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Effect of Sodium Silicate on Flocculation of Hematite with Starch in the Presence of Calcium

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ABSTRACT

Sodium silicate is used as a dispersant in the selective flocculation of iron ores with starch as the polymeric flocculant. The mechanism of its dispersive effect on quartz has been reported to be related to its ability to remove coagulants, such as calcium and magnesium ions, from the process water. The interaction between iron oxides and calcium and sodium silicate, which has not appeared in literature, is also an important factor that would contribute to the success of the selective flocculation process. To elucidate the nature of this interaction at pH 11, where selective flocculation of iron oxides is commonly carried out, the effect of calcium and sodium silicate on the flocculation–selective flocculation behavior of hematite was investigated. Abstraction of calcium and adsorption of starch by hematite at different concentrations of sodium silicate and calcium were determined. It was found that calcium silicate precipitates as well as

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sodium silicate prevented starch adsorption and, therefore, sodium silicate could only be used effectively below 10 mg/L calcium and 1000 mg/L SiO_2 concentrations while dispersing a hematite–quartz mixture.

Key Words: Hematite; Starch; Sodium silicate; Flocculation; Selective flocculation.

INTRODUCTION

Depletion of high-grade iron ores, together with increasing demand for higher-grade charges by iron makers, have forced iron-ore producers to enrich their ores. Mineral liberation at fine particle sizes or production of large quantities of ore fines as tailings and/or by-products of enrichment or preparation operations have necessitated the development of concentration methods applicable to finely ground ores.[1–4] Selective flocculation is one of the beneficiation methods applicable to very fine particles in pulp. The process is based on different settling velocities of different minerals. Enrichment is achieved by separating the settled (flocculated) fine particles of a certain mineral from the suspended particles of other minerals. Settling rates of mineral particles are controlled by the effective diameter, which can be altered by flocculation or dispersion of a particular mineral. For a successful selective flocculation process, the pulp must be fully dispersed prior to the addition of the flocculant. A polymeric flocculant, commonly corn starch for iron ores, is employed for the formation of flocs of iron-oxide minerals. Flocs, with their enlarged effective size, can settle much faster than the dispersed particles of other minerals, thus resulting in concentration separation. Several dispersants can be used for the dispersion of pulp, but the underlying mechanism involves reduction of the interparticle-attraction forces.[5–9]

Sodium silicate is a widely used dispersant in many mineral processing applications, including the selective flocculation of iron oxides to disperse silica. The studies with quartz have revealed that the mechanism of dispersion with sodium silicate is due to its ability to remove the coagulating constituents, namely calcium and magnesium ions, from mineral surfaces. It was also determined that sodium silicate was an effective dispersant only when calcium concentration was low. Above 15 mg/L calcium, excessive sodium silicate concentration needed to disperse quartz also resulted in the dispersion of iron oxides even in the presence of starch.[8]

Starch and its derivatives are also common reagents in mineral processing.[10–12] They are either used as a depressant in flotation or flocculant in selective flocculation. In both cases, strong affinity of starch molecules towards the mineral surfaces is the underlying reason for their use. This affinity has been related to a complex formation and hydrogen bonding between metal ions on the mineral surfaces and starch molecules.[11–14] The effectiveness of starch in the flocculation of iron oxides as a flocculant is dependent upon many factors, such as process water chemistry, presence of clayey constituents, the amount and the type of dispersants, etc.[7,15,16] Presence of sodium silicate in the selective-flocculation pulp has been reported to adversely affect the selective flocculation of hematite from a hematite–clay mixture.[15]

While the interaction between sodium silicate and quartz has been delineated,[8] little has been reported on the interaction between sodium silicate and hematite, which is equally important considering the fact that the flocculation of hematite by corn starch would be affected by the silicate–hematite interaction. In this paper, the results of the investigation on the effect of sodium silicate addition on starch adsorption and flocculation behavior of hematite at different Ca^{++} concentration levels will be presented.

MATERIALS AND METHODS

A purified and acid-cleaned Lac Jeanine specularite sample, analyzing 69.3% Fe and wet-ground to $-30\,\mu m$, was used as hematite. The quartz sample from Thompson, MN, was also acid-cleaned and dry-ground in a porcelain mill to $-30\,\mu m$. A commercial sodium silicate was used in liquid form. The sample had a SiO_2/Na_2O ratio of 3.22 and SiO_2 content of 28.7%. Globe Pearl Starch 3001 by CPC International, Westchester IL, was used as flocculant, and pH adjustments were made with NaOH.

Both the flocculation and selective flocculation tests were carried out with a pulp of 5% solids by weight; the selective flocculation feeds consisted of 50% hematite and 50% quartz. Abstraction tests were conducted with $-105 + 74\,\mu m$ hematite samples at 2% by weight solids concentrations. Complete descriptions are given elsewhere.[17] Calcium and SiO_2 were analyzed by AAS. Starch analysis was carried out using a phenol–sulfuric acid method.[18] A Pen Kem Model 501 Laser Zee Meter (USA) was used for the zeta potential measurements.

RESULTS

In order to study the effect of sodium silicate on flocculation and selective-flocculation behavior of hematite and the mechanism of the observed effects, flocculation tests on hematite and selective flocculation tests on an artificial mixture of hematite and quartz in the presence of calcium and sodium silicate were carried out. Calcium abstraction and starch adsorption by hematite were investigated. All tests were performed at pH 11 the level at which selective flocculation is generally practiced.

Flocculation Tests

Flocculation behavior of hematite with and without starch as a function of sodium silicate concentration in the presence of several calcium concentration levels was studied. The results are given as settling rate and suspended-solids curves in Fig. 1.

As can be seen in Fig. 1, in the absence of starch and calcium, sodium silicate addition did not affect the flocculation–dispersion behavior of hematite, which remained dispersed. At 10 and 40 mg/L calcium concentration, hematite flocculated with no sodium silicate addition. The coagulated pulp at 10 mg/L calcium concentration became dispersed above

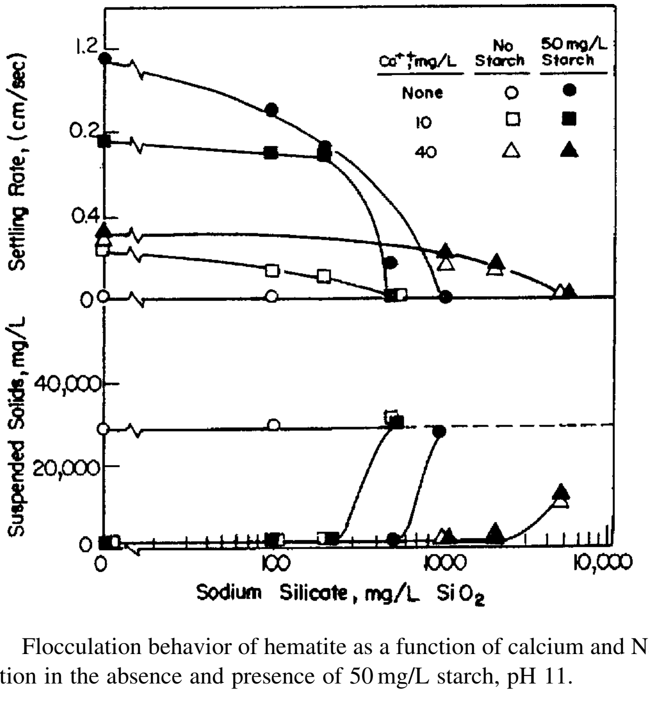

Figure 1. Flocculation behavior of hematite as a function of calcium and Na-silicate concentration in the absence and presence of 50 mg/L starch, pH 11.

200 mg/L SiO_2, a much higher SiO_2 concentration, 5000 mg/L, was required to disperse the pulp at 40 mg/L calcium concentration. Upon the addition of 50 mg/L starch in the pulp at zero and 10 mg/L calcium concentrations, a pronounced increase in the settling rate and a corresponding decrease in the suspended-solids content were observed as starch flocculated hematite. When the calcium concentration was increased to 40 mg/L, even though suspended solids remained low, the settling rate of flocs decreased. It can be noted in the figure that starch can act as an effective flocculant for hematite below 1000 mg/L SiO_2 concentration in the absence of calcium, and below 500 mg/L SiO_2 in the presence of 10 mg/L calcium. It is interesting to also note that the pulp in the presence of 40 mg/L calcium, when fully dispersed with sodium silicate, cannot be flocculated with 50 mg/L starch, indicating that at high calcium concentrations, starch will not be an effective flocculant for hematite, whose flocculation–dispersion behavior will be governed by the behavior of calcium and silicate ions.

Selective Flocculation Tests

In order to investigate the selective flocculation behavior of a hematite–quartz mixture in the calcium and sodium silicate concentration regions outlined above, selective flocculation tests were performed in the presence of 10 mg/L calcium at 0, 100, 200, and 800 mg/L SiO_2 equivalent sodium silicate concentrations. Another test at 200 mg/L SiO_2 concentration in the absence of calcium was carried out to see the effect of sodium silicate alone. The results are given in Fig. 2 as grade–recovery curves.

It is seen that the hematite was selectively flocculated using 30 mg/L starch without any addition of either calcium or sodium silicate, which is characterized by the high grade and recovery values throughout the characteristic curve. However, the mixture was indiscriminately flocculated at 10 mg/L calcium in the absence of sodium silicate, indicated by the clustered grade–recovery points in the upper left-hand corner of the figure. No improvement in selectivity was achieved at this calcium concentration after the addition of 100 mg/L SiO_2. Increasing the sodium silicate concentration to 200 mg/L resulted in some selectivity at 10 mg/L calcium concentration, although markedly poorer than the results obtained in the absence of calcium and silicate ions. At 800 mg/L SiO_2 and 10 mg/L calcium, the pulp was indiscriminately dispersed as seen from the close proximity of the grade–recovery curve to the line of no selectivity.

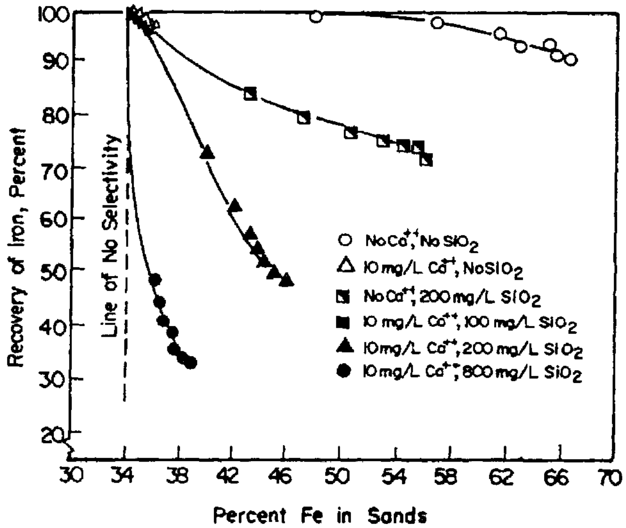

Figure 2. Selective flocculation of an artificial hematite–quartz mixture in the presence and absence of calcium and Na-silicate, 30 mg/L starch, pH 11.

It was also found that the addition of 200 mg/L SiO_2 in the absence of calcium resulted in a significant reduction in selectivity, indicating the adverse effect of sodium silicate on selective flocculation when used alone.

Calcium Abstraction Tests

In order to investigate the interaction between calcium and hematite in the presence of sodium silicate, calcium abstraction by hematite at pH 11 and 40 mg/L initial calcium concentration as a function of sodium silicate concentration was determined. The results are given in Fig. 3. Zeta potentials of calcium silicate precipitates and hematite under selected conditions and flocculation behavior of hematite are also included in the figure. It is seen that in the absence of sodium silicate, hematite abstracted around 0.35×10^{-2} g Ca^{++}/cm^2, Fig. 3a. As sodium silicate concentration increased, calcium abstraction by hematite also increased, reaching a maximum at around 1600 mg/L SiO_2. At this point, abstraction was 3×10^{-2} g Ca^{++}/cm^2 and decreased thereafter. Hematite flocculated up to 1600 mg/L SiO_2 concentration and dispersed at higher sodium silicate concentration, as depicted with the increase in the suspended solids in Fig. 3b. Results of zeta potential

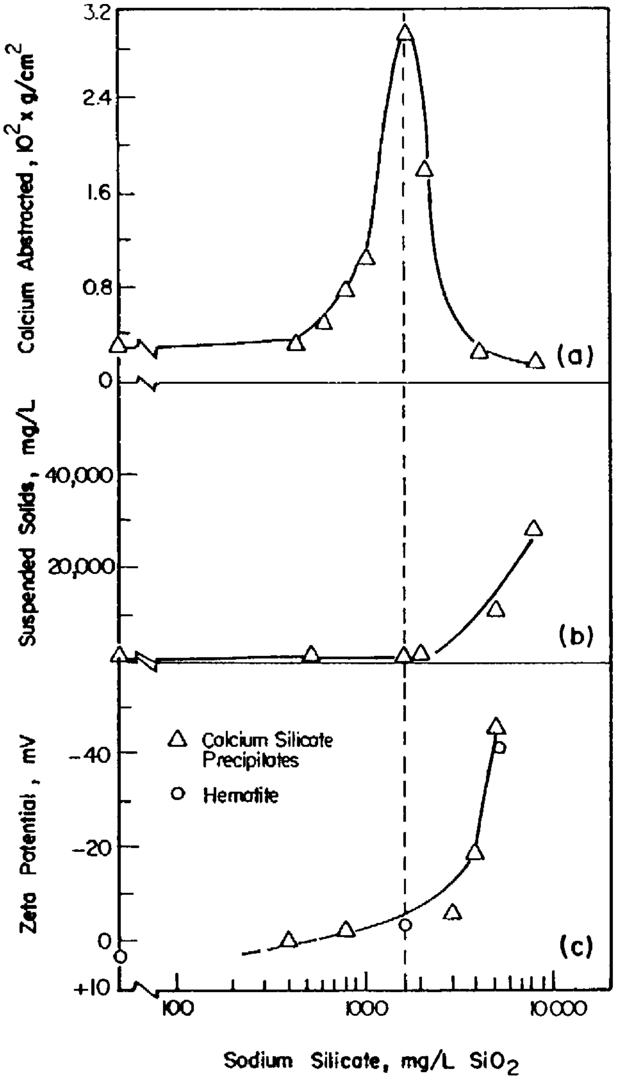

Figure 3. Calcium abstraction by and flocculation behavior of hematite and zeta potential of calcium silicate precipitates and hematite in the presence of 40 mg/L calcium as a function of Na-silicate concentration, pH 11.

measurements of hematite and calcium silicate precipitates, given in Fig. 3c, support the findings of calcium abstraction and flocculation of hematite. At low-sodium silicate concentrations, zeta potentials of calcium silicate precipitates and hematite were less than -20 mV, and thus, favoring heterocoagulation that would lead to higher calcium abstraction. As the sodium silicate concentration increased above 1600 mg/L SiO_2, zeta potentials of precipitates as well as hematite became more negative, and therefore, the two repulsed one another, resulting in reduced calcium abstraction by hematite and the dispersion of hematite pulp.

Starch Adsorption Tests

Flocculation behavior of hematite with starch in the presence of sodium silicate suggests that the interaction between hematite and silicate species influences adsorption of starch by hematite. To elucidate this point, starch adsorption by hematite was determined at 0, 10, and 40 mg/L calcium concentrations as a function of sodium silicate concentration. The results are presented in Fig. 4.

It was observed that starch was almost completely adsorbed at all calcium concentration levels in the absence of sodium silicate. Addition of sodium silicate resulted in a reduction of the starch adsorption at all calcium concentrations. However, the magnitude of reduction was the highest at 40 mg/L calcium and the lowest in the absence of calcium and intermediary at 10 mg/L calcium concentration. It was also found that regardless of the calcium concentration, hematite adsorbed nearly the same

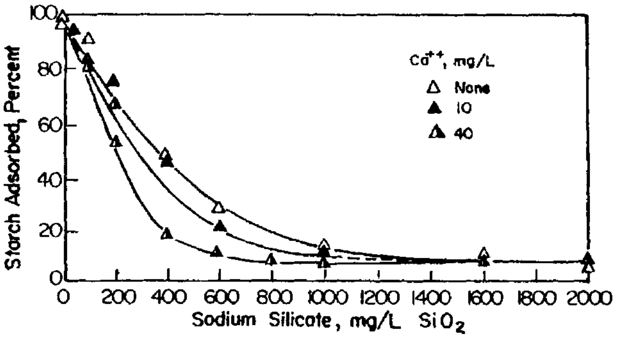

Figure 4. Starch adsorption by hematite in the presence of 0, 10, and 40 mg/L calcium ions as a function of Na-silicate concentration, 50 mg/L starch, pH 11.

and a very little amount of starch above 1000 mg/L SiO_2 silicate concentration.

DISCUSSION

The role of sodium silicate as a dispersant in the selective flocculation of iron ores has been shown to be related to its ability to remove calcium and magnesium ions from the process water.[8]

When sodium silicate is mixed with calcium chloride solution, calcium silicates precipitate instantaneously with a rapid decrease of free calcium ions in solution. The nature of precipitates can vary widely depending on such conditions as degree and manner of mixing, temperature, concentration of solutions, SiO_2/Na_2O ratio, and pH. Freshly formed precipitates are highly reactive due to their nascent, metastable nature, large surface area, and incompletely coordinated ions at the surface. In addition, presence of a substrate, such as mineral surfaces, for nucleation and growth plays a favorable role in the formation of surface precipitates. Interaction between mineral surfaces and precipitates is governed by their charges and specific affinity of the precipitates towards the surface. Sufficiently high surface potentials of precipitates and minerals would result in the detachment of precipitates from the surfaces depending on the presence and the magnitude of other forces.[19] At pH 11, both hematite and calcium silicate precipitates are negatively charged. Magnitude of the charge increases as the free calcium-ion concentration is lowered by increasing the sodium silicate concentration. When the zeta potentials of hematite and calcium silicate precipitates were sufficient in magnitude, say more than -20 mV,[5,20] Fig. 3c, calcium silicate precipitates detached from the hematite surface, Fig. 3a. Adsorption of starch on hematite was found to be very much related to the sodium silicate concentration, Fig. 4. With no sodium silicate present in the pulp, at 0, 10, and 40 mg/L calcium concentrations, starch was almost completely adsorbed by hematite. Addition of sodium silicate, at all calcium concentrations, caused significant reduction in starch adsorption. However, the magnitude of the reduction was more pronounced in the presence of calcium in the pulp. This can be related to the precipitation of calcium silicate on and thus shielding the starch molecules off the hematite surface. Further increase in the sodium silicate concentration in the pulp, although reduced calcium silicate coating of hematite surface, as clear from the calcium abstraction tests, did not improve starch adsorption. To the contrary, amount of starch adsorbed on hematite continued to decrease as the sodium silicate addition level increased in the presence and absence of calcium. Obviously, silicate ions, showing a complex hydroxide structure of multimeric nature in alkaline pH range[21,22] get adsorbed on the hematite surface before starch and prevent starch adsorption in a similar manner to earlier observations.[5,16,23]

The interactions depicted above between calcium, silicate, and hematite and between starch and hematite in the presence of calcium and silicate will govern the flocculation–dispersion behavior of hematite. These interactions may lead to coagulation as in the case of 10 and 40 mg/L calcium, flocculation caused by precipitates in the presence of calcium and low sodium silicate concentrations, polymer-induced flocculation in the presence of starch with no calcium and sodium silicate, and full dispersion with sodium silicate above a certain concentration level, which depends on calcium concentration. Each mechanism has a distinctly different settling behavior as seen in the settling rates under different conditions in Fig. 1. One single mechanism or a combination of the mechanisms and resulting settling behavior may prevail depending on the concentrations of the species under study. Successful selective flocculation of hematite will be possible only when hematite is flocculated with starch while quartz remains dispersed. In order to determine where this is possible in terms of calcium and sodium silicate concentrations, a simplified flocculation–dispersion map for the said minerals has been developed, Fig. 5. While developing the map, a suspension having more than

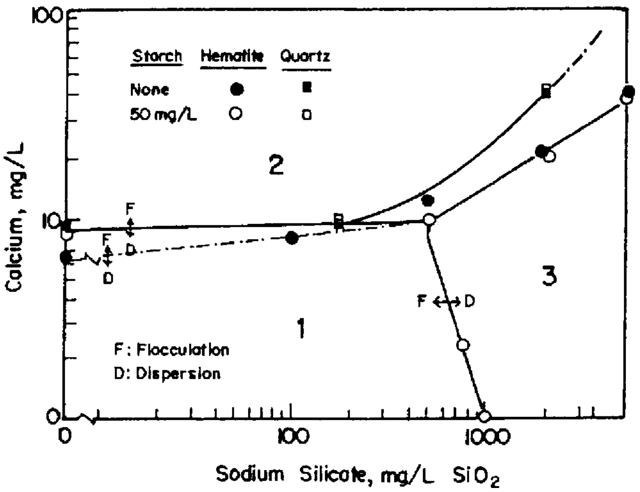

Figure 5. Flocculation–dispersion regions of hematite and quartz in the absence and presence of 50 mg/L starch as a function of calcium and Na-silicate concentration, pH 11.

30 g/L suspended solids was assumed dispersed and otherwise flocculated. As seen in the figure, there are three major flocculation and dispersion regions of hematite and quartz. In region (1), hematite and quartz remain dispersed in the absence of starch; in the presence of 50 mg/L starch, quartz continues to be dispersed while hematite flocculates. In region (2), both hematite and quartz flocculate, whereas in region (3), both minerals dispersed, both in the presence and absence of starch. It is obvious that selective flocculation of hematite with starch from a hematite–quartz mixture can only be possible in region (1) in which calcium and silicate concentrations should be kept below 10 mg/L and 800 mg/L as SiO_2, respectively. Region (2) results in indiscriminate flocculation while indiscriminate dispersion is expected in Region (3).

CONCLUSION

Dispersion of pulps in the selective flocculation of iron ores can be accomplished by using sodium silicate to remove coagulating multivalent cations, such as calcium and magnesium, from the process water. Sodium silicate was found to remove free calcium from the solution as calcium silicate precipitates, and thus, bring about dispersion. It was determined that there is a concentration of calcium, around 10 mg/L, above which dispersion with sodium silicate is not effective. Above this concentration, the amount of sodium silicate needed to disperse the pulp, or, in other words, remove the calcium from the hematite surface, was so much as to cause hematite surface to be covered by silicate ions. This coverage led to the prevention of starch adsorption on hematite and adversely affected selective flocculation.

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