

## THE DISPERSIVE EFFECT OF SODIUM SILICATE ON KAOLINITE PARTICLES IN PROCESS WATER: IMPLICATIONS FOR IRON-ORE PROCESSING

MARK MA

CSIRO Process Science and Engineering, Box 312, Clayton, Victoria, Australia 3168

**Abstract**—Kaolinite is a common gangue mineral in iron ore and sodium silicate has been used widely as a dispersant of silicate gangue minerals including kaolinite in various iron-ore flotation methods over a wide range of pH. Its actual dispersive effect on kaolinite under iron-ore flotation conditions has received very limited attention, however. The presence of hydrolyzable metal cations in process water further complicates sodium silicate–kaolinite interactions. In the present study, the dispersive effect of sodium silicate on kaolinite particles in distilled water as well as in  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions was investigated systematically through electrophoretic mobility and colloid-stability studies. The studies were based on controlled pH, which eliminated the dispersive effect of sodium silicate induced by increasing pulp pH, in order to simulate the conditions of iron-ore processing. With pH controlled at constant levels, sodium silicate dispersed kaolinite only when positively charged sites were present on kaolinite surfaces and the zeta potential of kaolinite was more negative than  $\sim -30$  mV. Over the pH range from 5 to 10.5, a significant dispersive effect of sodium silicate was only observed at pH 7. In process water, when Ca and Mg were present, the strong coagulation of kaolinite particles caused by the hydrolyzable metal cations could not be dispersed effectively with sodium silicate.

**Key Words**—Coagulation, Kaolinite, Sodium Silicate, Zeta Potential.

### INTRODUCTION

Australia is the world's largest exporter of iron ore. Kaolinite, a layered clay mineral of general chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , is a major gangue mineral in Australian iron ore. A large kaolinite content in iron ore results in a highly viscous slag and high coke rate and thus is detrimental to blast-furnace and sinter-plant operations. In the iron-ore industry, the process water contains Ca and Mg and their concentrations are often as much as 0.001 M (Iwasaki *et al.*, 1980). In previous work by Ma and co-workers (Ma, 2010, 2011; Ma and Bruckard, 2010), hydrolyzable metal cations in this concentration range caused fast coagulation of kaolinite; thus, effective dispersion of kaolinite in process water is of critical importance for the successful removal of kaolinite from iron ore.

In the iron-ore industry, sodium silicate is used widely as a dispersant of silicate gangue minerals in both direct and reverse flotation methods over a wide pH range. The actual dispersive effect on kaolinite in process water under the conditions of iron-ore flotation has received limited attention, however. Diz and Rand (1990) suggested that sodium silicate species adsorb on kaolinite through electrostatic attraction, hydrogen bonds, van der Waals attraction, and condensation.

Andreola *et al.* (2007) proposed that the polymeric species of sodium disilicate can precipitate on the surfaces of kaolinite. The theory of Amoros *et al.* (2010) was that sodium silicate disperses kaolinite by making the clay more negatively charged. In the work by Amoros *et al.*, however, the solution pH increased when sodium silicate was added to kaolinite suspensions. Whether the increased negative charge was caused by increased pH or the presence of anionic species of sodium silicate was not distinguished. According to Manfredini *et al.* (1987), the dispersive effect of sodium silicate on a mixture of clay and non-clay minerals is largely due to its effect on pH, rather than the action of its anionic species. Similar to Amoros *et al.* (2010), the work of Manfredini *et al.* (1987) was also conducted at natural pH, which depends on the dosage of sodium silicate and typically ranges between about pH 7 and 11. The actual pH of the suspensions depends on the dosage of sodium silicate.

In iron-ore flotation, the surface charge of iron and gangue minerals is regulated by adjusting pulp pH, using different flotation methods depending on the pH conditions, i.e. acidic, neutral, or alkaline, of the pulp. The sodium silicate-kaolinite interactions in process water at various pH values is, thus, of great interest to the iron-ore industry. The dispersive effect of sodium silicate on kaolinite in the presence of hydrolyzable metal cations with pH controlled at constant levels over a wide pH range and how these cations interfere with sodium silicate–kaolinite interactions have not been studied.

In the present study, the effect of sodium silicate on the colloid stability of kaolinite particles was investi-

\* E-mail address of corresponding author:

mark.ma@csiro.au

DOI: 10.1346/CCMN.2011.0590302

gated in a systematic manner. The pH of kaolinite suspensions was controlled at constant levels in order to simulate the conditions of iron-ore processing. Any pH change induced by sodium silicate was corrected using pH modifiers. This approach effectively eliminated the dispersive effect of sodium silicate induced by increasing the pulp pH.

## EXPERIMENTAL METHODS

### Materials

Kaolinite from Georgia, USA, was obtained from Ward's Natural Science Establishment. Quantitative X-ray diffraction (XRD) analysis showed it to contain 93.0% kaolinite and 7.0% illite. The particle-size distribution was determined using a Malvern Mastersizer 2000 (Worcestershire, UK) and the resultant  $d_{50}$  value was 4.2  $\mu\text{m}$ . The BET (Brunauer, Emmett, Teller) specific surface area of the sample, determined using a Micromeritics Tristar 3000 (Gosford, Australia) instrument, was 10.7  $\text{m}^2/\text{g}$ .

Sodium silicate (trade name N®-sodium silicate) with a  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 3.25 and a silica content of 28.7%, was obtained from PQ Corporation (Dandenong, Australia). Calcium chloride, magnesium chloride, sodium chloride, and sodium hydroxide were ACS-certified chemicals obtained from Ajax Finechem (Sydney, Australia).

### Methods

The colloid stability of the kaolinite particles was investigated through turbidity measurements using a Hach 2100AN turbidimeter (Loveland, Colorado, USA). Turbidity values were expressed in nephelometric turbidity units (NTU). In the turbidity tests, 1 g of kaolinite was first conditioned with 50 mL of salt solution (0.0001 M, 0.001 M, and 0.01 M) or distilled water for 20 min. Then 50 mL of a sodium silicate solution of known concentration, from 0.0001 M to 0.01 M, was added and the entire mixture was conditioned for a further 30 min. After conditioning, 30 mL of the sample was collected for turbidity measurements. Each measurement was repeated three times and the average value was used. The coefficient of variation in these experiments was 2–5%.

The electrophoretic mobility of kaolinite particles in aqueous suspension was studied with the use of a Zetacompact Z8000 model (CAD Instrumentation, France), using an electrostatic field of 80 V/cm. Particle movement was measured by an automated video analysis of the particles. Zeta potentials were calculated from electrophoretic mobility using the Smoluchowski equation (Smoluchowski, 1903). The pH was adjusted using NaOH and HCl. Each measurement was repeated three times and the average value used. The coefficient of variation in these experiments was 2–3%.

## RESULTS

Electrophoretic mobility measurements revealed the effect of sodium silicate on the zeta potential of kaolinite (Figure 1). From pH 8 to 10.5, sodium silicate did not interact with kaolinite and the slightly smaller zeta potential of kaolinite in the presence of 0.001 M sodium silicate was probably due to the compression of the electrical double layer by sodium silicate. At pH 7, however, the surfaces of kaolinite suddenly became significantly more negative in the presence of 0.001 M sodium silicate, with zeta potential becoming more negative, changing from  $\sim -28.9$  mV to  $\sim -36.4$  mV. A similar effect was observed at lower pH. Sodium silicate is known to form colloidal aggregates when its concentration is  $>0.005$  M (Harman, 1928). In the present study, the zeta potential behavior of sodium silicate colloidal aggregates was measured in 0.01 M sodium silicate solution (Figure 1). These colloidal aggregates were very negatively charged and independent of pH.

The zeta potential of kaolinite in the presence of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  at pH 10.5 (Figure 2) in the absence of sodium silicate become significantly more positive as the concentration of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  increased from 0 to 0.001 M. When the surfaces of kaolinite were negatively charged in  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions, sodium silicate had no effect on the coagulation of kaolinite particles. When kaolinite surfaces became positively charged in the presence of 0.001 M  $\text{MgCl}_2$ , however, the sodium silicate began to interact with the clay mineral and reversed its zeta potential from  $\sim +11.0$  to  $\sim -16.8$  mV. The effect of a low-molecular-weight polyacrylic acid (MW 1800) on the zeta potential of

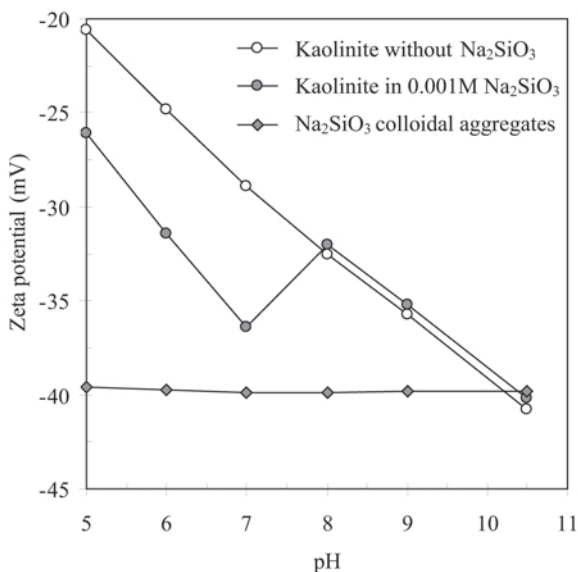


Figure 1. The zeta potential of sodium silicate (0.01 M) aggregates and the effect of sodium silicate on the zeta potential of kaolinite from pH 5 to 10.5 in 0.001 M NaCl solution.

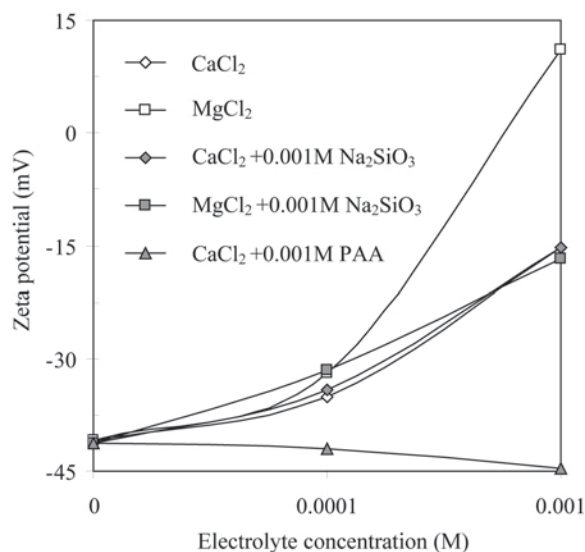


Figure 2. Effect of sodium silicate on the zeta potential of kaolinite at pH 10.5 in the presence of CaCl<sub>2</sub> and MgCl<sub>2</sub> using 0.001 M NaCl as a background solution.

kaolinite in the presence of CaCl<sub>2</sub> was measured for comparison.

The pH and ionic strength affect the colloid stability of kaolinite particles (Figure 3). From pH 3 to 7, fast coagulation of kaolinite particles occurred. In the pH range of 8 to 10.5, kaolinite particles were dispersed, with a sharp transition observed between pH 7 and 8.

The pH also influenced the effect of sodium silicate on the colloidal stability of kaolinite particles suspended in distilled water (Figure 4). Sodium silicate showed no significant effect on the coagulation of kaolinite particles from pH 8 to 10.5. At pH 7, however (when

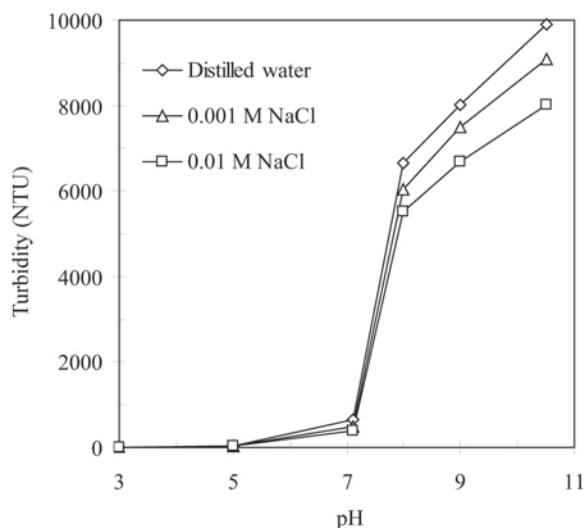


Figure 3. Effect of pH on the stability of kaolinite particles in distilled water.

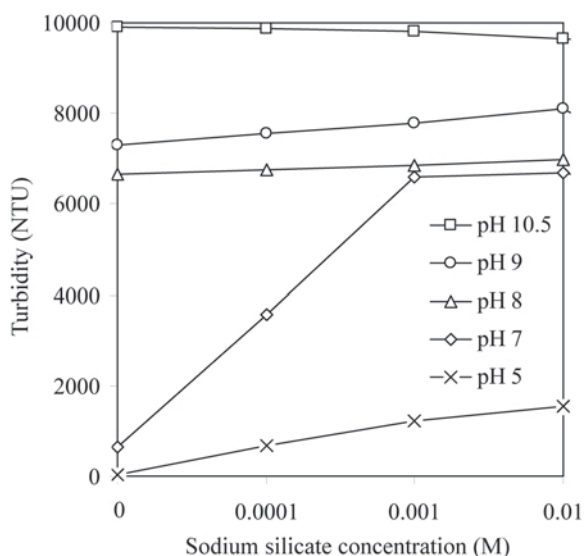


Figure 4. Effect of sodium silicate on the stability of kaolinite particles from pH 5 to 10.5 in distilled water.

fast coagulation of kaolinite particles occurred in the absence of sodium silicate, Figure 3), sodium silicate began to disperse kaolinite and this effect reached a plateau at a concentration of 0.001 M sodium silicate. At pH 5, when layer-edge surfaces were more positively charged, sodium silicate had no significant dispersive effect on the kaolinite.

Figure 5 presents the dispersive effect of sodium silicate on kaolinite in the presence of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> at pH 10.5. Except for 0.001 M MgCl<sub>2</sub> solution, the sodium silicate had no dispersive effect. On the contrary, the presence of sodium silicate facilitated the

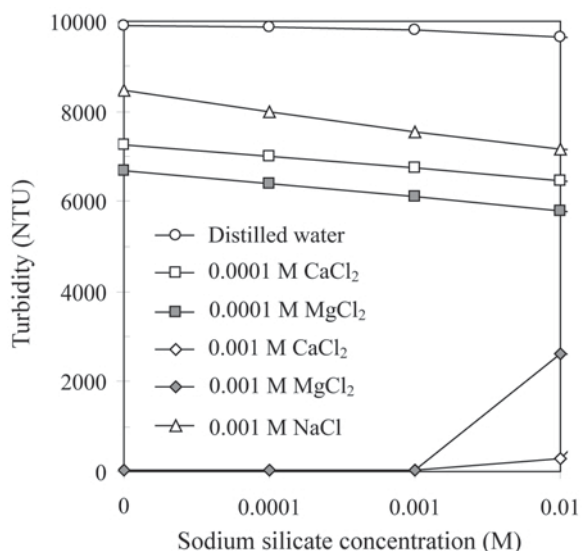


Figure 5. Effect of sodium silicate on the stability of kaolinite particles at pH 10.5 in distilled water and salt solutions.

coagulation of kaolinite particles, probably due to the compression of the electrical double layer by sodium silicate. In the presence of 0.001 M  $\text{MgCl}_2$ , sodium silicate dispersed kaolinite a little when its concentration was sufficiently high (0.01 M).

Figure 6 shows the correlation between zeta potential and colloid stability of kaolinite particles. When the zeta potential of kaolinite was  $< -30$  mV, fast coagulation of the clay particles occurred. At zeta potential values more negative than  $\sim -30$  mV, kaolinite was dispersed and its colloid stability increased as the zeta potential became more negative. In general,  $\sim -30$  mV may be viewed as a threshold for the coagulation/dispersion of kaolinite particles.

### DISCUSSION

The aqueous chemistry of sodium silicate is related to its concentration, pH, temperature, and  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio (Harman 1928; Lagerström, 1959; Ingri, 1959; Stumm *et al.*, 1967; Weldes and Lange, 1969; Harris and Newman, 1977; Sjöberg *et al.*, 1985; Svensson *et al.*, 1986; Bass and Turner, 1997; Osswald and Fehr, 2006). The presence of polymeric silicates increased with  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio and  $\text{SiO}_2$  concentration (Bass and Turner, 1997). According to Harman (1928), when the concentration of sodium silicate is  $> 0.005$  M, colloidal aggregates of sodium silicates are present in solution. The existence of such colloidal aggregates of sodium silicate was confirmed by Aveston (1965). The proposed structure of such aggregates was only speculative, however, and their electrophoretic mobility has not been reported (Leja, 1982). The present results (Figure 1) showed that the colloidal aggregates of

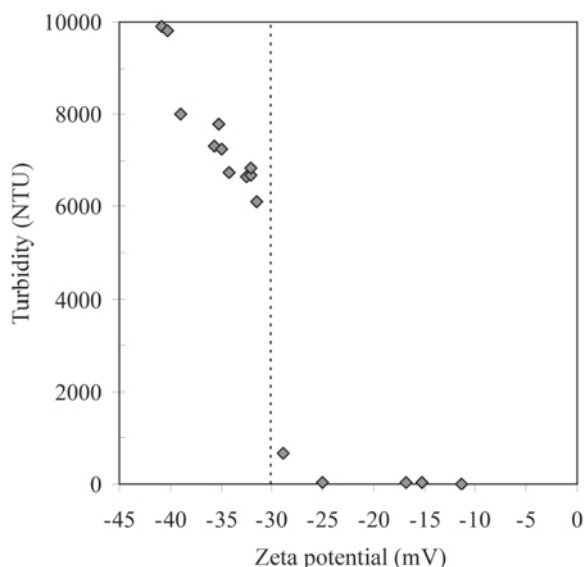


Figure 6. Correlation between zeta potential and colloidal stability of kaolinite.

sodium silicates were very negatively charged and independent of pH, which could exert a significant effect on the oppositely charged sites on the edges of kaolinite.

When such aggregates are present in solution, distinction between the zeta potential of colloidal aggregates of sodium silicate and that of kaolinite particles is difficult. The concentration of sodium silicate was thus always controlled at  $\leq 0.001$  M when measuring the zeta potential of kaolinite particles in this work.

According to Pushkarev (1956) and James and Healy (1972a), the adsorption of hydrolyzable ions on solids is correlated primarily with the hydrolysis characteristics of the ions rather than with the properties of the solid surfaces. Consequently, significant interaction of hydrolyzable ions and solid surfaces only occurs in a strongly alkaline medium. At pH 10.5, hydrolyzed  $\text{Ca}^{2+}$  species do not precipitate, allowing their adsorption onto kaolinite surfaces as  $\text{CaOH}^+$ . From the solubility products of  $\text{Mg}(\text{OH})_2$  species (Gjaldbæk, 1925), the  $\text{MgCl}_2$  concentration at which precipitation began at pH 10.5 was calculated to be  $1.2 \times 10^{-4}$  M. In a 0.0001 M  $\text{MgCl}_2$  solution, therefore, no precipitate of  $\text{Mg}(\text{OH})_2$  forms and Mg is adsorbed on kaolinite as  $\text{MgOH}^+$ . In a 0.001 M  $\text{MgCl}_2$  solution, however,  $\text{Mg}(\text{OH})_2$  forms and interacts with kaolinite through surface precipitation of colloidal hydroxides (James and Healy, 1972a, 1972b, 1972c).

Hydrolyzable metal cations and silicate anions form insoluble complexes in aqueous solutions (Hast, 1956). The zeta-potential results (Figure 2) indicated, however, that sodium silicate did not interact with the Mg or Ca sites on kaolinite when the mineral surfaces were negatively charged and only interacted with kaolinite when its surfaces were positively charged.

The inability of sodium silicate to adsorb on negatively charged kaolinite surfaces, in contrast to polyacrylic acid (Figure 2) which adsorbs on kaolinite by forming complexes with the edges (Zaman *et al.*, 2002), suggests that its adsorption mechanism on kaolinite is limited to electrostatic attraction only, without forming weak or chemical bonds with the mineral surfaces. Although Diz and Rand (1990) suggested that sodium silicate adsorbs on kaolinite through weak interactions including electrostatic attraction, hydrogen bonds, van der Waals attraction, and condensation, only electrostatic attraction was confirmed in the present study. Yang *et al.* (2008) reported that sodium silicate adsorbs readily on magnetite even when the mineral is very negatively charged at pH 11. The different phenomena observed for kaolinite indicate that the adsorption mechanism of sodium silicate on kaolinite differs from that on iron oxides.

Rossington *et al.* (1998) reported that at pH  $< 5$  when the edges of kaolinite are positively charged, the interactions between sodium silicate and kaolinite are

extremely weak; at  $\text{pH} > 6$ , when the edges of kaolinite are negatively charged, sodium silicate interacts strongly with kaolinite. This observation contradicts the generally accepted suggestion in the literature that electrostatic repulsion between sodium silicate and kaolinite at high pH hinders the dispersant's adsorption on kaolinite (Diz and Rand, 1990; Andreola *et al.*, 2007). Note that the samples used for zeta-potential measurements at different pH values were prepared separately in the present study because the adsorbed sodium silicate at low pH might be unable to desorb completely when titrating the same sample over a wide pH range. Rossington *et al.* (1998) provided no details of their zeta-potential measurements, which makes further discussion of their results difficult.

The application of Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory to the prediction of clay-colloid stability implies a large degree of uncertainty (Missanal and Adell, 2000), contradicting the findings of Rao *et al.* (2011) that kaolinite particles coagulate in the same way as normal colloidal particles. The colloid stability of kaolinite particles is related to their layered structure. In general, in acidic media, edge-to-face hetero-coagulation occurs through electrostatic attraction. In alkaline media, both edge and basal planes are negatively charged leading to electrostatic repulsion between kaolinite particles. The transition in coagulation occurs at the point of zero charge (PZC) of the edge planes.

The PZC of kaolinite edge planes reported in the literature ranges from pH 5 to 9, depending on the kaolinite used, the clay pretreatment, and the method used for measuring the PZC (Herrington *et al.*, 1992; Williams and Williams, 1978; Rand and Melton, 1975; Flegmann *et al.*, 1969; Melton and Rand, 1977; Diz and Rand, 1989). In the present study, the critical coagulation pH appears to be between pH 7 and 8 (Figure 2), which agrees well with the observations of Williams and Williams (1978), Johnson *et al.* (1998, 2000), and Miller *et al.* (2007).

As discussed above, the adsorption of sodium silicate on kaolinite surfaces is driven by electrostatic attraction only and this conclusion is supported by the turbidity results (Figure 4). The colloid stability of kaolinite particles was not affected by sodium silicate when kaolinite surfaces were negatively charged from pH 8 to 10.5 (Figure 4).

At pH 7, positively charged sites appeared on the edges of kaolinite, offering electric attraction to the anionic species of sodium silicate (Figure 1), which is responsible for the significant increase in the colloid stability of kaolinite (Figure 4). Further increase of the concentration of sodium silicate to 0.01 M led to the formation of very negatively charged colloidal precipitates of sodium silicate (Figure 1), which can be expected to adsorb on the positively charged edges and induce stronger dispersion of kaolinite. Such a phenom-

enon was not observed (Figure 4), however, indicating that the positive sites on kaolinite were probably already saturated by the anionic species of sodium silicate at 0.001 M and, thus, unable to accommodate further anionic species.

The dispersive effect of sodium silicate on the kaolinite particles coagulated by Ca and Mg was rather weak. As long as the surfaces of kaolinite (with adsorbed Ca/Mg) remained negatively charged, sodium silicate did not interact with kaolinite (Figure 2) and, thus, did not disperse the clay particles (Figure 5). When kaolinite surfaces were positively charged in the presence of 0.001 M  $\text{MgCl}_2$ , sodium silicate anionic species were attracted to kaolinite. In the presence of 0.001 M sodium silicate, the zeta potential of kaolinite was reversed from  $\sim +11$  mV to  $\sim -16.8$  mV (Figure 2), but still less than the critical zeta potential to disperse kaolinite ( $\sim -30$  mV). When sodium silicate concentration was increased to 0.01 M, the very negatively charged colloidal precipitates of sodium silicate appeared (Figure 1) and a slight dispersion of kaolinite was observed (Figure 5). Andreola *et al.* (2006) reported that the dispersive effect of sodium hexametaphosphate on kaolinite is greater than that of sodium disilicate. Because the work of Andreola *et al.* (2006) was only conducted at natural pH and the effect of the dispersants on the pH of kaolinite suspensions was not considered, to compare the effectiveness of sodium hexametaphosphate and sodium silicate in kaolinite dispersion with pH controlled at constant levels over a wide range of pH will certainly be of practical significance for the iron-ore industry.

In the present work, sodium silicate was only observed to disperse kaolinite in three cases: at pH 5 and 7 (in distilled water) and at pH 10.5 (in 0.001 M  $\text{MgCl}_2$  solution). In these three cases, positively charged sites were present on kaolinite surfaces.

## CONCLUSIONS

Electrophoretic mobility and colloid stability studies were conducted on sodium silicate-kaolinite systems. The studies were based on controlled pH, which eliminated the dispersive effect of sodium silicate induced by increasing the pH of kaolinite suspensions, in order to simulate the conditions of iron-ore processing. Under those conditions, the following conclusions can be drawn: (1) Colloidal aggregates of sodium silicate were observed when its concentration was 0.01 M. The colloidal aggregates were very negatively charged ( $\sim -40.0$  mV) and independent of pH. (2) A critical zeta potential ( $\sim -30$  mV) was observed as a threshold for the coagulation/dispersion of kaolinite particles. (3) Sodium silicate-kaolinite interactions are purely electrostatic. (4) Sodium silicate disperses kaolinite only when positively charged surface sites are available to the dispersant and the zeta potential of kaolinite is more negative than  $\sim -30$  mV. (5) Although sodium

silicate has been used widely as a dispersant of kaolinite in alkaline media in the iron-ore industry, significant dispersive effects were only observed at pH 7. At higher (8, 9, 10.5) or lower pH (5), no significant dispersive effect was found. The colloid stability of kaolinite decreased slightly with increasing sodium silicate concentration at pH 10.5, indicating that the dosage of sodium silicate to cause over deflocculation was reduced at high pH. (6) In process water, when Ca and Mg were present, the strong coagulation of kaolinite particles by these ions could not be dispersed effectively with sodium silicate.

#### ACKNOWLEDGMENTS

The author is grateful to the 'Minerals Down Under,' National Research Flagship of Australia, for support of this research.

#### REFERENCES

- Amorós, J.L., Beltrán, V., Sanz, V., and Jarque, J.C. (2010) Electrokinetic and rheological properties of highly concentrated kaolin dispersions: Influence of particle volume fraction and dispersant concentration. *Applied Clay Science*, **49**, 33–43.
- Andreola, F., Romagnoli, M., Castellini, E., Lusvardi, G., and Menabue, L. (2006) Role of the surface treatment in the deflocculation of kaolinite. *Journal of the American Ceramic Society*, **89**, 1107–1109.
- Andreola, F., Castellini, E., Lusvardi, G., Menabue, L., and Romagnoli, M. (2007) Release of ions from kaolinite dispersed in deflocculant solutions. *Applied Clay Science*, **36**, 271–278.
- Aveston, J. (1965) Hydrolysis of sodium silicate: ultracentrifugation in chloride solutions. *Journal of Chemical Society*, **1965**, 4444–4448.
- Bass, J.L. and Turner, G.L. (1997) Anion distributions in sodium silicate solutions. characterization by  $^{29}\text{Si}$  NMR and infrared spectroscopies and vapor phase osmometry. *Journal of Physical Chemistry B*, **101**, 10638–10644.
- Diz, H.M.M. and Rand, B. (1989) The variable nature of the isoelectric point of the edge surface of kaolinite. *British Ceramic Transactions and Journal*, **88**, 162–166.
- Diz, H.M.M. and Rand, B. (1990) The mechanism of deflocculation of kaolinite by polyanions. *British Ceramic Transactions and Journal*, **89**, 77–82.
- Flegmann, A.W., Goodwin, J.W., and Ottewill, R.H. (1969) Rheological studies on kaolinite suspensions. *Proceedings of the British Ceramic Society*, **13**, 31–45.
- Gjaldbaek, J.K. (1925) Untersuchungen über die Löslichkeit des magnesiumhydroxyds. *Zeitschrift für Anorganische und Allgemeine Chemie*, **144**, 269–288.
- Harman, R.W. (1928) Aqueous solutions of sodium silicates, part VIII. General summary and theory of constitution. Sodium silicates as colloidal electrolytes. *Journal of Physical Chemistry*, **32**, 44–60.
- Harris, R.K. and Newman, R.H. (1977)  $^{29}\text{Si}$  NMR studies of aqueous silicate solutions. *Journal of the Chemical Society – Faraday Transactions*, **73**, 1204–1215.
- Hast, N. (1956) A reaction between silica and some magnesium compounds at room temperature and at +37°C. *Arkiv för Kemi*, **9**, 343–360.
- Herrington, T.M., Clarke, A.Q., and Watts, J.C. (1992) The surface charge of kaolin. *Colloids and Surfaces*, **68**, 161–169.
- Ingrì, N. (1959) Equilibrium studies of polyanions, IV. Silicate ions in NaCl medium. *Acta Chemica Scandinavica*, **13**, 758–775.
- Iwasaki, I., Smith, K.A., Lipp, R.J., and Sato, H. (1980) Effect of calcium and magnesium ions on selective desliming and cationic flotation of quartz from iron ore. Pp. 1057–1082 in: *Fine Particles Processing* (P. Somasundaran, editor). Vol. 2, American Institute of Mechanical Engineers, New York.
- James, R.O. and Healy, T.W. (1972a) Adsorption of hydrolyzable metal ions at the oxide-water interface, part III. *Journal of Colloid and Interface Science*, **40**, 65–81.
- James, R.O. and Healy, T.W. (1972b) Adsorption of hydrolyzable metal ions at the oxide-water interface, part I. *Journal of Colloid and Interface Science*, **40**, 42–52.
- James, R.O. and Healy, T.W. (1972c) Adsorption of hydrolyzable metal ions at the oxide-water interface, part II. *Journal of Colloid and Interface Science*, **40**, 53–63.
- Johnson, S.B., Russell, A.S., and Scales, P.J. (1998) Volume fraction effects in shear rheology and electroacoustic studies of concentrated alumina and kaolin suspensions. *Colloids and Surfaces A*, **141**, 119–130.
- Johnson, S.B., Franks, G.V., Scales, P.J., Boger, D.V., and Healy, T.W. (2000) Surface chemistry–rheology relationships in concentrated mineral suspensions. *International Journal of Mineral Processing*, **58**, 267–304.
- Lagerström, G. (1959) Equilibrium studies of polyanions – the silicate ions in  $\text{NaClO}_4$  medium. *Acta Chemica Scandinavica*, **13**, 722–736.
- Leja, J. (1982) *Surface Chemistry of Froth Flotation*. Plenum Press, New York.
- Ma, X. (2010) Role of hydrolyzable metal cations in starch-kaolinite interactions. *International Journal of Mineral Processing*, **97**, 100–103.
- Ma, X. and Bruckard, W. (2010) Effect of pH and ionic strength on starch-kaolinite interactions. *International Journal of Mineral Processing*, **94**, 111–114.
- Ma, X. (2011) Effect of a low-molecular-weight polyacrylic acid on the coagulation of kaolinite particles. *International Journal of Mineral Processing*, **99**, 17–20.
- Manfredini, T., Pellacani, G.C., and Pozzi, P. (1987) Sodium silicates as deflocculating agents for clays. *Industrial Ceramics*, **7**, 85–87.
- Melton, I.E. and Rand, B. (1977) Particle interactions in aqueous kaolinite suspensions: II. Comparison of some laboratory and commercial kaolinite samples. *Journal of Colloid and Interface Science*, **60**, 321–330.
- Miller, J.D., Nalaskowski, J., Abdul, B., and Du, H. (2007) Surface characteristics of kaolinite and other selected two layer silicate minerals. *Canadian Journal of Chemical Engineering*, **85**, 617–624.
- Missanal, T. and Adell, A. (2000) On the applicability of DLVO theory to the prediction of clay colloids stability. *Journal of Colloid and Interface Science*, **230**, 150–156.
- Osswald, J. and Fehr, K.T. (2006) FTIR spectroscopic study on liquid silica solutions and nanoscale particle size determination. *Journal of Materials Science*, **41**, 1335–1339.
- Pushkarev, V.V. (1956) Adsorption of radioactive isotopes on ferric hydroxide. *Russian Journal of Inorganic Chemistry*, **1**, 176–185.
- Rand, B. and Melton, I.E. (1975) Isoelectric point of the edge surface of kaolinite. *Nature*, **257**, 214–216.
- Rand, B., Diz, H.M.M., Li, J., and Inwang, I.B. (1988) Deflocculation of kaolinitic clay suspensions by sodium silicate. *Science of Ceramics*, **4**, 231–236.
- Rao, F., Ramirez-Acosta, F.J., Sanchez-Leija, R.J., Song, S., and Lopez-Valdivieso, A. (2011) Stability of kaolinite dispersions in the presence of sodium and aluminum ions. *Applied Clay Science*, **51**, 38–42.
- Rossington, K.R., Senapati, U., and Carty, M. (1998) A critical evaluation of dispersants for clay-based systems. *Ceramic*

- Engineering and Science Proceedings*, **19**, 77–87.
- Sjöberg, S., Öhman, L.-O., and Ingri, N. (1985) Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. 11. Polysilicate formation in alkaline aqueous solution. A combined potentiometric and  $^{29}\text{Si}$  NMR study. *Acta Chemica Scandinavica*, **39**, 93–107.
- Smoluchowski, M. (1903) Contribution à la théorie de l'endosmose électrique et de quelques phénomènes corrélatifs. *Bulletin International de l'Académie des Sciences de Cracovie*, **1**, 182–199.
- Stumm, W., Huper, H. and Champlin, R.L. (1967) Formation of polysilicates as determined by coagulation effects. *Environmental Science & Technology*, **1**, 221–227.
- Svensson, I.L., Sjöberg, S., and Öhman, L. (1986) Polysilicate equilibria in concentrated sodium silicate solutions. *Journal of Chemistry Society – Faraday Transaction*, **82**, 3635–3646.
- Weldes, H.H. and Lange, R.R. (1969) Properties of soluble silicates. *Industrial and Engineering Chemistry*, **61**, 29–44.
- Williams, D.J.A. and Williams, K.P. (1978) Electrophoresis and zeta potential of kaolinite. *Journal of Colloid and Interface Science*, **65**, 79–87.
- Yang, X., Roonasi, P., and Holmgren, A. (2008) A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy. *Journal of Colloid and Interface Science*, **328**, 41–4.
- Zaman, A.A., Tsuchiya, R., and Moudgil, B.M. (2002) Adsorption of a low-molecular-weight polyacrylic acid on silica, alumina, and kaolin. *Journal of Colloid and Interface Science*, **256**, 73–78.

(Received 25 January 2011; revised 1 August 2011; Ms. 538; A.E. P. Malla)