Influence of dispersing agents and solution conditions on the solubility of crude kaolin

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Abstract

Experiments measuring the solubility of kaolin particles in terms of the concentration of aluminum and silicon ions in supernatant were carried out as a function of the pH of the slurry over a wide range of dosages of different dispersing agents varying from 0.5 to 12 mg/(g solids). The concentrations of the metal ions in supernatant were found to be strongly affected by the type and the dosage of the dispersants and pH of the solution. In this study, the mechanism of the reaction between the dispersing agents and kaolin particles was studied and the dissolution capacities of metal ions (aluminum and silicon) were identified from kaolin particles in the absence and presence of dispersing agents. The three anionic dispersing agents used were sodium polyacrylate (Na-PAA), sodium hexametaphosphate (Na-HMP), and sodium silicate (Na-silicate), based on the industrial application of these agents and their ability to produce a stable dispersion for this purpose.

Keywords: Kaolin clay; Solubility of kaolin; Sodium polyacrylate; Sodium hexametaphosphate; Sodium silicate

1. Introduction

Kaolin is widely used in industries such as paper manufacture, paints, pigments, ceramics, and concrete and also as a filler in polymers and other industrially important materials. Kaolin is used as a paper coating to enhance the brightness, opacity, smoothness, and printability of paper (e.g., [1]). In most of the above-mentioned applications highly concentrated stable kaolin dispersions of controlled fluidity and stability are needed, which can be achieved through the addition of inorganic and organic dispersing agents to the system. Rheological behavior and stability of kaolin dispersions are greatly affected by the solubility of kaolin particles and the concentrations of the dispersing agents, soluble salts, and metal ions arising from the solubility of the particles in the suspending media [1]. Therefore, the adsorption of the dispersants onto the surfaces of the particles, the mechanism of interaction of dispersing agents with the active sites of the particles and their effect on the solubility of kaolin, and also the reaction mechanism of dispersants with soluble ions from the particles become of significant importance.

Kaolinite crystal with the unit cell chemical composition Si₂Al₂O₅(OH)₄ consists of alternating layers of silica tetrahedra and alumina octahedra, and each kaolinite particle consists of several sheets of twin layers held together with hydrogen bonds. The aspect ratio of kaolin particles, which are platelike in shape, may vary from 5 to 15 depending upon the mechanical treatment of the particles [1–3].

There is a significant charge difference between the basal plane and the edge of the particles due to the difference between them in chemical composition. Kaolin edges contain both silica- and alumina-like charge sites but the faces contain only silica-like charge sites, which are expected to remain negatively charged above pH 3.0. The edges are positively charged at low pH, but progress through an isoelectric point to possess a negative charge at high pH [4,5]. As a result of this difference, in the absence of dispersing agents, electrostatic edge-to-face attraction causes agglomeration of the particles in the form of a card-house type structure (even at very low volume fractions) depending on the pH of the dispersion [6]. In applications such as paper coatings, the solids concentration of kaolin dispersions can be as high as
60–70% solids (wt) and the slurry is required to be well-dispersed, with acceptable flow characteristics for processibility [3]. Well-dispersed kaolin slurries may be achieved by increasing the pH of the suspension above the isoelectric point of alumina (IEP) through the addition of an alkali substance to the dispersion. Under this condition, the surface of the particles will be negatively charged, causing an increase in electrostatic repulsion between the particles, which may result in a well-dispersed suspension [6]. However, electrostatic stabilization may not be effective at high solids loadings, and also, increase in pH may not be desirable due to difficulties in processing the materials at high pH levels.

Kaolinite is a hydrophilic material and can be dispersed in water using anionic inorganics, polyelectrolytes, and surfactants. Adsorption of polymers and surfactants on the surface of kaolin as a function of pH, ionic strength, and polymer charge has been studied in the past (e.g., [7,8]). Understanding the mechanism of interaction of the dispersants with the active sites on the surface of the particles, the effect of the dispersants on the solubility of the clay particles, and the mechanism of reaction between the dispersing agents and the dissolved ions from the particles is important in terms of (1) control of the stability and rheological behavior of the dispersion, (2) proper selection of the currently available dispersants, and (3) design of new dispersing agents for mineral slurries of particles of heterogeneous surfaces.

Since stability and rheology of clay dispersions are affected by the concentration of the ions resulting from the solubility of the particles in the suspending media, our main objective in this study is to investigate the effect of dispersing agents on the solubility of kaolin particles and to understand the mechanism of reaction between different dispersants and dissolved metal ions in the supernatant. It is believed that stability and rheology of clay dispersions are affected by the dissolution capacity of the particles and the concentration of metal ions in the dispersion. Results are presented and discussed in terms of the effect of the dosage of the dispersing agents and pH on the concentration of aluminum and silicon ions in the supernatant.

2. Materials and methods

2.1. Materials

The kaolin used in this investigation was a high-purity-grade East Georgia crude kaolin without any pretreatment of the mineral surfaces, which was supplied by Engelhard Corporation. The sample was first characterized for moisture content, density, surface area, particle size distribution, and chemical composition.

The BET nitrogen specific surface area of the particles was determined (using a Quanta Chrome NOVA 1200 instrument) to be 20.32 m²·g⁻¹. Also, the surface area of the powder was measured using a mercury porosimeter (Quanta Chrome) and found to be nearly equal to the BET surface area, indicating that the micropores on the particles are not significant and all the surface area is available to dispersing agent molecules. The density of the powder was measured to be equal to 2.72 g cm⁻³ using a helium ultrapycnometer. The particle size analysis was conducted using a SediGraph 5100, which determines the diameter of the particles based on Stoke’s law using sedimentation velocity. Analysis of the data indicates that d₅₀ of the particles based on this method is nearly equal to 0.50 µm. Fig. 1 represents the size distribution of the kaolin particles used in this work. The particles were dispersed in a solution of Na-PAA and then loaded into a SediGraph 5100 for particle size analysis.

Chemical analysis of the powder, as will be discussed later, indicated a relatively pure sample with insignificant amounts of Mg²⁺, Ca²⁺, Na⁺, and other impurities.

Three anionic dispersing agents used in this study were (1) the sodium salt of a low-molecular-weight polyacrylic acid (MW = 3400, polydispersity index = 1.18 and 43.1% wt solids) which was provided by Vining Industries Inc. and used as received, (2) sodium hexametaphosphate (Na-HMP, 30% wt solids), and (3) sodium silicate (Na-silicate, 37.5% wt solids). Ultrapure water (Millipore) of specific resistivity greater than 18 MΩ·cm⁻¹ was used to prepare the suspensions in this investigation.

2.2. Methods

Stock solutions of dispersing agents were prepared to a concentration of 15,000 ppm by mixing the required amounts of each dispersing agent and ultrapure water for at least 2 h using a magnetic stirrer to achieve complete dissolution. All experiments were conducted using suspensions with a total volume of 60 cm³ contained in a 100-cm³ screw-capped centrifuged tube. Depending upon the volume fraction of kaolin and the dispersant dosage, the corresponding stock solution was diluted with ultrapure water to the desired concentration and used as the suspending fluid. The required mass of dry kaolin was then slowly added to the solution while the sample was mixed by shaking and vibration. After all the particles were added, the pH of the suspension was adjusted to the desired value using Fisher brand HCl and Na₂CO₃ as pH modifiers. Adjustment of pH was per-
formed in one direction only. After addition of kaolin, the suspensions were vigorously shaken by hand and the pH checked and readjusted, after which the samples were agitated using a Burrell Model 75 wrist action shaker for at least 17 h for equilibrium to be reached. Then, the samples were centrifuged at 15,000 rpm for 15 min and the supernatant was carefully withdrawn. Supernatants were then analyzed for the dissolved metal ions, mainly aluminum and silicon, using a Perkin–Elmer plasma (ICP-AES) instrument. The metal ions concentrations are reported as mg/l (ppm) in the supernatant.

Chemical analysis of the kaolin powder was conducted using the following procedure:

To remove the moisture from kaolin, the powder (about 5 g) was dried in an oven at 100–110°C for at least 1 h and then cooled in a dry chamber to room temperature. In order to decompose the chemical structure of kaolin, 0.5 g of the powder was completely mixed with 5 g of Na₂CO₃ (or a mixture of Na₂CO₃ and K₂CO₃) in a platinum crucible and then left in a preheated furnace at 900°C for 30 min. After the platinum crucible was removed from the oven, it was cooled to room temperature in a dry chamber and then transferred into a glass beaker containing 50 ml of 1/1 HCl (vol.) solution. After the completion of the chemical reaction, the platinum crucible was washed for several times with distilled water inside the beaker and then was removed from the medium. The contents of the beaker were boiled to evaporate all the water and then dissolved in another 50 ml of 1/1 HCl solution. Upon completion of the dissolution, the solution was filtered using ashless filter paper (Watman Number 40). The glass beaker was washed several times with distilled water while the solution was filtered at the same time. Washing of the filter paper was continued until the filtered solution became colorless; then the filter paper was placed in an empty preweighted clean porcelain crucible and left in a preheated furnace at 900°C for at least 1 h, cooled to room temperature, and weighed to determine the amount of acid insoluble (AI) in the sample. The volume of the filtered solution was completed to 1000 ml and a certain amount was used for chemical analysis employing a Perkin–Elmer plasma (ICP-AES) instrument. Chemical analysis of the sample indicates that the kaolin used in this work contains 38.54% Al₂O₃ and 46.34% SiO₂ as the main constituents, with very small amounts of TiO₂ (1.16%) and Fe₂O₃ (0.20%) as impurities. As can be observed, the ratio of SiO₂ to Al₂O₃ in the sample is equal to 1.20, which is very close to its theoretical value in kaolinite crystal (1.18), indicating a relatively pure sample.

Zeta potential measurements were conducted using a Matec AcoustoSizer Instrument (Matec Applied Science, Hopkinton, MA). The instrument consists of 400 cm³ volume sample cell, a variable speed stirrer, built-in conductivity and pH probes, a dual syringe module for precise reagent titration, and a thermostate to measure the temperature of the sample. The acoustic response of the dispersion subjected to an external, alternating electric field at different frequencies is measured using this instrument and the dynamic mobility and the particle size distribution of the particles is determined from the acoustic response. The advantage of the technique is that it is not limited to dilute suspensions.

3. Results

3.1. Solubility of kaolin in the absence of dispersing agents

The solubility reaction of kaolinite can be expressed as

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \equiv 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O} \quad (1)
\]

and

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{OH}^- + 5\text{H}_2\text{O} \equiv 2\text{Al(OH)}_4^- + 2\text{H}_4\text{SiO}_4 \quad (2)
\]

in acidic and basic conditions, respectively. Solubility of kaolin in terms of the concentration of the dissolved metal ions in supernatant was investigated in the absence of dispersing agents as a function of solids content and pH of the slurry.

Results indicated that in the absence of dispersants, while the concentration of the released silicon ions in supernatant increases with increasing the concentration of solids, aluminum ions do not appear significantly in supernatant over the entire range of solids loadings studied. Effects of pH and dispersant dosage on the solubility of kaolin particles have been reported in an earlier publications [9], but due to their importance, they need to be discussed in more detail. Results of the past study [9] indicate that in the absence of dispersing agents, while the concentration of silicon ions in supernatant decreases with increasing pH, aluminum ions do not appear in the solution over the entire pH range studied. This may be due to (1) formation and precipitation of Al(OH)₃, the solubility of which in water is very small in the pH range 4.5–8.5 [10,11], and (2) formation and precipitation of an aluminosilicate gel [12].

Due to the amphoteric nature of aluminum hydroxides, these materials are soluble in strong acids and bases, but at room temperature, they have a very low solubility over the pH range 4.5–8.5. Outside this range, solubility of Al(OH)₃ as a function of pH has a steep slope, meaning that a small change in pH can cause considerable supersaturation and, consequently, rapid precipitation of aluminum hydroxide. It is believed that in acidic solutions below pH 4, mononuclear Al³⁺ ions exist in the solution. As the pH is increased, a series of hydroxy–aluminum complexes is formed [10]. Yuan et al. [12] have explained the reduction in the concentration of silicon ions in terms of the formation of insoluble aluminosilicate gel that will be precipitated with solids during the centrifugation process. Also, the formation of an aluminosilicate gel layer on the surface of kaolin may prohibit dissolution of the particles, which will result in a decrease in the concentration of the released ions in supernatant.
In addition to the possible production of aluminosilicate gel, formation of aluminum hydroxide with negligible solubility in the pH range 4.5–8.5 that precipitates with solids may be another reason for the decrease in the concentration of Al\(^{3+}\) ions in supernatant. The solubility reactions of aluminum hydroxide in acidic and basic environments are [11]

\[
\begin{align*}
\text{Al(OH)}_3(s) + 3\text{H}_2\text{O}^+ &\rightleftharpoons \text{Al}^{3+}(aq) + 6\text{H}_2\text{O}, \\
\text{Al(OH)}_3(s) + \text{OH}^- &\rightleftharpoons \text{Al(OH)}_4^-(aq).
\end{align*}
\]

3.2. Solubility of kaolin in the presence of dispersing agents

The concentration of metal ions in supernatant resulting from the solubility of kaolin particles is significantly affected by the dosage of the dispersing agents used to prepare the slurry. Results presented in an earlier paper [9] indicate that Na-PAA and Na-HMP have similar effects on the solubility of kaolin particles for dosage levels up to 5 mg/(g solids). When the dosage of the dispersing agent is increased above 5 mg/(g solids), the concentration of aluminum ions in the supernatant is considerably higher in the presence of Na-HMP than in the case where Na-PAA is used as dispersing agent. The phosphorus ions have a strong affinity to aluminum ions and will compete with OH\(^-\) for aluminum ions to form water-soluble complex ions. Similar behavior was observed by Yuan et al. [12], who studied the influence of different dispersants on solubility of calcined kaolin and concluded that these complexes can displace the H\(_2\)O or OH\(^-\) ligand in the first coordination sphere of Al\(^{3+}\), inhibiting Al(OH)_3 crystallization and precipitation. It has been shown by Hsu [13] that the phosphate’s ability to form stable complexes is so strong that crystalline Al(OH)_3 cannot develop even at pH levels above 9–10 and therefore, almost all Al\(^{3+}\) will stay in the dissolved form.

When Na-PAA and Na-HMP are used as the dispersing agents, the concentration of the released aluminum ions in supernatant increased significantly with increasing the polymer dosage in the system. In an earlier study, we [14] have shown that PAA adsorbs on alumina sites present on the edges of kaolin particles and not on the silica sites, which are present on the basal planes of the particles. PAA contains ionizable carboxylic acid groups, which are capable of dissociation depending on the pH of the solution. Since kaolinite consists of silica-like charge sites on the basal planes and alumina-like and silica-like charge sites on the edge, understanding the adsorption behavior of PAA on the surface of pure alumina and silica and also interaction mechanism of this agent with the dissolved silicon and aluminum ions may help to (1) understand and reveal the adsorption of PAA on the surface of kaolin and (2) determine the effect of dispersants on the solubility of kaolin particles at different conditions. Therefore, it is briefly reviewed in this work.

Gebhardt and Fuerstenau [15] examined the adsorption of PAA onto silica and concluded that PAA does not adsorb onto silica due to electrostatic repulsion. In a later study by Ravishankar et al. [16] it was suggested that dissociated carboxylic acid groups (COO\(^-\)) adsorbed onto alumina surface by chelation with Al\(^{3+}\) surface sites, while undissociated carboxylic acid groups (COOH) adsorb via hydrogen bonding between the PAA carboxyl group and surface hydroxyls. Hence at lower pH values the adsorption mechanism is predominantly hydrogen bonding in nature. Similarly, for the PAA/alumina system, Santhiya et al. [17] suggested that below pH 4, PAA adsorbed via hydrogen bonding, while complexation occurred at high pH. The adsorption mechanism of PAA onto alumina has thus been described in the literature as both hydrogen bonding and chemical in nature, the contribution of each driving force being a function of solution pH.

Elfarissi et al. [18] measured a drop in pH when PAA at pH 5 was mixed with an aqueous solution of aluminum ions at the same pH, thereby suggesting the formation of a PAA–Al\(^{3+}\) complex in solution. These authors also studied changes in the zeta potential due to the interaction of PAA complexed with Al\(^{3+}\) ions. Their results indicate that below a critical concentration of polyelectrolyte, zeta potential is positive and shifts to lower values as the polymer concentration is increased further. Above the critical concentration of polyelectrolyte, zeta potential is negative and its magnitude increases with increasing the polymer concentration in this region.

In a recent study, Vermöhlen et al. [19] used DRIFT spectroscopy and ab initio calculations to show that PAA did indeed adsorbs onto the surface of alumina via complexation. These results along with the results of our earlier work on the adsorption of PAA on the surface of alumina, silica, and kaolin [14] show that negatively charged dispersing agents such as Na-PAA and Na-HMP adsorb on alumina sites of kaolin particles. The high concentration of aluminum ions in supernatant in the presence of these dispersing agents in the system suggests that aluminum ions form a water-soluble complex with each of these dispersing agents which remains in supernatant and therefore, can be detected by ICP measurements. As shown by Subramanian et al. [20], the pH of the dispersion has a significant role on the adsorption density of the dispersing agents onto the surface of the particles and therefore, on the reaction mechanism between the dissolved metal ions and the dispersants, as will be discussed later.

When Na-silicate was used as the dispersing agent, the concentration of aluminum ions in supernatant was very small as compared with those of the other two dispersing agents. Aluminum ions were not detectable in supernatant for Na-silicate dosage levels up to 4 mg/(g solids). Above this level, an increase was observed in the concentration of aluminum ions in the supernatant, which appeared to reach a plateau at higher levels of Na-silicate dosage. The low concentration of aluminum ions in supernatant (as compared with the cases of Na-PAA and Na-HMP) may be attributed to the formation of insoluble aluminosilicate gel as was explained earlier. It is reported by Okamoto et al. [21] and Iler [22] that as aluminum becomes available in solution, it will inhibit the release of silicon from kaolin, which may be
attributed to the formation and participation of aluminosilicate gel on the surface of solids.

### 3.3. Effect of pH

The effect of the pH of the dispersion on the concentration of aluminum and silicon ions in the supernatant for dispersions of kaolin particles of 35% solids (wt) prepared using 5 mg/g solids of dispersing agents are shown in Figs. 2 through 5. Figs. 2 and 3 represent aluminum ion concentration as a function of pH in the presence of Na-PAA and Na-HMP and Figs. 4 and 5 show the effect of pH on the concentration of silicon ions in the supernatant in the presence of the above mentioned dispersing agents. As can be observed from Figs. 2 and 3, the concentration of aluminum ions in the supernatant in the presence of both Na-PAA and Na-HMP strongly depends on the pH of the dispersion. The concentration of the ions in the supernatant is a maximum over a pH range of 5.5–7.0 in both cases. It appears that in the presence of dispersing agents, the released aluminum and silicon ions remain in the suspending liquid in water soluble forms. As was discussed earlier, in the absence of dispersants, aluminum ions were not detectable in the supernatant due to precipitation in the form of Al(OH)₃ and/or formation of insoluble aluminosilicate gel. The phosphorus ions and PAA polymer will compete with OH⁻ for Al³⁺ to form water-soluble complex ions, thus interfering with the dissolution and precipitation process of Al(OH)₃. As the pH of the dispersion is increased above the level of 6.5 or decreased below the level of 5.5, the concentration of aluminum ions in the supernatant decreases in the presence of both Na-PAA and Na-HMP.

Dissolution and precipitation kinetics of pure kaolinite in the absence of dispersing agents as a function of pH and chemical affinity and solution composition have been studied by Devidal et al. [23] and several other investigators. By changing the inlet solution composition (concentration of aluminum and silicon ions in the feed) to the reactor, dissolution and precipitation rates were found to be an inverse function of aqueous aluminum concentration at acidic and inverse function of aluminum and silicon concentrations at alkaline conditions.

Studies conducted by Devidal et al. [23] and Nagy et al. [24] indicate that steady state kaolinite dissolution is stoichiometric with respect to Al/Si ratio in both acidic and basic conditions at temperatures ranging from 60 to 230 °C. Carroll and Walther [25] have shown that at 25 °C, aluminum was released at a faster rate than Si during initial dissolution of kaolinite.

Figs. 4 and 5 show the effect of the pH of the dispersion on the concentration of silicon ions in supernatant when Na-PAA and Na-HMP are used as dispersing agents to stabilize kaolin dispersions respectively. In both cases, the concen-
tation of silicon ions in supernatant decreased significantly when the pH of the slurry was increased.

The data presented in this section indicate that the concentration of metal ions in supernatant in the presence of dispersing agents is strongly pH-dependent. Change in pH of the slurry will affect the association and dissociation of dispersing agents and the charge on different adsorption sites of kaolin particles. At pH levels below 4, the alumina sites present on the edge of the particles are highly positively charged. The loss of protons from PAA for the formation of negatively charged carboxylic acid functionalities will thus result in an electrostatic attraction of the polymer for the positively charged alumina sites on kaolin surfaces. The level of dissociation of PAA decreases as the pH of the slurry is decreased which will decrease the level of interaction between PAA molecules and aluminum ions in the solution. Therefore these ions may precipitate in the form of aluminum hydroxide and/or form aluminosilicate gel with the dissolved silicon ions.

Elfarissi et al. [18] have studied changes in the zeta potential due to the interaction of PAA complexed with Al$^{3+}$ ions and alumina by mixing PAA at pH 5 with an aqueous solution of aluminum ions at the same pH. Their results show that for low concentrations of PAA–Al$^{3+}$ complex, there was an increase in the magnitude of the zeta potential, presumably as a result of the magnitude of the positive charge of complexed Al$^{3+}$ ions outweighing that of negative charges being generated due to undissociated carboxylic acid groups forming complexes with surface aluminum ions. These observations confirm the results of this work on the decrease in the concentration of aluminum ions in supernatant at low levels of pH. Increase in the pH of the slurry will be in the favor of negative charge generation and hence complex formation, which will be accompanied by an increase in the concentration of aluminum ions in supernatant over a pH range which is believed to be in the range of the iso-electric point of the edge of the kaolin particles. Above this pH range, the overall charge on the edge of the particles becomes negative causing an increase in the overall repulsion between dissociated PAA molecules and negatively charged kaolin particles. This will not be in the favor of the dissolution of the particles and also, formation of PAA–Al$^{3+}$ complexes, which in any case is accompanied by a reduction in the concentration of aluminum ions in supernatant.

4. Effect of dispersants dosage on the fluidity of kaolin dispersions

The viscosity behavior of kaolin dispersions varies significantly with different factors including type of the stabilization method, and the amount and type of dispersing agents added to the dispersion. In the absence of dispersing agents, interparticle interactions between the edges and the basal planes of the particles promote aggregation of the particles into edge-to-edge, edge-to-face, or face-to-face structures, causing a significant increase in the viscosity of the dispersion, and therefore it is not possible to prepare concentrated kaolin dispersions without adding dispersing agents to the system. Dispersants can adsorb on the surface of the particles and produce a barrier that may prevent adhesion and agglomeration of the particles, which will result in a well-dispersed dispersion of low viscosity. The effect of Na-HMP on the viscosity of kaolin dispersions of 55% wt solids is presented in Fig. 6, which is a plot of viscosity as a function of the dosage of Na-HMP used to prepare the slurry. As can be observed, there is a decrease of several orders of magnitude in the viscosity of the dispersion as the dosage of Na-HMP is increased to 5 mg/(g solids) in the system. The results of our earlier work [14] indicate the negatively charged dispersing agents such as Na-PAA and Na-HMP adsorb on alumina sites present on the edge of kaolin particles and the dosage of 5 mg/(g solids) corresponds to the saturation adsorption of the dispersants on the surface of the edge of the particles.

Effect of the dosage of Na-HMP on the Smoluchowski zeta potential of dispersions of kaolin particles (suspension pH 7) is shown in Fig. 7 and as can be observed, over the entire range of dispersant dosage, the zeta potential values indicate a strong negative charge on the surface of the particles. The magnitude of the Smoluchowski zeta potential increases significantly as the dispersant molecules gradually covers the surface of the particles and reaches a plateau corresponding to the value of saturation adsorption density. The Smoluchowski zeta potential of the bare kaolin surface at pH 7.0 is approximately equal to $-16 \text{ mV}$. It can be observed
that, as the amount of Na-HMP added to the dispersion is increased to 5 mg/(g solids), the Smoluchowski zeta potential approaches a plateau value of approximately −46 mV, corresponding to the saturation adsorption and critical concentration of Na-HMP added to the dispersion for minimal viscosity.

5. Summary and conclusions

The objective of the present work was to investigate the effect of different dispersing agents and solution conditions on solubility of particles of heterogeneous surfaces using kaolin as a model system. The ultimate objective of this study is to investigate the effect of the released metal ions on stability and rheology of the system to develop more effective dispersing agents for engineered slurries of particles of heterogeneous charges. Three different anionic commercially available dispersing agents used in this work were (1) sodium salt of a low-molecular-weight polyacrylic acid (Na-PAA), (2) sodium hexametaphosphate (Na-HMP), and (3) sodium silicate (Na-silicate). In the absence of dispersing agents, while the concentration of silicon ions in supernatant showed a decrease with increasing pH, aluminum ions did not appear in the solution over the entire pH range studied. This was explained in terms of the formation and precipitation of aluminum hydroxide and/or formation of insoluble aluminosilicate gel in the system.

It appears from the data that the concentration of the metal ions in supernatant is highly affected by the dosage of the dispersing agents and pH of the slurry. The concentration of aluminum ions in supernatant in the presence of both Na-PAA and Na-HMP is maximum over a pH range of 5.5–6.5. Results indicate that Na-PAA and Na-HMP have similar mechanisms of reaction with kaolin particles. The high concentration of aluminum ions in supernatant in the presence of these dispersing agents in the system suggests that aluminum ions form a water-soluble complex with each of these dispersing agents which remains in supernatant. In the presence of Na-silicate, aluminum ions were not detectable in supernatant for Na-silicate dosage levels of up to 4 mg/(g solids), which is attributed to the formation, and precipitation of insoluble aluminum hydroxide and/or aluminosilicate gel.

Overall, the amount of the released aluminum and silicon ions in supernatant is largely related to the type and dosage of the dispersing agents and pH of the dispersion. The results of the current paper will be used to study the effect of the solubility and reaction between the dispersing agents and the dissolved ions on the performance of the slurry in terms of stability and flow properties of the system.

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References