

CRUDE KAOLIN DISSOLUTION IN THE ABSENCE AND PRESENCE OF SODIUM POLY(ACRYLIC ACID), SODIUM HEXAMETAPHOSPHATE, AND SODIUM SILICATE UNDER DIFFERENT EXPERIMENTAL CONDITIONS

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Abstract—The influence of anionic dispersing agents, such as sodium poly(acrylic acid), sodium hexametaphosphate, and sodium silicate on the dissolution of crude kaolin was examined by measuring the dissolved metals produced in the absence and presence of dispersing agents. For this purpose, the rheological and structural changes caused by the dissolution of kaolin metal constituents were studied in batch mode using several parameters, namely, solids (wt.%), pH, contact time (aging), and dispersing agent dose. A noteworthy increase in kaolin dissolution was caused by the presence of dispersing agents, particularly poly(acrylic acid) and sodium hexametaphosphate. These agents produced conspicuously large amounts of dissolved Al in comparison to the other experimental treatments. Little dissolved Si was measured under similar conditions in distilled water, but the amount of Si released using dispersing agents was nearly double that observed in distilled water only. Excess dispersing agents interacted with kaolin and dissolved accessory elements in the kaolin (*i.e.* Fe, Ca, Mg) and thus released enough Fe to form a stable Fe–dispersant complex. The present study showed that this phenomenon also contributed to a significant increase in the release of dissolved Al and Si through complexation.

Key Words—Anionic Dispersing Agents, Kaolin Dissolution, Release of Dissolved Al and Si, Sodium Hexametaphosphate, Sodium Poly(acrylic acid), Sodium Silicate.

INTRODUCTION

Kaolinite is a significant clay mineral that has been widely used due to the whiteness, fine particle size, and plate-like structure. It is very feasible for use as a coating, carrier, or diluent in fertilizers and pesticides and as a functional filler, extender, ceramic raw material, and pigment. Therefore, it is broadly used in the paper, paint, rubber, plastic, ceramic, cosmetic, and dye industries with new applications being discovered in a wide variety of industrial and non-industrial fields (Murray and Kogelb, 2005; Konta, 1995; Ayadi *et al.*, 2011). It also has significant applications as a raw material in refractories, catalysts, concrete, and fiberglass. The increasing demand for high quality paper and paper products has led to the use of kaolin in papermaking for many years, both as a coating pigment and as a filler to replace fiber because it possesses desirable optical properties. Because kaolinite is chemically inert and relatively inexpensive compared to other minerals, it holds advantages that lead to wide use.

Kaolinite and other kaolin group minerals are hydrated aluminum silicates with a chemical formula of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and have a 1:1 structure with one octahedral alumina sheet and one tetrahedral silica sheet.

It is a plentiful and naturally available mineral that occurs in the form of thin, roughly hexagonal platelets, and the aspect ratio (length-to-thickness ratio) of the particles usually varies from 5–15, depending on the mechanical treatment (Solomon and Hawthorne, 1983). The octahedral alumina and tetrahedral silica sheets share one of the four oxygen atoms of the octahedral sheet to form one layer of kaolinite. The layers of kaolinite in a particle are bound together through hydrogen bonding and each particle consists of approximately 50 alternating layers (Lagaly, 2006).

The effective control of the rheological behavior of concentrated kaolin suspensions is a noteworthy challenge due to the formation of intractable card-house-type agglomerates that are encountered during industrial operations. Agglomerates can cause unforeseen sol–gel transitions that can have a clear effect on dispersion flow behavior, such as pumpability and processability. In most practical applications, such as paper coating, highly concentrated stable kaolin dispersions of controlled fluidity and stability are required for processability (Zaman *et al.*, 2003; Bossard *et al.*, 2007; Loginov

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et al., 2008). Thus, organic and inorganic dispersants are added to the system to obtain suspensions at the desired stable viscosity. The dispersants resolve significant and common industrial problems of suspensions by modifying the charge of particles and allowing the preparation of suspensions at high solid loadings in terms of the rheological behavior and convenient processability (Yuan *et al.*, 1998; Johnson *et al.*, 2000; Penner and Lagaly, 2001; Moan *et al.*, 2003; Mark, 2011). The use of negatively charged polyelectrolytes is regarded as promising with the merits of simplicity, high efficiency, ease of operation, and applicability to kaolin suspensions because the kaolin particle edges account for approximately 20% of the total kaolin surface area (Zaman *et al.*, 2001; Ayadi *et al.*, 2011). Polyelectrolytes modify particle surfaces to produce a uniformly charged state by either polymer and surfactant adsorption onto kaolin particle surfaces, by adjustment of the surface charge through compression of the electrical double layer or by ion shielding of the surface charge with electrolytes (Benchabane and Bekkour, 2006; Desai *et al.*, 2010).

Kaolin dissolution in the absence and presence of dispersing agents has been widely investigated because this process is believed to play a significant role in governing the colloidal behavior of kaolin dispersions. Thus, Chin and Mills (1991) examined the effect of protons and low-molecular-weight organic ligands on the kinetics and mechanisms of kaolinite dissolution. Their investigations showed that the rate of dissolution increased as H^+ concentrations were increased and that the Si dissolution rate was generally faster than that of Al in the absence of organic ligands. The presence of low-molecular-weight organic ligands, however, noticeably increased the dissolution rates of both Al and Si. In other studies performed by Carroll-Webb and Walther (1988) and Carroll and Walther (1990), kaolinite dissolution over the 1 to 12 pH range was investigated by employing malonic acid to sustain Al ions in solution at pHs between 5 and 10. Their results revealed that the initial dissolution rate was nonstoichiometric and the steady-state period was quasi-stoichiometric between pH 2 and 9. Wieland and Stumm (1992) studied dissolution kinetics in the pH 2 to 6.5 range, which revealed that the dissolution reaction was not stoichiometric and favored release of Si over Al. The dissolution reaction was, therefore, stoichiometric in the presence of oxalate as an Al-complexing ligand. They claimed that Al ions that were detached from kaolinite structural surfaces and simultaneously re-absorbed on distinct surface sites during dissolution caused the experimentally observed non-stoichiometry. The use of oxalate and salicylate not only formed surface complexes with alumina centers, but also promoted the release of both alumina and silica centers during dissolution. Another investigation performed by Devidal *et al.* (1997) and Nagy *et al.* (1991) showed that the steady state dissolution of kaolinite was stoichiometric with respect to the Al/Si ratio in both

acidic and alkaline suspensions between 60 and 230°C. Huertas *et al.* (1998, 1999) studied the dissolution of an aqueous kaolinite suspension at pH 1–13. They claimed that the mechanism of kaolinite dissolution depends on the behavior of multi-site particle surfaces that produce the charged surface complexes. The surface complexes were formed by protonation/deprotonation of surfaces in different pH ranges and were the precursors of the detachment step in the dissolution reaction. Studies conducted by Yuan *et al.* (1998), Zaman *et al.* (2003), and Zaman and Mathur (2004) on the solubility of metal ions extracted from kaolinite particles using different dispersing agents found that the Al and Si concentrations were substantially affected by the dispersing agent type, dose, and suspension pH. A significant increase in dissolved metals was observed in the supernatants, particularly in the presence of sodium poly(acrylic acid) (NaPAA) and sodium hexametaphosphate (NaHMP). In another study performed by Altioikka and Hoşgün (2003), the dissolution rate of calcined kaolin in HCl solution was highly sensitive to the reaction temperature. Andreola *et al.* (2004) examined the role of NaHMP in the dissolution of kaolinite and kaolin and found that it significantly affected metal release from the kaolinite/kaolin structure and surfaces that depended on the clay material and on the NaHMP dose. Andreola *et al.* (2007) also investigated deflocculated suspensions of kaolinite that had previously been treated with NaHMP and sodium disilicate and determined that the nature of the treatment affects metal solubility for a kaolinite previously treated with sodium disilicate. It significantly reduced the accessibility of the HMP molecules to alumina sites on the clay surface due to the competitive presence of adsorbed silica derivatives. Yang and Steefel (2008) investigated kaolinite dissolution and precipitation kinetics at 22°C, 1 bar pressure, and pH 4 as a function of reaction affinity. Their results revealed that the dissolution rates near equilibrium exponentially decreased in comparison to the dissolution rate far from equilibrium. This implies that the activated complexes that were involved in the rate-limiting step for kaolinite dissolution contained either a single Al or Si atom.

All of these studies greatly contributed to an understanding of the complex dissolution actions observed in suspensions with and without different dispersing agents and under different experimental conditions. Although many investigations have been performed on the dissolution of kaolin by dispersants, no exact elucidation of the dissolution mechanism and reaction kinetics has been achieved.

In this study, the dissolution of crude kaolin was investigated in NaPAA-kaolin, NaHMP-kaolin, and Na-silicate-kaolin suspension systems that were prepared over a wide range of solid loadings, dispersant doses, and aging times. The effect of several parameters, namely, solids (wt.%), dispersant dose, pH, and contact

time (aging) were tested in batch mode. The objective of this study was to identify the dissolution action of dispersants on kaolin in terms of the dissolved kaolin constituents by evaluating apparent viscosity measurements, pH variations, and the concentrations of metals released from suspensions prepared in the absence and presence of dispersing agents under various experimental conditions.

MATERIALS AND METHODS

Materials

East Georgia crude kaolin was supplied by the Engelhard Corporation (Georgia, USA) and was used without any organic or inorganic additives. The East Georgia crude kaolin contained impurities, such as oxides of titanium and iron, and may also contain small amounts of mica, quartz, and other ancillary minerals. The Fe_2O_3 content ranged from 0.17 to 1.1 wt.% and almost all of this Fe_2O_3 was in the kaolin structure. Most of the TiO_2 was present as anatase that contains small amounts of iron oxides (Stucki *et al.*, 1988).

The kaolin sample was used as received without any further purification to prevent possible modification of the surface characteristics. All of the samples were out-gassed on a Quantachrome AUTOSORB-1 model AX1C-MP-LP gas adsorption analyzer (Quantachrome Instruments, Boynton Beach, Florida, USA) for 24 h at 110°C under vacuum prior to measurement. The kaolin powder has a specific surface area of $20.3 \text{ m}^2 \text{ g}^{-1}$ as determined by N_2 adsorption (BET) using a Quantachrome NOVA 1200 gas adsorption analyzer (Quantachrome Instruments, Boynton Beach, Florida, USA). A Quantachrome Poremaster Hg porosimeter

(Quantachrome Instruments, Boynton Beach, Florida, USA) was also used to determine the specific surface area of the kaolin powder which was found to be almost equal to the BET N_2 specific surface area. This indicates that micropores on the particle surfaces were not significant such that all of the surface area was available for adsorption by the dispersing agent molecules. A Quantachrome Ultrapycnometer (Quantachrome Instruments, Boynton Beach, Florida, USA) was used to determine an absolute powder density of 2.72 g cm^{-3} with a kaolin powder moisture content of $0.86 \pm 0.07 \%$. The kaolin particle size distribution was determined using a Coulter LS 230 instrument (Beckman Coulter, Inc., Brea, California, USA) which utilizes the light-scattering technique, a small volume module, and characteristic diameters (d_{10} , d_{50} , and d_{90} determined to be 0.301, 3.363, and 13.37 μm , respectively). The shape of the kaolin particles was determined using a JEOL JSM 6330F (JEOL USA, Inc. Peabody, Massachusetts, USA) field emission scanning electron microscope (SEM) (Figure 1). The observed particles were characteristically thin, roughly hexagonal platelets.

All of the dispersing agents employed in this investigation were supplied by Vinings Industries, Inc. (Atlanta, Georgia, USA) and were used as received without any treatment. The sodium poly(acrylic acid) (NaPAA) is a low-molecular-weight anionic polyelectrolyte containing 43.1 wt.% solids with a molecular weight of $3,400 \text{ g mol}^{-1}$ and a polydispersity index of 1.18. The sodium hexametaphosphate (NaHMP) contained 30 wt.% solids and the sodium silicate (Na-silicate) contained 37.5 wt.% solids. All of the suspensions were prepared using ultrapure water produced by a Millipore filtration system (EMD Millipore Corporation,

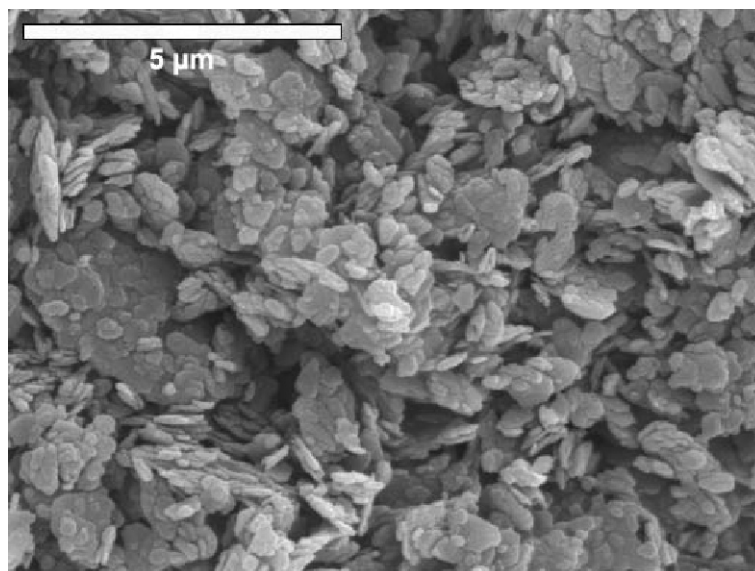


Figure 1. SEM image of crude kaolin particles. Bar = 5 μm .

Merck KGaA, Darmstadt, Germany) with a resistivity $>18.2 \text{ M}\Omega\text{-cm}$ and $<7 \text{ ppb}$ carbon.

Chemical analysis of the crude kaolin was conducted at the beginning of the investigation using the analysis procedure detailed in Demir (2015). The chemical composition of the kaolin sample was found to be 38.04% Al_2O_3 , 46.44% SiO_2 , 1.19% TiO_2 , 0.18% Fe_2O_3 , and 14.15% Loss on Ignition (L.O.I). No CaO or MgO was detected, which indicates a relatively pure kaolin sample with insignificant amounts of Ca, Mg, Na, and other impurities.

Preparation of kaolin suspensions

Three different stock solutions were prepared by mixing 15.0 g (dry basis) of NaPAA, NaHMP, or Na-silicate with 1000 cm^3 of ultrapure water. To achieve complete dissolution of the dispersion agents, the stock solutions were stirred using a magnetic stirrer for at least 2 h in a volumetric flask. All of the kaolin suspensions used in this investigation were prepared with a total volume of 60 cm^3 in 100 cm^3 screw-cap centrifuge tubes. The stock solution of each dispersing agent was diluted with ultrapure water to the selected concentration. The selected concentrations depended on the kaolin volume fraction and the dispersion agent dose. These diluted dispersing agent solutions were used as the dispersing fluids. The dispersing fluid was initially poured into the centrifuge tube and the kaolin powder was slowly added in the required amounts to the solution while stirring with a vortex mixer to ensure efficient mixing. After preparing the suspensions under the desired conditions, the solutions were agitated using a Burrell Model 75 Wrist-Action Shaker (Burrell Scientific, Pittsburgh, Pennsylvania, USA) for at least 24 h to reach equilibrium.

Measurement of metals dissolved from the kaolin particles

For the dissolution studies, the kaolin suspensions were prepared as described in *Preparation of kaolin suspension* and was equilibrated for 24 h. Then, the kaolin suspensions were centrifuged at $25,200 \times g$ for 15 min using a Beckman Model J2-21 Centrifuge (Beckman Instruments, Inc., Palo Alto, California, USA) to sediment the kaolin. The clear supernatants were carefully removed and poured into small glass test tubes. All of the supernatants were set aside overnight in a refrigerator to allow the remaining suspended particles to settle because the presence of even a few particles could adversely affect the subsequent analysis. The Al and Si dissolved from the kaolin particles were measured in the supernatants using a Perkin Elmer Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) instrument (PerkinElmer, Inc., Norwalk, Connecticut, USA) and the concentrations were reported as mg/L (ppm). Both Al and Si had detection limits of less than 0.1 mg/L.

Rheological measurements

To determine viscosity changes in the kaolin suspensions immediately after equilibration, the absolute viscosities were measured using a Paar Physica UDS 200 Rheometer (Anton Paar, Ashland, Virginia, USA) as the shear rate was changed from low to high and the results were recorded at shear rates of 10, 100, and 1000 s^{-1} . The pH of the kaolin suspensions varied between 4.5 and 8.9 and the temperature was isothermal at $25 \pm 1^\circ\text{C}$ during the measurements. Two different geometries, a plate (MP31) measuring 50 mm in diameter and a cone (MK24) measuring 75 mm in diameter, were used according to the rheological behavior of the suspension. For highly viscous suspensions, the MP31 plate was used and the gap size was adjusted according to suspension loading. When the viscosity was very low, the MK24 cone was used and the gap size was kept constant at 0.05 mm. A wet cover was placed around and on top of the aqueous suspension when it was in the rheometer in order to reduce water evaporation. For all measurements, the shear rate was changed from 0.01 to $10,000 \text{ s}^{-1}$ and this procedure was repeated for each sample.

RESULTS AND DISCUSSION

Effect of solids loading on the dissolution of crude kaolin

First, kaolin dissolution studies in the absence of dispersing agents (Figure 2) were performed by measuring dissolved metal concentrations lost from the kaolin particles as a function of suspension % solids without any additives or adjustments. However, the suspensions were only allowed to reach 48.48 wt.% solids and did not exhibit the intended rheological behavior because of charge heterogeneity on the kaolin particle surfaces. The results revealed that dissolved Si increased with the kaolin suspension solids concentration; however, the dissolved Al concentration seemed unaffected by solids concentration over the entire solids loading range. This result was expected due to the absence of dispersing agent in the kaolin suspension to interact with the kaolin surfaces to form water-soluble Al-dispersant complex ions. Huertas *et al.* (1999) suggested that when dissolution reactions occur at solid–water interfaces, protons, hydroxyls, water molecules, other ions, or organic ligands are capable of reacting with cations at fully hydrated kaolinite surfaces to form a precursor surface complex that can be involved in the cation detachment step. Because the Huertas *et al.* (1999) experiments were conducted at neutral pH without any dispersing agent, no Al ions were produced and the dissolution was nonstoichiometric. Huertas *et al.* (1999) suggested that this nonstoichiometric dissolution was caused by Al precipitation after congruent dissolution. Therefore, Al ions dissolved from the kaolin powder might have precipitated as an Al–hydroxide phase

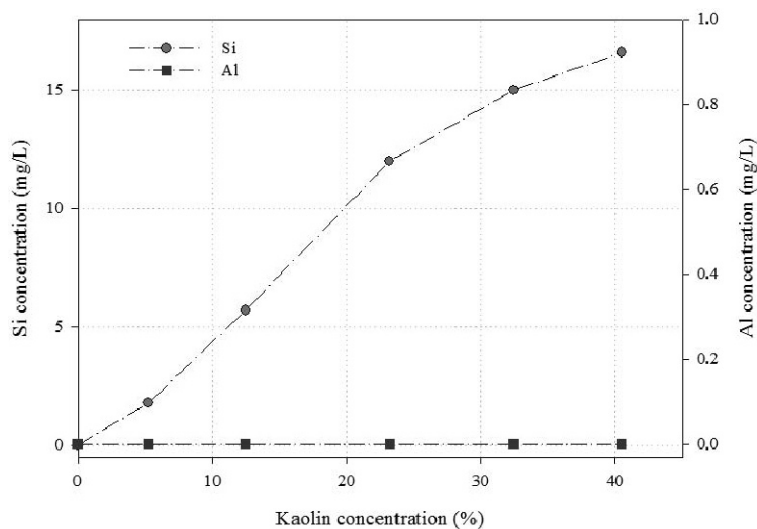
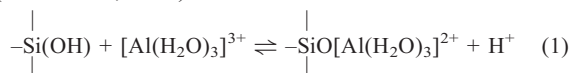


Figure 2. Dissolution of Al and Si from kaolin particles in the absence of dispersing agents.

because Al hydroxides have very low solubility product values of $\sim 1.3 \cdot 10^{-33}$ at pH values of 4 and 10 and can form colloidal $Al(OH)_3$ precipitates at room temperature (Yuan *et al.*, 1998; Zaman and Mathur, 2004; Feng *et al.*, 2008) or the Al can be re-adsorbed to the particle surface (Wieland and Stumm, 1992; Huertas *et al.*, 1998). Dissolved Al ions can readily be precipitated as $Al(OH)_3$ by increasing the pH to neutral or slightly alkaline values. In addition to the low dissolved Al concentrations, dissolved Si (Figure 3) also decreased at higher pH values due to the formation of an insoluble aluminosilicate gel (equation 1), which was likely removed with the kaolin solids during centrifugation (Yuan *et al.*, 1998).



Moreover, the aluminosilicate gel could create a surface layer on the kaolin that can inhibit dissolution of the kaolin particles. The term $-Si(OH)$ in the equation represents the reactive silica surface and $-SiO[Al(H_2O)_3]^{2+}$ represents the aluminosilicate gel. These results are consistent with the studies of Chin and Mills (1991), Xie and Walter (1992), Yuan *et al.* (1998), Huertas *et al.* (1998, 1999), and Zaman *et al.* (2003).

In studies with dispersing agents conducted prior to the dissolution experiments, the critical (optimum) doses of NaPAA, NaHMP, and Na-silicate were determined to be 5 mg of dispersing agent/g of solids from the apparent viscosity of kaolin suspensions as a function of dispersant dose. Critical or optimal dispersant dose was

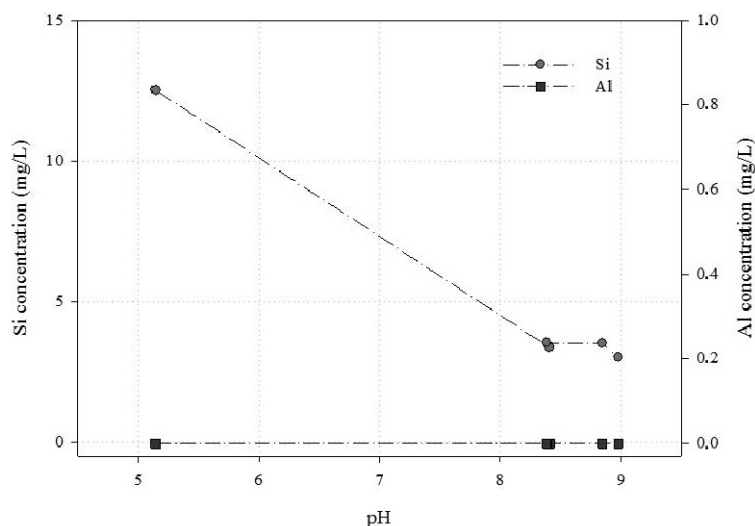


Figure 3. Effect of pH on dissolution of metals from kaolin particles at a fixed solid concentration of 35 wt.% solids in the absence of dispersant.

Table 1. Concentration (mg/L) of dissolved metals in kaolin suspensions with 5 mg dispersant/g kaolin solids and NaPAA, NaHMP, and Na-silicate dispersants at various wt.% solids and 24 h contact times.

Wt.% solids	NaPAA						NaHMP						Na-silicate					
	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca
5.25	9.84	1.91	0	0	0	0	8.13	3.76	0	0	0	0	0.837	63.3	0	0	0	0
12.5	23.2	5.6	0	0	0	0	20.6	10.2	0	0	0	0	2.32	102	0	0	0	0
23.2	42	14	0	0	0	0	39.3	18.9	0	0.059	0	0.437	5.03	129	0	0	0	0
32.43	62.6	18.3	0	0	0	0	57.3	25.8	0	0.338	0.847	1.7	7.67	139	0	0	0	0
40.48	84.2	25.3	0	0	0.911	0	74.2	35.9	0	0.697	2.04	3.27	18.4	162	0	0	0	0
53.83	112	37.9	0	0.879	3.13	0	101	55.4	0	1.12	4.72	6.58	18.1	138	0	0	0	0
64.46	142.5	55	0	0	0.382	0	133	86.8	0	1.78	10.7	13.5	24.05	114	0	0	0.278	0
68.99	NA	NA	NA	NA	NA	NA	151	98	0	1.96	14.4	17.6	NA	NA	NA	NA	NA	NA

determined using a deflocculation curve with different dispersant doses at the same kaolin loading. The optimum dispersant dose was the value which produced the minimum viscosity. Various concentrations of kaolin suspensions were prepared using the critical dispersant dose and the dissolved element concentrations are summarized in Table 1. The rheological measurements (Figure 4) were made at a shear rate of 1000 s^{-1} . Results indicated that suspension concentrations as high as 68.99 wt.% solids had good flow behavior and were stable at the desired viscosity.

In general, the dissolved Al concentrations using NaPAA and NaHMP clearly increased as the kaolin suspension concentration was increased. A similar behavior was observed for Na-silicate, but the suspended solids values were less than for the other dispersants. The Al concentration at 53.83 wt.% solids for NaPAA and NaHMP, for example, was approximately 105 ppm, whereas the Al value for Na-silicate was only 20 ppm at the same wt.% solids. Similar to Al, the Si concentra-

tions for the dispersants also increased, except for Na-silicate. Moreover, an inversion in the solubility ratios of Al and Si relative to distilled water was observed. Dissolved Mg slightly increased at suspension levels above 53.83 wt.% solids, but only for NaHMP.

To evaluate more accurately the influence of solids loading on elemental release from the kaolin powder at the critical dispersant dose, normalized concentrations of Al and Si were calculated (Figures 5 and 6) on the basis of measured Al and Si concentrations. The values were based on the fraction of the dissolved Al and Si that corresponded to the kaolin solids content of the suspensions. The results indicate that the dissolved Al concentrations in the solution were nearly the same and followed the same pattern as solids loading for NaPAA and NaHMP (Figure 5). This suggests that similar amounts of PAA and HMP acted in the same manner for adsorption to the same sites on the kaolin particles, where positively charged alumina sites of kaolin particles were modified and covered through adsorption

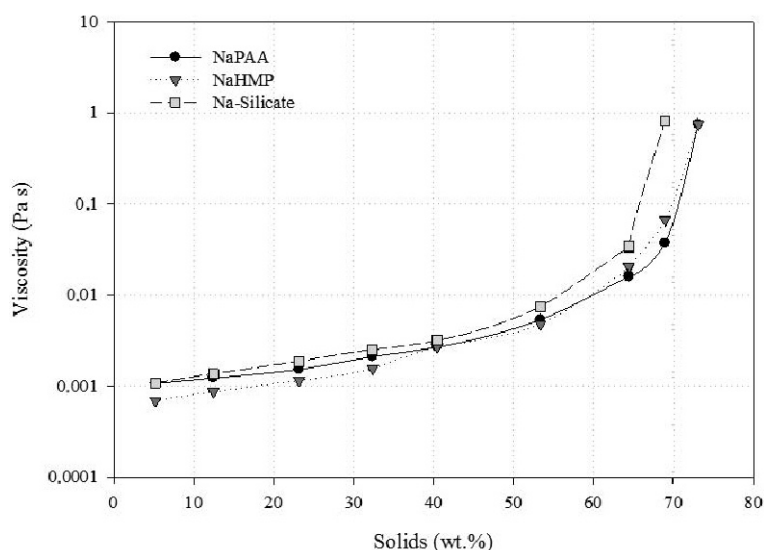


Figure 4. Variations in kaolin suspension viscosities at a shear rate of 1000 s^{-1} in the presence of dispersing agents at various wt.% solids and 5 mg dispersant/g kaolin solids at the critical dispersant dose.

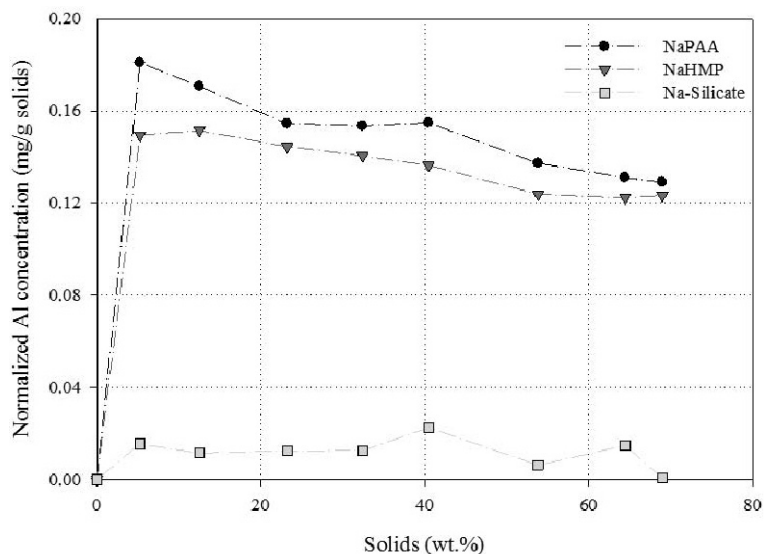


Figure 5. Normalized Al concentrations as a function of wt.% solids in kaolin suspensions at a fixed 5 mg dispersant/g kaolin solids.

of these anionic polymers. The greater extraction of Al was caused by NaPAA and NaHMP additions because dissociation of these compounds in solution yielded negatively charged PAA carboxylate groups ($-\text{COO}^-$) and HMP phosphate groups that had a strong affinity towards Al ions. The PAA and HMP adsorbed on particle edges to form water-soluble complexes of the Al dispersant that could be measured using ICP. The HMP adsorption mechanism suggested by Andreola *et al.* (2007) involved the formation of an inner sphere complex that included kaolinite surface Al ions and HMP oxygen(s). Yuan *et al.* (1998) also suggested an adsorption mechanism for HMP and claimed that phosphate ions could displace the H_2O or OH^- ligand in the first coordination sphere of Al ions, thereby

preventing $\text{Al}(\text{OH})_3$ crystallization and precipitation. In summary, the PAA and HMP compete with hydroxide ions for the Al ions to form water-soluble complex ions.

Because one of the kaolin basal planes is composed of silica, these surfaces are silica-like or negatively charged within the working pHs. The PAA and HMP did not interact with the silica surface of kaolin, thus, small amounts of Si were extracted into the supernatant during treatment (Figure 6). The amount of released Si was, however, nearly double that observed in distilled water because of the surface complexes formed between the alumina centers and PAA or HMP promoted the release of the silica centers and the detachment of Al ions that might open the silica structure to the attack of hydroxyls during the dissolution process. The studies of Wieland

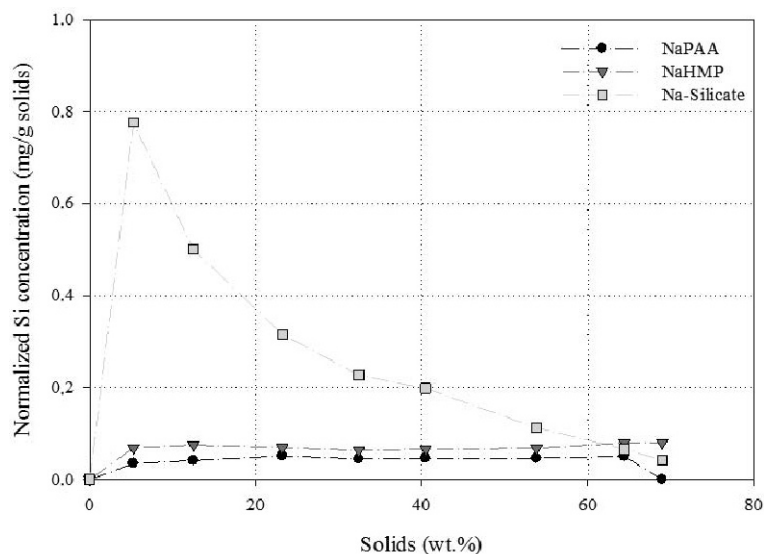


Figure 6. Normalized Si concentrations as a function of wt.% solids in kaolin suspensions at a fixed 5 mg dispersant/g kaolin solids.

and Stumm (1992) and Huertas *et al.* (1999) affirmed that the detachment of Al from the kaolin surface can open the silica structure.

The Na-silicate caused a slight increase in dissolved Al, but at much lower concentrations than the two other dispersants (Figure 5). The kaolinite and Na-silicate interaction mechanism proposed by Andreola *et al.* (2004) was between Na-silicate silanol groups and kaolinite surface hydroxyls through a condensation reaction in addition to hydrogen and van der Waals bonds. Amorós *et al.* (2010) also reported that Na-silicates contributed Na ions to the suspension, which replaced Ca gegen ions with Na ions, and thus changed the edge charge from positive to negative by polyanion adsorption. This resulted in a pH increase in the suspension, which produced negative edge charges that produced more dissolved Al. This test demonstrated, therefore, that the release of small amounts of dissolved Al stemmed from these phenomena.

The amount of Si released from the Na-silicate was excessively high at a low solids loading because of the Na-silicate contribution to dissolved Si, but then regressed with an increased solids concentration because Na-silicate is an alkaline material and it thus significantly increased the pH of the suspensions. Thus, an insoluble aluminosilicate gel was formed and was removed with the kaolin solids during centrifugation.

Effect of varying the dispersing agent dose on crude kaolin dissolution

The suspension viscosity was high at low dispersing agent doses due to insufficient coverage or modification of the positively charged alumina surfaces of the kaolin particles. These interactions between particle edges and basal planes promoted the formation of card-house structures, which depended on the chemical characteristics of the system as documented by Demir (2015). Further additions of dispersing agent significantly decreased the suspension viscosity and, thus, the critical dispersant dose was determined by the minimum viscosity and resulted in a well-dispersed suspension. To evaluate the contributions of NaPAA, NaHMP, and

Na-silicate to kaolin dissolution, suspensions were prepared with dispersant doses that ranged from 0.5 to 12 mg/g solids and the dissolution results are summarized in Table 2.

As expected, NaHMP produced a remarkably high amount of dissolved Al due to the better ability to form soluble complex ions in comparison to Na-silicate. Hsu (1989) reported that, because phosphate anions have a very strong ability to form soluble complex ions with Al, they inhibit Al(OH)₃ crystallization and precipitation. Hence, crystalline Al hydroxide cannot develop even at high pH levels and, thus, almost all of the Al released from kaolin powder was dissolved Al. The test results strongly support this conclusion because the use of NaHMP with 10 and 12 mg/g solids critical doses leads to a significant and incessant increase in Al dissolution (Table 2). Large amounts of soluble Al at dispersant concentrations over the critical dose can also be explained by progressive solubilization and continuous phosphate reaction with the positively charged edges of kaolin particles. The following processes contributed to kaolin dissolution: reactions with the lower layers or edge surfaces of kaolin particles, phosphate reaction with and destruction of previously formed Al hydroxides, and elemental loss due to cation exchange. The rather high dissolved Fe, Ca, and Mg contents (Table 2) support this explanation and indicate the contribution of kaolin edge surfaces and interlayers to dissolution through chemical reaction with kaolin accessory minerals at dispersant doses of 10 and 12 mg/g kaolin solids. Otherwise, because the positively charged alumina surface is covered by HMP adsorbed at the critical NaHMP dose, Al dissolution should not have been this high and should have either decreased or slightly increased. Andreola *et al.* (2004) obtained analogous results from their study and suggested that in addition to the strong complexing ability exerted by polyphosphates towards Al kaolinite, which could lead to the production of more dissolved Al. The Al contributed through the chemical reaction of accessory minerals with polyphosphates should also partially account for the high Al concentrations.

Table 2. Concentration (mg/L) of dissolved metals in the kaolin suspensions with added NaPAA, NaHMP, and Na-silicate at 55 wt.% solids and 24 h contact time.

Dose, mg/g solids	NaPAA						NaHMP						Na-silicate					
	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca
0.5	0	25.8	0	0	0	0	1.23	31.2	0	0	5.21	5.71	0	100	0	0	1.86	2.29
1	0	21.7	0	0	2.52	0	2.37	38.7	0	0	3.2	3.57	0	137	0	0	0.377	0.676
2	1.04	19.8	0	0	1.36	0	9.39	46.8	0	0	1.88	2.14	0	147	0	0	0	0
3	0.224	19.5	0	0	0.504	0	25.1	49.9	0	0	2.07	2.6	0.992	137	0	0	0	0
4	35.6	41.3	0	0	0.696	0	59.2	52.2	0	0	3.36	4.51	8.4	118	0	0	0	0
5	136	51.3	0.588	2.3	4.08	0	116	56.6	0	1.47	6.22	8.4	16.6	150.5	0	0	0	0
10	200	50.8	1.61	4.72	46.4	5.02	285	68.4	0.11	13.6	36.8	51.4	23.5	270	0	1.34	0	0
12	196	51.6	3.24	5.63	61.9	6.56	314	71.8	0.228	18.2	48	66.2	26.9	503	0	1.75	0	0

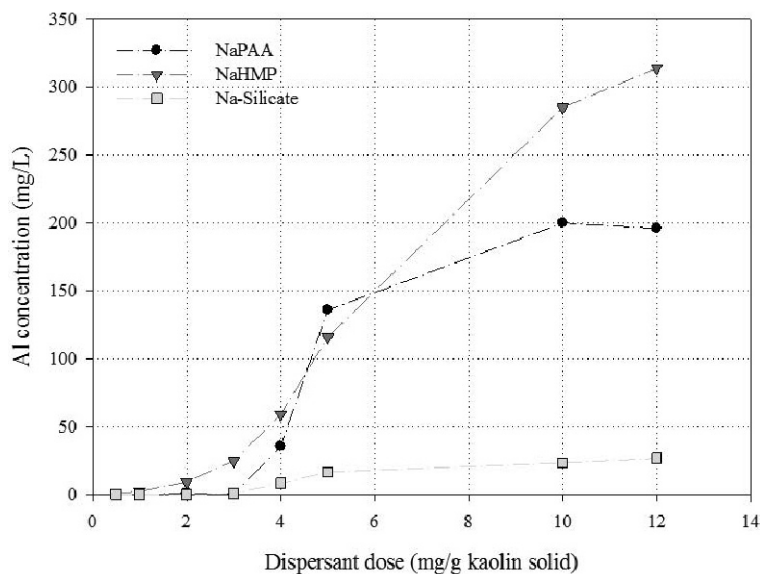


Figure 7. Concentration of dissolved Al as a function of dispersant dose in kaolin suspensions at a fixed 55 wt.% solids.

The same phenomenon was observed for NaPAA because it also has a strong affinity for Al to form complexes with PAA like the phosphate complexes with HMP and interfere with the Al hydroxide dissolution/precipitation. However, the concentrations of Al released by HMP into the supernatant were greater than the Al released by NaPAA. The optimum concentration of PAA produced lower Al concentrations than HMP, especially at high NaPAA doses, which indicates that PAA can react with Al on kaolin edge sites to form a stable, soluble complex. However, the complex was not sufficiently strong for the chemical reaction with kaolin edge surfaces and interlayers to dissolve kaolin accessory minerals

(Figure 7). The lower concentrations of dissolved Fe, Ca, and Mg confirmed this phenomenon (Table 2).

The lowest Al dissolution occurred with Na-silicate (Figure 7) in comparison to the other dispersants because Na-silicate has no affinity for Al nor does it react chemically with accessory minerals. The dissolved Al was due to the high suspension pHs when Na-silicate was used (Figure 9). After the critical Na-silicate dose was used, the Al dissolution immediately began to reach a plateau, which suggests that fewer cation exchange interactions occurred at kaolin particle edges and cation exchange of Na^+ for Al^{3+} was almost at equilibrium and remained constant at greater Na-silicate doses.

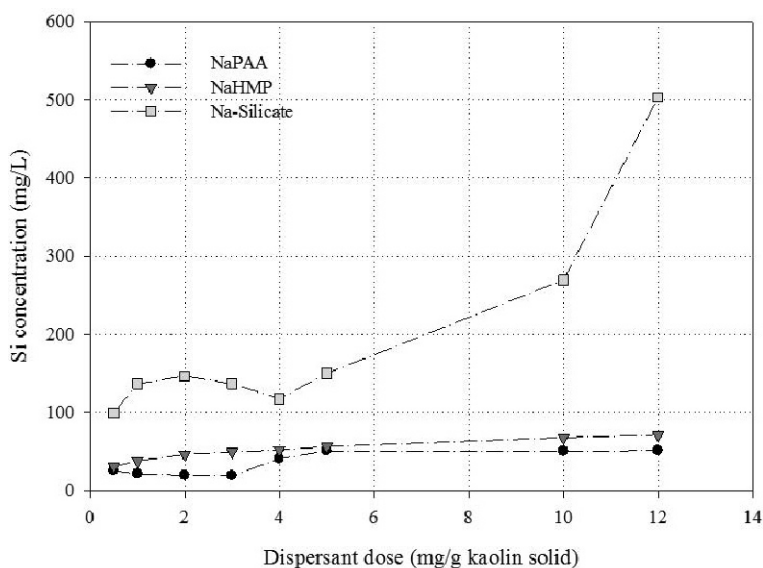


Figure 8. Concentration of dissolved Si as a function of dispersant dose in kaolin suspensions at a fixed 55 wt.% solids.

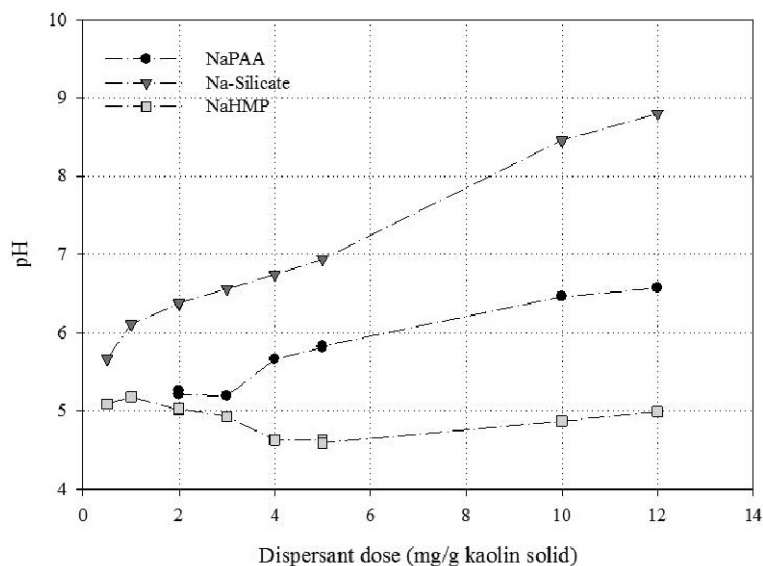


Figure 9. Variation of pH in kaolin suspensions at various dispersant doses at a fixed 55 wt.% solids.

The change in dissolved Si concentrations with increased NaPAA and NaHMP doses produced a comparable contribution, but did not substantially increase dissolved Al because the chemical affinity of polyphosphates and PAA towards the octahedral Al sheets in the kaolin structure were more prominent than the affinity for silica tetrahedral sheets. The Si solubility (Figure 8) increased to some extent with critical dispersant doses because the alumina-center surface complexes opened the silica framework to hydroxyl ion attack and then reached a plateau, which indicates that a complex was formed. Because Na-silicate contains a large amount of Si, the Si concentration was highest in the suspension as dispersant dose was increased, particularly after the critical dose was attained due to the lack of further interactions in the system.

Effect of aging on the dissolution of crude kaolin in the presence of dispersing agents

To examine the dissolution rate of kaolin in the presence of dispersing agents, the concentrated suspensions were prepared at a dose of 5 mg dispersant/g solids

and 65 wt.% kaolin solids and then were aged for 0, 12, 24, 48, 96, and 192 h at room temperature. The 65 wt.% solids value was chosen for the aging test for convenience because industries are required to prepare and use stable suspensions at high solids loading for use over long times. Thus, reaction mechanisms were elucidated to explain the interactions between kaolin and dispersing agents. After each aging interval, the dissolved metal concentrations in samples were measured in the supernatants and are summarized in Table 3. The variation in sample pHs was also presented as a function of time (Figure 12).

In the presence of NaPAA, the dissolved Al underwent adsorption and complex ion formation for up to 24 h. Then, time-dependent alterations involving the dissolution of kaolin accessory mineral components, such as Fe, presumably caused a sudden jump and then a gradual increase in the Al concentration during the long aging time (Figure 10). The increased amounts of dissolved Fe were presumably caused by dissolution of kaolin accessory minerals by PAA and the formation of a stable Fe–PAA complex, which contributed to the production of dissolved Al, especially after the 24 h

Table 3. Concentration (mg/L) of dissolved metals in kaolin suspensions with 5 mg dispersant/g kaolin solids with NaPAA, NaHMP, and Na-silicate dispersants at 65 wt.% solids.

Time (h)	NaPAA						NaHMP						Na-silicate					
	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca	Al	Si	Ti	Fe	Mg	Ca
0	192	65.4	1.52	2.14	9.28	14	163	32.8	0	2.1	11.2	15.15	47	295	0	0	0.273	0.689
12	190	84.9	1.84	3.57	8.28	12.1	156	71.9	0	1.94	10.9	14.2	53.4	183	0	0	0.538	0.655
24	194	98.3	2.74	4.45	8.06	11.6	142	88.3	0	1.44	10.5	13.7	31.9	166	0	0	0.538	0.685
48	234	147	4.92	7.99	8.08	11.5	136	115	0	1.55	10.9	13.95	28.1	122	0	0	0.494	0.604
96	217	140	3.01	9.33	7.88	11	112	120	0	0.631	11.6	14.7	20.9	95.4	0	0	0.538	0.663
192	243	161	4.59	11.3	7.92	11.1	111	134	0	0.714	11.9	15.2	8.73	76.6	0	0	0.599	0.722

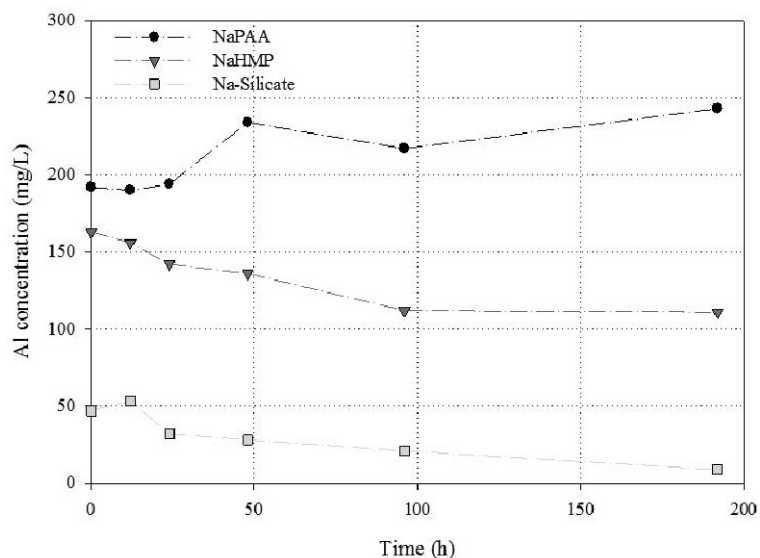


Figure 10. Concentration of dissolved Al as a function of time in kaolin suspensions at a fixed 5 mg dispersant/g kaolin solids and 65 wt.% solids.

aging time. The Ca and Mg cations released by cation exchange remained nearly constant in the kaolin supernatants and showed no time dependence or contribution to the dissolution reaction over the aging time. The pH values of the suspensions also remained nearly constant, which indicates that no significant peculiar behavior occurred during the aging process. Parallel increases in dissolved Al and Si verified that Si dissolution resulted from the formation of complex ions that caused the Si concentrations to increase continuously (Figure 11).

The aging test performed to examine the influence of NaHMP on kaolin dissolution (Figure 12) revealed that

NaHMP showed a peculiar behavior, probably due to the pH increases during the first 48 h. As Al concentrations slightly decreased, the Si concentrations increased, particularly during the first 48 h and concentrations reached a plateau during the remainder of the aging time (Figure 10 and 11). The dissolved Ti, Fe, Ca, and Mg did not show any time dependence and remained constant in the solution throughout the aging time. Andreola *et al.* (2006) demonstrated that NaHMP concentrations in solution decreased with increased aging time up to 6 h and then reached an apparent plateau followed by a gradual decrease. The study considered the first 48 h of

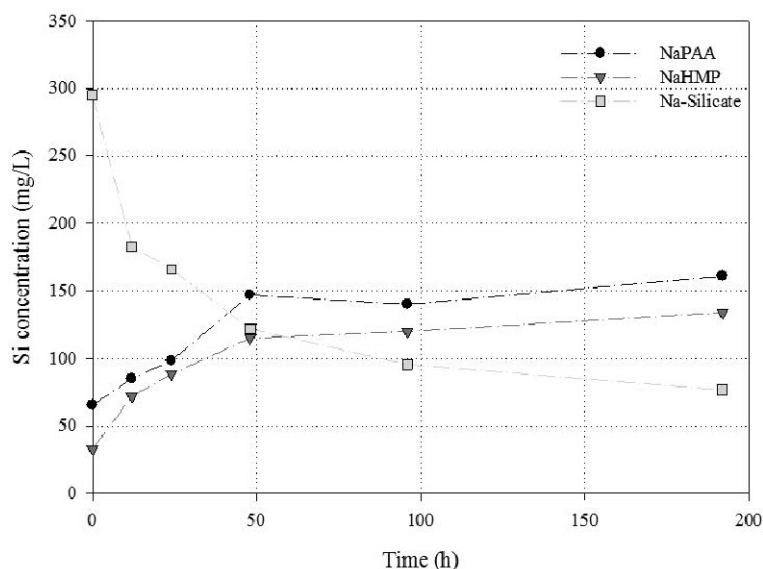


Figure 11. Concentration of dissolved Si as a function of time in kaolin suspensions at a fixed 5 mg dispersant/g kaolin solids and 65 wt.% solids.

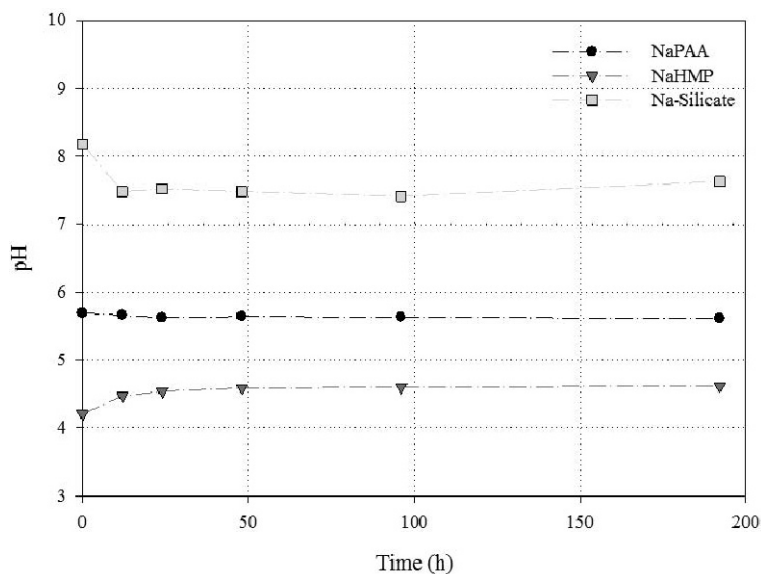


Figure 12. Variation of pH with time in kaolin suspensions at a fixed 5 mg dispersant/g solids and 65 wt.% solids.

aging for ceramic grade kaolin suspensions at 30°C. Because adsorption, complexation, and aluminosilicate gel formation processes create equilibrium conditions, solution properties, such as pH, were also evaluated for any effects on dissolution. The dissolved Si significantly increased in the presence of NaHMP during the first 48 h because of increased pH values (Figure 12). Hence, the direction of the aluminosilicate gel formation reaction was presumably from left to right in equation 1 and caused a decrease in the Al concentration (Figure 10). A slight pH increase in the kaolin suspension from 4.2 to 4.6 might also affect the chemisorption of phosphates and result in fewer Al complex ions due to a change in the apparent isoelectric point (IEP) of the particle edges. In addition, although phosphate ions have a very strong affinity to form complexes with Al ions and $\text{Al}(\text{OH})_3$, precipitation may have been involved due to a solution pH change. At the beginning of the interaction, a large number of complex ions were produced. These complex ions were, however, later converted to $\text{Al}(\text{OH})_3$ by hydroxyl ions. Thus, the dissolved Al concentrations decreased in the suspensions (Figure 10).

When Na-silicate was studied, the results indicated that while the phenomenon of congruent dissolution was observed for the Al dissolution rate (less than the other dispersing agents), an opposite phenomenon for the Si dissolution rate with increased aging time was observed. This was explained by the action of Na-silicate. The Na-silicate changed the edge charge of the kaolin particles from positive to negative and was adsorbed as a polyanion. This yielded complexes with kaolin cations and the substitution of cations in the electric double layer of kaolin particles with Na cations to increase the pH of the suspensions (Andreola *et al.*, 2004; Amorós *et al.*, 2010). Figure 12 shows pH variation with time in the

kaolin suspensions with added Na-silicate. This action presumably produced a notable amount of soluble complex ions with the Al of the kaolin due to the high pH (Figure 10). However, Figure 11 clearly shows that the change in dissolved Si concentration with aging time was strongly dependent on the use of Na-silicate and a sharp decrease was observed for short aging periods (0–48 h) compared to other dispersing agents. Because Na-silicate is composed of a large amount of Si, large amounts of Si initially appeared in the suspensions. The most obvious decrease in Si solubility occurred for the aging times of 0 and 12 h, where the most relevant increases in solution pH occurred. The dissolved Al indicates that the Si contributed to the formation of stable Al-SiO_4 complexes via adsorption, and then, depending on the Al concentration in the alkaline medium, the Al-SiO_4 was precipitated by Al adsorption onto the surface of the silica, which gradually decreased Si concentrations in the suspension (Figure 11). The continuous decrease of Si concentrations over the aging period might also involve dispersing agent deterioration through a hydrolysis reaction. The kaolin accessory minerals did not contribute because kaolin constituents were not released by the addition of Na-silicate (Table 3).

CONCLUSIONS

In this study, the dissolved metal constituents of crude kaolin (Al, Si, Ti, Fe, Mg, and Ca) were measured to elucidate kaolin dissolution in the absence and presence of Na-poly(acrylic acid), Na-hexametaphosphate, and Na-silicate under different experimental conditions. The main conclusions and observations are briefly summarized below:

(1) In the absence of dispersing agent, the dissolved Si concentrations increased as the solids concentration was increased. However, the dissolved Al concentrations were unaffected by the solids concentration over the entire range of solids loading, which indicates nonstoichiometric dissolution caused by the precipitation of Al.

(2) The normalized results did not show any dependence between the elements extracted from crude kaolin and increased solids loading at equivalent critical doses of dispersing agents.

(3) The use of dispersing agents remarkably promoted the release of dissolved Al but only slightly increased dissolved Si due to the lack of any significant interactions with the basal silica surface of the kaolin particles. The dissolved Si was attributed to the release of silica centers by surface complexes between the alumina centers and PAA or HMP and the detachment of Al that might open the silica structure of kaolin to the attack of hydroxyls during dispersion.

(4) The increase in the dissolution of the kaolin accessory minerals presumably caused an increase in kaolin edge surfaces or interlayers, which leads to greater dissolved metal concentrations.

(5) The aging effects were related to different phenomena, which included (i) changes in adsorption due to pH variations around the IEP of the kaolin particle edges in the presence of NaHMP; (ii) presumed shifts in the direction of the aluminosilicate gel formation reactions induced by the higher pHs, which thereby produced more dissolved Si and resulted in less soluble Al in the presence of NaHMP; and (iii) the contribution of dissolved Fe in accessory minerals to the release of dissolved Al, which thereby released soluble Si through complexation in the presence of NaPAA.

This investigation contributed to an understanding of the effects of anionic dispersing agents, such as NaPAA, NaHMP, and Na-silicate on kaolin dissolution by determining variations in kaolin suspension viscosities and the concentrations of elements dissolved from kaolin particles. The results obtained from this investigation may contribute to the design of effective suspension preparation strategies to produce a minimum viscosity and control stability and fluidity. Moreover, this investigation may assist in deciding the feasibility of using dispersing agents for particles that have surface charge heterogeneities, such as kaolin minerals, in the field of colloidal hydrodynamics.

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