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Research paper

Experimental studies on the desorption of adsorbed sodium poly(acrylic acid) from crude kaolin particles

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ABSTRACT

Background: The controlled stability and fluidity of highly concentrated kaolin dispersion is a crucial problem when kaolin is used in industry due to the charge heterogeneity of its surface. To solve the common industrial problems of dispersions prepared at high solid loadings in terms of their rheological behavior, some organic and inorganic dispersing agents have to be added into the system to modify the particle surfaces.
Objective: Adsorption and desorption behaviors of sodium poly(acrylic acid) (NaPAA) on the surface of kaolin particles were investigated to elucidate the adsorption mechanism of the PAA–kaolin dispersion system within the scope of the rheology and the colloidal stability. We also investigated the structural changes in the kaolin particles due to the extraction of Si^{4+} and Al^{3+} ions when a dispersing agent was used.
Method: Kaolin dispersions were prepared using NaPAA, and investigated in terms of the adsorption and desorption behaviors, the rheological and the electrokinetic properties and the extracted Al^{3+} and Si^{4+} ions from the particles.
Results: As expected, PAA was strongly adsorbed on the positively charged alumina sites of the particles. According to the results obtained in the experiments of adsorption density, viscosity, ζ-potential and the dissolution of metal ion measurements for the adsorption/desorption, a strong and irreversible adsorption was observed between PAA and the surface of the kaolin surface, indicating the existence of unbreakable chemical bonds. This is due to the adsorption of negatively charged carboxylic acid groups ($-COO^-$) from the PAA onto the positive alumina sites on the edges of the kaolin surface by electrostatic attraction. Due to the negative charge, no adsorption was observed on the silica surface of the particles within the working pH range of 5.3 to 8.4.
Conclusion: The adsorption mechanism of PAA–kaolin interaction is attributed to chemical adsorption with the formation of chemical bonds between the charged carboxylic acid groups ($-COO^-$) of the polymer and the alumina sites on the edges of the kaolin.

1. Introduction

Kaolin is an important clay mineral and is widely used in the paper, paint, rubber, plastic, ceramic, cosmetic, and dye industries, and new applications are found incessantly. In the paper industry, kaolin is used as a filling and coating component to enhance paper qualities such as brightness, opacity, smoothness, and printability (Murray, 2000; Murray and Kogelb, 2005). Kaolin is used in the plastic industry in applications such as plastic covers, foils, water pipes, tubes, and cables (Konta, 1995). Kaolin–polyelectrolyte and kaolin–surfactant interactions are relevant to a broad variety of applications such as soil stabilization, paper manufacturing, nanocomposite manufacturing, the mining industry, water–wastewater treatment and mud preparations for drilling oil walls (Liu, 2007; Sanchez-Martin et al., 2008; Ayadi et al., 2011). Kaolin usage in the United States in 2002 was estimated to be 54% in the paper industry, 17% in refractories, and 29% in other industries (Zaman, 2006).

Kaolinite crystal has the chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; it consists of one octahedral alumina and one tetrahedral silica sheet, and is a 1:1 pure clay mineral. These sheets share one of the four oxygen atoms of the octahedral sheet, and they form one layer of the kaolinite mineral. The layers are bound together through hydrogen bonding, and each particle consists of approximately 50 alternating layers (van Olphen, 1977; Lagaly, 2006). Kaolinite is a non-swelling clay mineral because of these alternating layers that are bound together by hydrogen bonding (Addai-Mensah and Ralston, 2005; Addai-Mensah, 2007; Li et al., 2008). The aspect ratio of kaolin particles, which are plate-like in shape, may vary from 5–15 depending upon the mechanical treatment of the particles (Sjoberg et al., 1999).

Kaolinite has a complicated surface chemistry because of the heterogeneity of the charged edges and faces (Herrington et al., 1992; Tombácz and Szekeres, 2006). Its edges comprise both silica and

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alumina-like sites and their charges are pH dependent. They are positively charged at low pH, but, beyond the isoelectric point, they are negatively charge at high pH. Kaolinite faces comprise only silica-like charge sites and remain negatively charged across the pH range. The isoelectric points of silica and alumina are in the pH ranges of 2.0–3.5 and 8.5–10.4, respectively. Thus, within the working pH range of 3.5–9.5 for industrial application, the basal plane of kaolin is negatively charged, and the alumina-like charged sites on the edge are positively charged. This particle charge difference causes an electrostatic face-to-face, edge-to-edge and edge-to-face attraction and forms card–house type agglomerates that coagulate the suspension at the high kaolin loadings.

The controlled stability and fluidity of highly concentrated kaolin dispersion is a crucial problem when kaolin is used in the industry due to the charge heterogeneity of its surface (Sjoberg et al., 1999; Addai-Mensah, 2007; Marco and Llorens, 2007). Especially in paper coating, the solid concentration of a kaolin dispersion can usually go up to 60 or 70% (by wt.), and the dispersion is required to be well-dispersed, have a stable viscosity, and have good flow characteristics for processability (Zaman et al., 2003; Bossard et al., 2007; Loginov et al., 2008). To solve the common industrial problems of dispersions prepared at high solid loadings in terms of their rheological behavior and convenient processability, some organic and inorganic dispersing agents have to be added into the system to modify the particle surfaces (Stenius et al., 1990; Jogun and Zukoski, 1996; Yuan et al., 1998; Johnson et al., 2000; Penner and Lagaly, 2001; Moan et al., 2003). These dispersing agents can usually be anionic polyelectrolytes, surfactants and electrolytes, and they modify the particle surfaces to form a uniformly charged state by either adsorption of polymers and surfactants onto the surface of the kaolin particles or charge adjustment around the surface with electrolytes (Benchabane and Bekkour, 2006; Desai et al., 2010). Modifications are usually made by the negatively charge adjustments because the edges of the kaolin are estimated to occupy approximately 20% of the whole kaolinite surface (Zaman et al., 2001; Ayadi et al., 2011), and these modifications result in well-dispersed kaolin slurries by increasing the electrostatic repulsion between the particles (Diz and Rand, 1989, 1990; Gupta et al., 2011; Cao et al., 2012).

Many studies have been performed by using different dispersing agents on kaolin suspensions to investigate the adsorption of polymers and surfactants on the kaolin particle surfaces. The studies have usually focused on the achievement of rheologically stable dispersion (Husband, 1998; Mpofu et al., 2003; Ma, 2011; Rao et al., 2011), the electrokinetic properties of the system (Braggs et al. 1994; Alkan et al., 2005; Lagaly, 2006; Chassagne et al., 2009; Amorós et al., 2010; Duman et al., 2012; Leong et al., 2012), the adsorption isotherms (Backfolk et al., 2001; Marco and Llorens, 2005; Hoch and Bandara, 2005; Backfolk et al., 2006; Kwan et al., 2006, 2011; Totland et al., 2011), and the identification of the reaction mechanism causing the dissolution of metal ions from the particles (Huertas et al., 1998, 1999; Yuan et al., 1998; Zaman et al., 2003). Dodson and Somasundaran (1983) studied the desorption of polyacrylamide and hydrolyzed polyacrylamide from the kaolinite surface. Adsorption of non-ionic polymers on the kaolin surface have also been investigated to elucidate the polymer adsorption characteristics and determined that non-ionic polymer molecules interact with the surface of kaolinite particles via polymer bridging (Chaplain et al., 1995; Carasso et al., 1997; Backfolk et al., 2006; Besra et al., 2006; Lagaly, 2006; Kim and Palomino, 2009). However, there are almost no reports on the desorption of polymers adsorbed onto the kaolin surface, especially using PAA and its effect on rheological behavior.

In this study, we performed a systematic investigation of the desorption of PAA–kaolin dispersion systems prepared by the adsorption of the polymer on the crude kaolin particles. The objective of this study was to elucidate the adsorption mechanism of the PAA–kaolin interaction using results obtained from the desorption studies of adsorption density, viscosity, ζ-potential and the measurements of metal ion dissolution. The aim of this work was to produce a rheologically stable dispersion and to develop a new dispersing agent for mineral slurries of heterogeneous particles.

2. Materials and methods

2.1. Materials

The kaolin used in this study was high purity-grade East Georgia crude kaolin and was supplied by Engelhard Corporation in Georgia, USA, without any organic or inorganic additives. The kaolin sample was used without any further treatment to avoid possible modification of its surface characteristics. All samples were out-gassed on the gas adsorption analyzer for 24 h at 110 °C under vacuum prior to measurement. The BET nitrogen specific surface area of the particles was determined to be 20.3 $m^2 g^{-1}$ using a Quanta Chrome NOVA 1200 instrument. The surface area of the powder was also determined using a mercury porosimeter (a Quanta Chrome instrument) and was found to be nearly equal to the BET nitrogen specific surface. These results indicate that there are no significant micropores on the particle surface, and all of the surface area is available for adsorption by the dispersing agent molecules. The density of the powder was measured to be 2.72 $g \cdot cm^{-3}$ using a Quanta Chrome Ultrapycnometer, and the humidity was 0.86 ± 0.07%. Particle size analysis of the kaolin particles was conducted by a Coulter LS 230 instrument utilizing the light-scattering technique with a small volume module, and Fig. 1 shows the size distribution curve of the dispersion as a function of differential volume at pH 10. SEM image of kaolin particles is shown in Fig. 2.

The NaPAA used in this study as a dispersing agent was a low molecular weight anionic polyelectrolyte and was provided by Vinings Industries, Inc. The NaPAA contained 43.1% (wt.) solids of molecular weight 3400 $g \cdot mol^{-1}$ with a polydispersity index of 1.18. The NaPAA was used as received. All dispersions were prepared using ultrapure water, produced by a millipore filtration system, including less than 7 ppb carbon and specific resistivity greater than 18.2 MΩ cm^{-1}.

2.2. Chemical analysis of crude kaolin

5 g of kaolin powder was dried in an oven at 100–110 °C to remove moisture at least 1 h before analysis and then cooled in a dry chamber until room temperature. Then, 0.5 g of dry powder was analyzed and mixed with 2.5 g Na_2CO_3 and then with an additional 2.5 g Na_2CO_3 in a platinum crucible. To decompose the kaolin, the kaolin:Na_2CO_3 mixture was placed in a preheated furnace at 900 °C for 30 min. After the sample was removed from the 900 °C oven, it was cooled to room

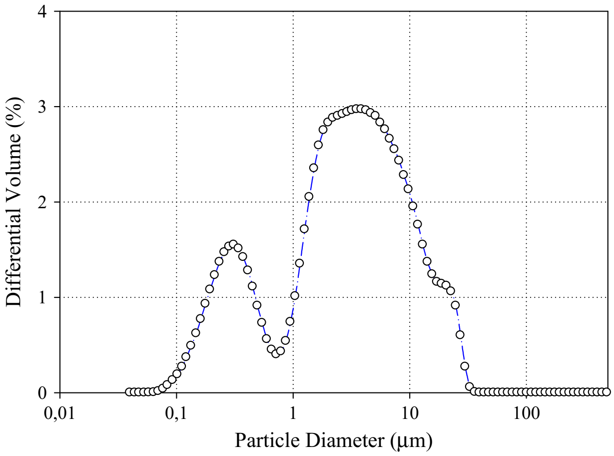

Fig. 1. Particle size distribution of kaolin particles (pH = 10).