₃	14.9	30.4	39.1
%Na ₂ O	7.2	0.4	3.0
%K ₂ O	1.8	3.1	2.7
%CaO	0.9	0.3	0.1
%MgO	0.2	0.5	0.9
%Fe ₂ O ₃	0.7	1.2	0.4
%TiO ₂	–	1.1	–
%Ignition loss	0.6	9.0	1.5

decyltrimethylammonium bromide (10C), dodecyltrimethylammonium bromide (12C), hexadecyltrimethylammonium bromide (16C), octadecyltrimethylammonium bromide (18C) and didodecyltrimethylammonium bromide with two alkyl chains of 12 carbons (24C). The solid content in all the analyzed slurries was 70 wt.% and pH of slurry was fixed to 9.0. Preliminary experiments indicated that the viscosities are lower when pH ranges from 8.8 to 9.2 and this is just the pH range in the industrial process. The concentration of sodium metasilicate and organic dispersant was the same in all the analyzed slurries: 0.321 and 0.107 wt.% (dry basis) respectively. We tested slurries with the addition of a single polyacrylate (PA-2, PA-10 or PA-70) and with the addition of a mixture of polyacrylate PA-2 and each of the QAS (e.g., PA-2 and dodecyltrimethylammonium bromide, PA-2+10C). The molar ratio of QAS/acrylate monomer was 3.14·10⁻³ for PA-2+12C. In order to increase dispersion, the slurries were sonicated for 5 min and kept at rest at room temperature for 24 h in sealed flasks in order to assure the equilibrium, in the process of deflocculant adsorption, and make behavior more reproducible.

2.2. Rheological measurements

Rheological measurements were carried out using a controlled rate rheometer (Haake CV20 Rotovisco) with a Mooney-Ewart (45 mm in diameter, 1 mm gap) concentric cylinder sensor. All measurements were performed at 25 °C. Non-steady rheological measurements or thixotropic analyses were performed using a hysteresis loop test, where the hysteresis loop was generated by increasing and decreasing the shear rate linearly over time. Stress history can have effect on the test rheological measurements. To ensure that no such history was recorded in the material, all samples have been presheared at 100 s⁻¹ for 10 min and then kept at rest for 60 min to instate a uniform starting condition. Then the shear rate was linearly increased from rest to maximum over 15 min, maintained for 30 min in order to reach steady shear stress, and finally linearly decreased to 0 s⁻¹ over 15 min. Three maximum shear rates were tested: 20, 100 and 500 s⁻¹.

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