Adsorption Properties of Ca\(^{2+}\) on Na-Kaolinite and Its Effect on Flocculation Using Polyacrylamides

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ABSTRACT

Adsorption behavior of calcium ions on Na-kaolinite and the adsorption and flocculation behavior of Na-kaolinite by polyacrylamide in the presence of calcium species in solution have been investigated. Parameters examined in calcium adsorption experiments include pH, conditioning time of the suspension with calcium, and calcium concentration. The effect of calcium on adsorption of polyacrylamide and hydrolyzed polyacrylamide by the kaolinite and on its flocculation is determined. Also the effect of the polymer on calcium adsorption is examined.

Adsorption of calcium occurs only under pH conditions where it hydrolyzes to CaOH\(^+\) and Ca(OH)_2. Calcium adsorption (abstraction) is sensitive to the presence of polymer as well as to stirring conditions. Interestingly, above pH 8, stirring and addition of polymer (HPAM 33) were found to cause calcium desorption suggesting detachment of precipitate from the kaolinite surface.

INTRODUCTION

Mineral fines can be flocculated by reducing the electrostatic repulsion between particles, e.g. by using inorganic salts, and by using polymers which are capable of bridging the particles with one another. Polyacrylamides are widely used as a flocculating agent for fine particle suspensions and their adsorption has been generally characterized [1-4]. Most of these systems can also contain ionic species which may alter the surface physicochemical properties of the particles significantly [5,6]. For example, ions such as Ca\(^{2+}\) and Mg\(^{2+}\) have been reported to change the zeta potential of quartz [7,8] as well as to affect its flocculation characteristics. Such effects can in turn drastically affect industrial selective flocculation processes [6,9].

In the last decade, a number of studies of cation adsorption have been conducted [10,11]. Many of these have shown the important role of pH in controlling cation adsorption on hydrous metal oxides [12]. In some cases,

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increased uptake of the metal ion occurs in a narrow pH range. This is particularly true for strongly hydrolyzable cations [13,14]. For these systems, adsorption has been correlated primarily with the hydrolysis characteristics of the adsorbing ion rather than with the charge properties of the mineral. On the other hand, a recent work detailing the effect of conditions in the double layer has shown that in a number of cases, phenomena attributed to adsorption can in fact be explained by surface precipitation [15].

Some work has been done in the past on the adsorption of inorganic ions on kaolinite. For example, the selectivity sequence on kaolinite is found to be $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ [16,17]. However, there is little information on divalent cation selectivity on kaolinite [18,19]. There has also been some work on the adsorption of and flocculation by polymers on kaolinite [1-4,20]. Both of these processes have been shown to depend significantly on the charge characteristics of the polymer and the mineral as determined by the pH and ionic strength. Indeed, the behavior of these systems is extremely complex when both the inorganic and polymer species are present and almost no information is available for such cases even though both are invariably present in most flocculating systems.

In this study, the adsorption* response of calcium on Na-kaolinite and the adsorption and flocculation of Na-kaolinite by polyacrylamides in the presence of calcium in solution have been investigated. Results obtained for adsorption and flocculation are discussed with the help of electrokinetic data.

**EXPERIMENTAL**

*Material*

**Mineral Na-kaolinite**

A well-crystallized sample of Georgia kaolinite of 9.94 m² g⁻¹ surface area was obtained from the clay repository at the University of Missouri. A homoionic sample of sodium kaolinite was prepared from this using an ion-exchange treatment discussed elsewhere [20,21].

**Polymers**

The $^{14}$C-labeled nonionic polyacrylamide (PAM) of $5.2 \times 10^6$ molecular weight and 33% hydrolyzed polyacrylamide (HPAM 33) of $6.6 \times 10^5$ molecular weight used here were synthesized and characterized by American Cyanamid Company.

*The word adsorption is used somewhat loosely here as it is clear there may also be precipitation in the system. It might be more correct to use "calcium abstraction" to include both the calcium which adsorbs and that which precipitates. However, for simplicity, "adsorption" is used and the likelihood of precipitation is kept in mind.
**Inorganic reagents**

Fisher certified HCl and NaOH were used to adjust the pH of the suspension. Amend Drug and Chemical Company reagent grade NaCl (99.96% pure) was used to prepare the $3 \times 10^{-2}$ kmol m$^{-3}$ salt solution used in all the experiments to control ionic strength, $I$.

**Methods**

**Flocculation procedure**

For flocculation tests, 5 g samples of Na-kaolinite were pre-conditioned in 150 cm$^3$ salt solution in 250 cm$^3$ Teflon bottles for 2 h using a wrist-action shaker and for an additional 30 min after adding desired amounts of calcium salt. Polymer which is in 40 ml salt solution was then added and the pulp stirred for 10 min using a 1 inch diameter propeller at 1200 rpm. These conditions were identified as sufficient to achieve equilibrium adsorption (i.e., no additional change measured). Sedimentation tests were carried out in 250 cm$^3$ beakers at 2.5% (by weight) pulp density. The slurry was allowed to settle for 30 s and then 100 ml of the supernatant was removed using a suction device. The pH of the pulp was measured at the end of each test.

**Polymer determinations**

Supernatant samples were centrifuged for 10 min at 10,000 rpm, using an IEC centrifuge and analyzed for residual polymer using a Beckman Liquid Scintillation Counter (LSC).

**Calcium determination**

Supernatants were analyzed for total calcium, CaT, also using the LSC to count $^{45}$Ca. Ca$^{2+}$ concentration in some of the samples was also determined by measuring the calcium potential using a Ca$^{2+}$ selective electrode. The effect of the presence of the hydrolyzed (anionic) polymer on the calcium measurement was also monitored and taken into account in the calibrating system (Fig. 1). There is significant interference but only above 100 ppm polymer. Evidently the anionic polymer quenches the calcium to a certain extent or there is some precipitation of calcium with the negatively charged polymer.

**Electrokinetic studies**

Electrokinetic mobility of Na-kaolinite was measured using a Zeta-Meter in mineral supernatants at 0.1% solids content.
RESULTS AND DISCUSSION

Adsorption

Results obtained for adsorption of calcium by Na-kaolinite are given in Figs 1 and 3 as a function of calcium concentration and pH, respectively. Calcium adsorption density increases with concentration and is higher at elevated pH (Fig. 2). The more interesting feature, however, is the sharp rise in adsorption
above pH 10 (Fig. 3). Similar behavior has been observed in the past for calcium adsorption on silica [22]. The sudden increase in adsorption may be attributed to formation of calcium-hydroxide complexes in solution and at the
Fig. 5. Zeta potential values of Na-kaolinite after adsorption of calcium as a function of concentration of calcium as Ca²⁺.

Fig. 6. Effect of conditioning time of the suspension with calcium on adsorption.
The presence of calcium also causes significant change in zeta potential above pH 9 (Figs 4 and 5). While increasing calcium concentration causes some reduction in negative zeta potential at pH 7.5, the effect is dramatic at pH 11.3 (Fig. 5). Such zeta potential change has been proposed to be due to adsorption of the hydroxy complex, CaOH\(^+\), by hydrogen bonding or water forming reactions between the complex and protons on the solid surface [13]. It has been shown, however, that under these conditions there can be surface precipitation of Ca(OH)\(_2\) [15]. The negative potential in the interfacial region gives rise to an excess of Ca\(^{2+}\) and the solubility product is exceeded then at the interface before the bulk solution attains the critical concentration. The precipitated Ca(OH)\(_2\), which has a point of zero charge above 12 [23], will impart positive potential to the surface which accounts for the observed increase in zeta potential above pH 9.

There is another possible explanation for the observed behavior. Carbonate in solution open to atmospheric CO\(_2\) (g) increases dramatically at high pH and can lead to calcium carbonate precipitation [24]. Formation of CaCO\(_3\) is thermodynamically favored over Ca(OH)\(_2\) and it too has a higher PZC than kaolinite [24]. Presence of either of these species on the kaolin surface will reduce measured zeta potential.

The effect of conditioning time of the suspension in calcium salt solution on Ca adsorption by kaolinite at pH 7.4 and 11.4 is shown in Fig. 6. While conditioning time had no effect on Ca adsorption at pH 7.4, a sudden marked rise in adsorption resulted at pH 11.4 at 2 h followed by a steady decrease thereafter. The reasons for the sharp rise in calcium adsorption are not evident at present. It is suggested that it may be due to onset of precipitation of calcium species at the surface followed by some detachment of crystallites.

Flocculation

Calcium alone has only a small effect on kaolinite aggregation. When the percent solids settled is compared in the absence and presence of calcium (Fig. 7), there is a small decrease (dispersion) below pH 11 and a measurable increase above pH 11. This latter is evidently due to the decrease in zeta potential caused by the calcium in alkaline solutions. At pH 11, the zeta potential is reduced from \(-55\) mV to \(-20\) mV in the presence of 100 ppm calcium.

The results in Fig. 7 show the flocculation of the clay by nonionic polyacrylamide in the presence of calcium and as a function of pH. Adsorption of the polymer in these systems was total at the tested level (50 ppm) both in the absence and presence of calcium and was independent of pH. As expected, the polyacrylamide caused considerable flocculation of the kaolinite and, interestingly enough, addition of calcium a further increase in flocculation.

Flocculation of kaolinite by anionic polymer, HPAM (33% hydrolyzed), in
Fig. 7. Effect of PAM on flocculation of Na-kaolinite in the presence of calcium (CaT, total calcium (without distinguishing among species); Ci, initial concentration; S/L, solid/liquid ratio; I, ionic strength).

Fig. 8. Effect of HPAM on flocculation of Na-kaolinite in the presence of calcium.
Fig. 9. Adsorption of calcium by Na-kaolinite before and after adding polymer.

Fig. 10. Effect of calcium, polymer or both on pH response of zeta potential of Na-kaolinite.
the absence and presence of calcium was investigated as a function of pH. Polymer enhances flocculation only at quite low pH and calcium has no additional effect. Solids settled is the same as with calcium addition (no polymer) up to pH 10. Results obtained for polymer adsorption and flocculation are also given in Fig. 8. It can be seen from this figure that the adsorption of the polymer was increased by the addition of calcium above pH 9. However, there was insignificant change in the flocculation as measured by the solids settled.

In order to study this phenomenon further, the effect of polymer on Ca adsorption by kaolinite was also examined. Adsorption of calcium before and after polymer addition was determined. Results obtained are presented in Fig. 9. As seen from this figure, addition of the hydrolyzed polymer did cause desorption of calcium. To determine the nature of desorption or detachment, control experiments were carried out in the absence of polymer. It can be seen from Fig. 9 that the stirring process itself (without polymer) does produce measurable desorption of calcium from the clay.

These results suggest that calcium depletion from solution might be due to surface precipitation of calcium species which can be detached by stirring. It appears that HPAM enhanced the detachment possibly due to increased particle–particle abrasion in the flocculated system. It is also likely that the calcium species form a complex with HPAM and then detach from the surface. In this regard, it is interesting that the flocculation of kaolinite by the anionic polymer was not affected by the presence of calcium.

The zeta potential of kaolinite in the presence of both calcium and HPAM as a function of pH is given in Fig. 10. These results show that polymer alone reduces the magnitude of the zeta potential only slightly. The addition of polymer with calcium causes complex zeta potential response. However, above pH 10, the negative potential is restored at least partially, suggesting that some of what adsorbed or precipitated on the surface was removed by the polymer.

**SUMMARY**

Clay flocculation by calcium, by nonionic and anionic (33% hydrolyzed) polyacrylamide and by mixtures of calcium and polymer has been studied. Calcium adsorption and polymer adsorption have been examined as well. Electrokinetic data support the results.

Calcium has its maximum effect at high pH where kaolinite aggregation is slightly enhanced, the magnitude of zeta potential is reduced and calcium adsorption shows a sharp increase. These effects are attributed to the formation and adsorption of CaOH⁺. At high pH, surface precipitation of the hydroxide or carbonate can occur but additional stirring is able to cause some subsequent desorption.

Nonionic polyacrylamide flocculates the clay and this is enhanced by the
addition of calcium even though calcium has no effect on polymer adsorption. Calcium may be increasing bridging among particles.

The anionic polyacrylamide has no effect on flocculation except at very acidic pH. The addition of calcium does not affect these results significantly even though it seems to lead to higher polymer adsorption at high pH. Adsorbed calcium species may provide additional adsorption sites for the anionic polymer but due to repulsive effects, do not lead to flocculation. Zeta potential results at high pH support the hypothesis that the anionic polymer interacts with calcium species, removing them from the surface.

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REFERENCES