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Influence of two dispersants on the rheological behavior of kaolin and illite in concentrated calcium hydroxide dispersions

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Abstract

The influence of an alkylammonium surfactant and a negatively charged grafted block copolymer (CTP) onto the threshold stress value of illite and kaolinite dispersions was investigated in a strongly alkaline environment.

For both clay minerals, addition of hexadecyl trimethylammonium (HDMA) promotes the release of calcium ions. For kaolin KF, this release is linked at low HDMA/ kaolinite ratio with an increase of the threshold stress, and at high HDMA/kaolinite ratio with a decreasing viscosity of the dispersion. Low cationic additive concentrations coagulated the dispersions while at high additive content, repulsion between the surfactant counter ions on the particle surfaces stabilized the dispersion.

In contrast, although addition of a comb-type copolymer with an anionic backbone (CTP) reduced viscosity of both dispersions, no calcium ion release was observed. This result indicated that CTP stabilized the dispersions by a steric mechanism.

Keywords: Threshold stress; Adsorption; Alkylammonium ions; Superplasticizer; Surfactants

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1. Introduction

In concrete, the presence of clay minerals in the granulates often perturb the setting parameters. In particular, the setting time cannot always be accurately predicted. Moreover, clay influences the rheological behavior of cement and can modify the placing conditions (Schmidt and Rostasy, 1993). Thus, we were interested in understanding the influence of clay minerals onto a cementitious environment, and in particular in understanding the ion sorption at the clay surfaces. In a precedent publication, we showed that in a strongly alkaline environment, kaolinite and illite adsorb calcium and hydroxide ions, and that the large amount of adsorbed calcium and hydroxide ions cannot be attributed solely to bonding to clay mineral particle edges (Konan et al., 2007). The proposed mechanism implies participation of the particle faces in the adsorption process: at high calcium hydroxide concentrations, on siliceous clay mineral faces, a Ca^{2+}, $2OH^-$, $4H_2O$ layer is adsorbed, and the particle edges are weakly electronegative due to the screening of the silanol and aluminol groups through adsorption of hydrated calcium cations Ca^{2+}, 6 H_2O. Thus, the adsorption of calcium hydroxide modifies the interactions between the clay mineral particles. We are now interested in characterizing the influence of this adsorption onto the rheological behavior of clay minerals.

Natural clay mineral samples are usually very polydisperse in both shape and size. Rheological properties, like viscosity, depend on particle shape, particle anisotropy and particle size distribution (Michot et al., 2001; Matijasic and Glasnovic, 2002). Results obtained for aqueous polystyrene latex dispersions with nearly the same average particle sizes but varying degrees of polydispersity demonstrated a significant effect of particle size distribution on the rheological properties of

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Table 1
Chemical composition (mass %) of the raw materials

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	Na_2O	CaO	MgO	Ignition loss (at 1000 °C, weight %)
Kaolin KF	51.6	34.7	0.7	0.3	0.1	0.1	-	0.1	12.7
Illite	53.3	19.9	5.8	5.0	1.3	-	3.6	3.2	9.5

particles: a noticeable reduction in the viscosity, yield value, elastic moduli, and loss moduli was observed for very polydisperse systems compared to a monodisperse one. In a very broad distribution case, small particles can fit between the larger ones to minimize the particle interactions, and this reduces the yield value (Luckham and Ukeje, 1999). Based on these results, the two highly polydispersed and anisotropic raw materials investigated exhibit most probably lower threshold stress values than those that could be observed for the corresponding pure clays.

Interactions taking place between dispersed clay mineral particles are changed by the presence of ionic species or molecules on the clay surface. Cationic surfactant, such as ions belonging to the alkylammonium family, are known to replace cations at the clay mineral surface and favor the release of mono- and divalent positive species (Lagaly, 1986). Two major mechanisms are proposed for the adsorption of cationic surfactants onto different clay, earth and zeolite minerals: ion exchange and van der Waals interaction (Luckham and Rossi, 1999). The former is indicated by stoichiometric release of inorganic cations accompanying alkylammonium adsorption, when the alkylammonium loading is well below the quantity necessary to saturate the outer surfaces of the clay minerals (Xu and Boyd, 1994). The latter is characterized by a fast rising adsorption exceeding the CEC of the minerals (Xu and Boyd, 1995; Li, 1999).

Other types of surface modifier commonly used in concrete formulation are superplasticizers. This class of additives reduces the porosity of the hardened concrete by allowing the fresh material to become workable with less water (Sakai and Daimon, 1995; Uchikawa et al., 1997; Yoshioka et al., 1997; Flatt, 2001; Kirby and Lewis, 2004; Laarz et al., 2006). This greatly enhances the durability and also makes possible to substitute substantial volumes of cement with industrial waste materials, e.g. slag or fly ash (Ramachandran et al., 1998). New generation superplasticizers are comb-like copolymers with an anionic backbone, commonly having carboxylic and/or sulphonate groups that charge the polymer negatively, and uncharged poly(ethylene oxide(PEO))-based chains of variable length grafted onto the anionic backbone at regular intervals (Kjeldsen et al., 2006). Superplasticizers adsorb at the solid-liquid interface, and can impart a repulsive inter-particle force of electrostatic or steric origin that reduces or eliminates the adhesion between particles at close proximity. The relative importance of the double-layer and the polymer–induced contributions in reducing the degree of flocculation has been an issue in several studies. The high ionic strength and the relative low surface charge density in cement-silica or limestone granulates suggest that the steric stabilization should be dominating, in particular for the new comb-type copolymers (Sakai and Daimon, 1995; Yoshioka et al., 1997; Flatt, 2001). For steric stabilisation to occur, the dispersant requires some portion of its chain to extend into the solvent to increase repulsion and prevent collision with other particles (Hunter, 1987). Numerous granulates contain a small amount of clay minerals, which influence on the rheological behaviour of the cement–based paste is not yet clearly established.

Thus, in the following publication, we will explain the influence of two dispersants onto the rheological behavior of clay minerals containing kaolinite and illite in concentrated calcium hydroxide suspensions with respect to the binding mechanisms of the surfactants to the clay minerals.

2. Materials and methods

The chemical and mineralogical compositions of the clay minerals used in this study, i.e. kaolin KF and illite (Damrec, France) are given in Tables 1 and 2. The chemical composition has been obtained using Inductively Coupled Plasma Atomic Emission Spectoscopy (ICP-AES, Iris instrument fromThermo Jarrell). Prior to analysis, clay minerals samples were solubilized in a fluorhydric acid / nitric acid mixture (28 /68% in volume) using a microwave (CEM, MARS 5). The specific surface area of the clay minerals has been determined by the Brunauer-Emmet-Teller (BET) method using adsorption of nitrogen at 77 K (Micromeritics Flow Sorb II 2300). All dispersions were prepared using deionised water and analytical grade calcium hydroxide (Merck, purity above 96%).

Two liquid additives (Fig. 1) were tested in this study: hexadecyl trimethylammonium chloride (HDMA) with a molar mass of 320 and a grafted negative polymer. The latter additive is composed of a polymethacrylic backbone and grafted side chains of polyethylene glycol (PEG) with a molar mass determined by gas phase chromatography of 1100.

Calcium ion desorption measurements were conducted on 50% (by mass) dispersions of clay minerals equilibrated with a freshly prepared lime saturated solution, where the initial calcium ion concentration was equal to 2.1×10^{-2} mol. L^{-1} ($pH_0 = 12.6$). The dispersions were then hermetically sealed in polyethylene tubes and stored under nitrogen to avoid carbonation. Samples were stirred for 25 minutes, centrifuged for 20 minutes at a speed of 10 000 rpm. The total contact time between lime solutions and clay mineral samples was 45 min, which is the minimum time required to equilibrate the clay dispersion with the calcium hydroxide solution. In this time period, other processes, such as dissolution of the clay mineral, are negligible (Konan et al., 2007). Aliquots of surfactants were then added to the dispersions, and after mixing, equilibration and centrifugation, the supernatant was subsequently collected for measurements of calcium concentration using the Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) technique with an Iris (Thermo Jarell) equipment.

Rheological measurements were carried out on concentrated dispersions mimicking the cementitious environment with a controlled-stress rheometer (CARRIMED CSL 100) equipped with a parallel-plate geometry (gap: 1 mm, diameter: 10 mm). All measurements were performed at 20±0.1 °C. Prior to

Table 2
Estimated mineralogical composition (mass %) and specific surface areas of the raw materials

Mineral	KF Kaolin	Illite
	Soro, 2003	Bouchet and Sammartino, 2002
Kaolinite	83	5
Illite	6	87
Calcite	-	4
Quartz	10	3
Specific surface area ($m^2.g^{-1}$)	11±1	90±7