

THE INFLUENCE OF SODIUM SILICATE IN NONMETALLIC FLOTATION SYSTEMS

by M. C. Fuerstenau, G. Gutierrez and D. A. Elgillani

The zero-points-of-charge of apatite, calcite, and fluorite are pH 6.4, 10.8, and 10.0, respectively. Scheelite is negatively charged above at least pH 3. In this article, the flotation responses of these minerals in the presence of potassium oleate and sodium silicate are described and compared with electrokinetic data. Colloidal silica appears to be the species principally responsible for calcite depression, while silicate anion is the species responsible for fluorite depression. Additions as high as 1×10^{-3} mole/liter silicate have no effect on the flotation responses of apatite and scheelite.

Selective flotation of nonmetallic minerals is difficult to achieve with fatty acids or soaps by themselves. As a result, specific reagents are added to aid these separations, and one of the reagents commonly employed for this purpose is sodium silicate. Flotation separations of various calcium-bearing minerals such as fluorite from calcite¹⁻³ and scheelite from calcite^{2,4} and apatite,^{2,5} for example, almost always involve the use of sodium silicate.

The mechanisms by which sodium silicate functions as a depressant are still not understood, probably for a number of reasons. For one thing, the dissolution process of sodium silicate is complex, giving rise to a number of ionic and colloidal species.⁶ Moreover, the type and concentration of these species depend on the ratio of Na_2O to SiO_2 , the concentration of sodium silicate, and the pH of the system.⁶ At the present time, it is not known which species, colloidal silica or silicate anion, is responsible for depression. If colloidal silica is the species that is adsorbing, then adsorption must occur by electrostatic attraction between the colloid and the mineral surface. Silicate anion, on the other hand, may adsorb either physically or chemically. The objective of this paper is to determine first the active species of sodium silicate

and then the conditions under which this species will adsorb and function as a depressant.

EXPERIMENTAL MATERIALS AND METHODS

Pure samples of apatite (Durango), calcite (Iceland-spar), fluorite, and scheelite were used in this investigation. Pure potassium oleate was used as collector, while reagent-grade HCl and KOH were employed for pH adjustment. The sodium silicates used were samples obtained from the Philadelphia Quartz Co. In one series of experiments, various sodium silicates containing different ratios of SiO_2 to Na_2O were added to calcite systems. These sodium silicates contained SiO_2 -to- Na_2O ratios of 3.75 to 1, 3.22 to 1, 2.40 to 1, and 1.60 to 1. All other experiments were conducted with the sodium silicate containing the ratio of 3.22 to 1, which is the one that is normally used in industry.

Flotation experiments were conducted with 2½-g charges of 48 × 150-mesh material in conductivity water with an apparatus and technique described previously.⁷

Electrokinetic experiments were conducted with both a Zeta Meter and streaming potential apparatus. Particle size was 48 × 65 mesh for the streaming potential experiments.

EXPERIMENTAL RESULTS

The first series of experiments involved flotation of scheelite in the absence and presence of sodium silicate. As shown in Fig. 1, flotation response was not affected with even the relatively high addition of 1×10^{-3} mole per liter sodium silicate. Interestingly though, no flotation was effected below pH 6 with this collector addition.

The responses of apatite to flotation under these same conditions are given in Fig. 2. Similarly, no depression was obtained in basic media under these conditions.

Similar experiments were conducted with fluorite, and in this case, depression was noted above about pH 11 with 1×10^{-3} mole per liter sodium silicate (Fig. 3).

When calcite was floated with these same levels of addition of sodium silicate, essentially no flotation was possible above pH 7 (Fig. 4). The effect of collector addition with a constant addition of sodium

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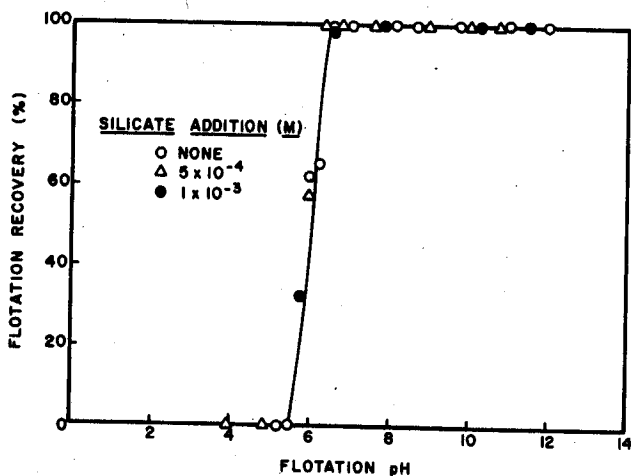


Fig. 1 - Flotation recovery of scheelite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the absence and presence of sodium silicate.

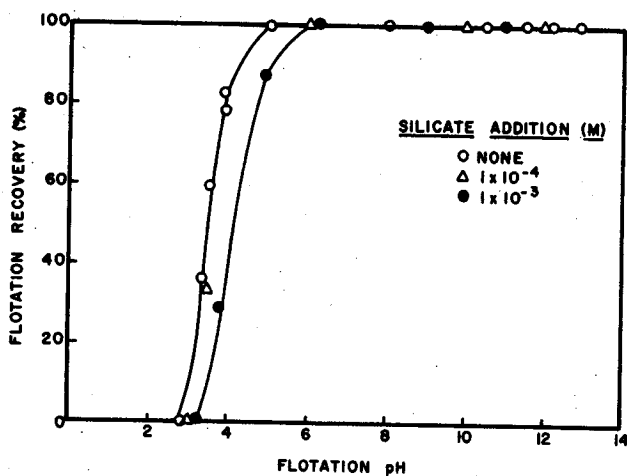


Fig. 2 - Flotation recovery of apatite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the absence and presence of sodium silicate.

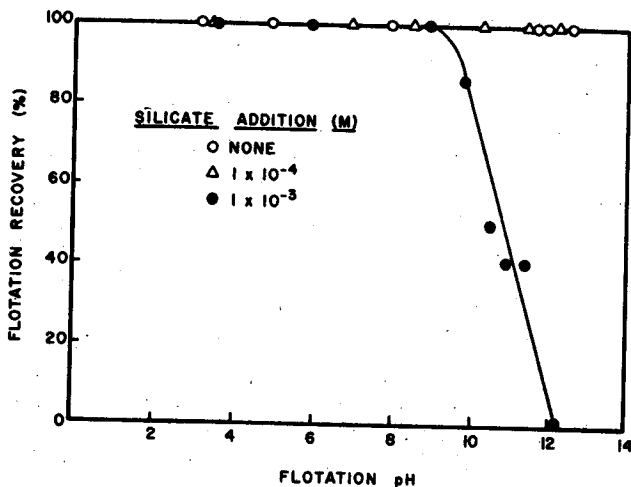


Fig. 3 - Flotation recovery of fluorite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the absence and presence of sodium silicate.

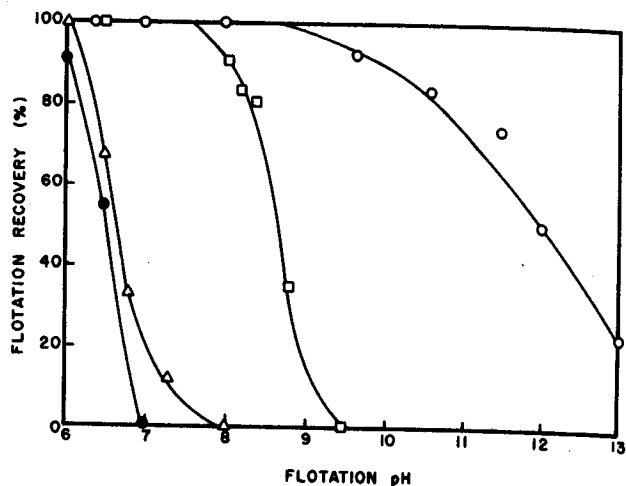


Fig. 4 - Flotation recovery of calcite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the absence and presence of sodium silicate. Light circles = none; squares = 1×10^{-6} M; triangles = 1×10^{-4} M; dark circles = 1×10^{-3} M.

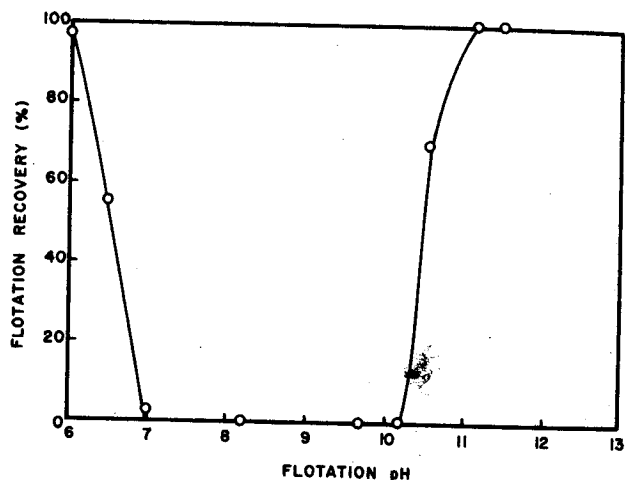


Fig. 5 - Flotation recovery of calcite as a function of pH with 5×10^{-4} mole per liter potassium oleate in the presence of 5×10^{-4} mole per liter sodium silicate.

silicate can be noted by comparing the data in Fig. 4 with that in Fig. 5.

The influence of the colloidal silica content of sodium silicate was also examined. The data presented in Fig. 6 show that as the ratio of SiO_2 to Na_2O is increased, depression is obtained sooner with the same level of addition of sodium silicate. It should be noted that the greater the ratio of SiO_2 to Na_2O in a sodium silicate, the greater is the colloidal silica content.⁶

Acidifying sodium silicate solutions results in the formation of more colloidal silica in the silicate solution, and flotation experiments were conducted in which the silicate additions were made from silicate solutions whose pH values ranged from pH 2 to 10.7. As shown in Fig. 7, the lower the pH of the silicate solution, the more effective is the depressing action. This phenomenon has been observed before.²

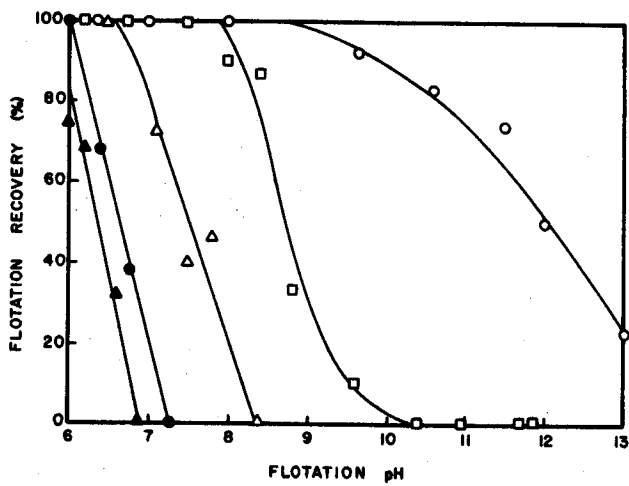


Fig. 6 - Flotation recovery of calcite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the absence and presence of sodium silicates (5×10^{-4} mole per liter) containing various ratios of SiO_2 to Na_2O . Light circles = none; squares = 1.60; light triangles = 2.40; dark circles = 3.22; dark triangles = 3.75.

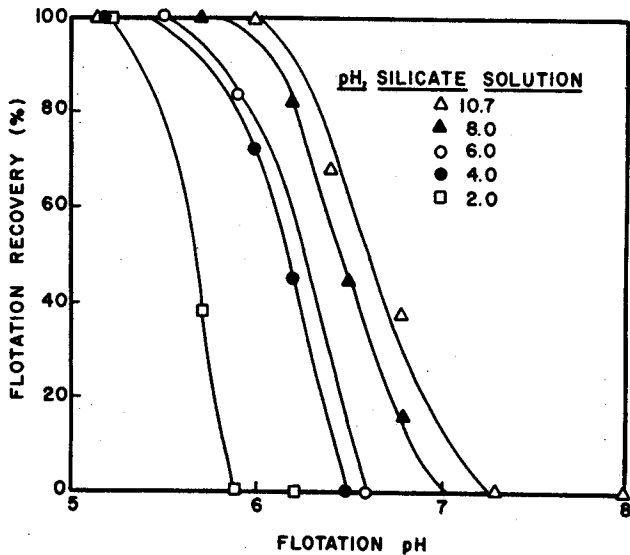


Fig. 7 - Flotation recovery of calcite as a function of pH with 1×10^{-4} mole per liter potassium oleate in the presence of various sodium silicates. The pH values of the sodium silicate solutions were adjusted to the values as shown.

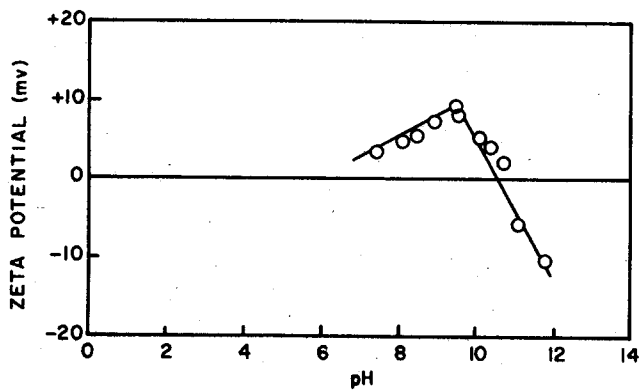


Fig. 8 - Zeta potential of calcite as a function of pH.

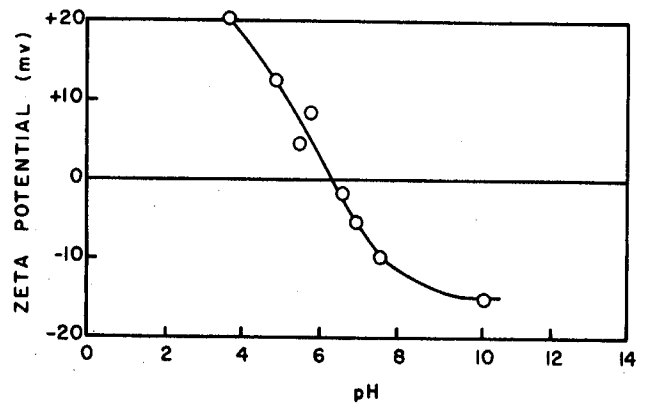


Fig. 9 - Zeta potential of apatite as a function of pH.

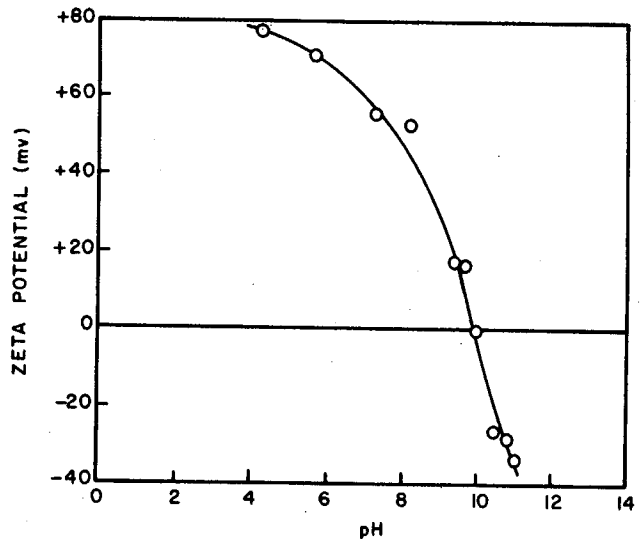


Fig. 10 - Zeta potential of fluorite as a function of pH.

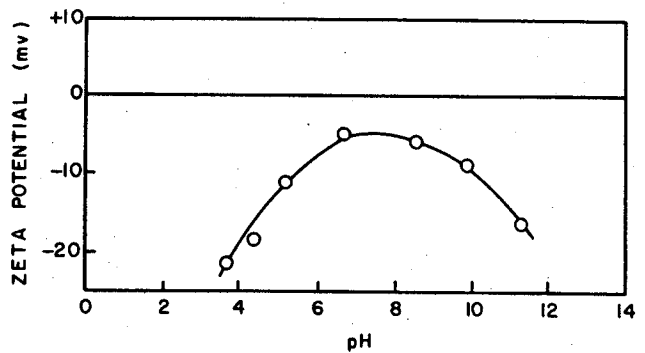


Fig. 11 - Zeta potential of scheelite as a function of pH.

Electrokinetic studies were conducted with each of the minerals to determine their zero-points-of-charge. As shown in Figs. 8, 9, 10, and 11, the zpc's of apatite, calcite, and fluorite are pH 6.4, 10.8, and 10.0, respectively. The zeta potentials of scheelite are negative over the pH range investigated, which is in agreement with the observation of O'Conner.⁹

The data for calcite presented in Fig. 8 were determined with a streaming potential apparatus due to

the solubility of calcite. These data agree well with that of Somasundaran and Agar.¹⁰ Electrokinetic experiments on apatite, fluorite, and scheelite were made with a Zeta Meter.

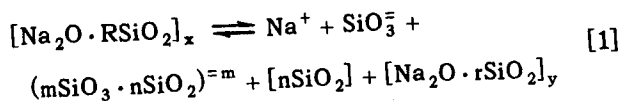
DISCUSSION OF RESULTS

The adsorption of oleate on calcite and fluorite has been shown with infrared techniques to be chemical in nature.¹¹ In view of the fact that flotation occurs well with oleate above the zero-points-of-charge of apatite and scheelite, it can be concluded that chemisorption of oleate is also occurring on these two minerals.

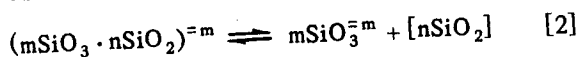
The individual flotation responses of these minerals in the absence of sodium silicate are quite different in acid media and would seem to be related to mineral solubility and perhaps to surface charge in the case of scheelite. Owing to the extreme solubility of calcite, no experiments were conducted with calcite much below neutral pH. With scheelite, no flotation is possible below about pH 6. Scheelite is negatively charged at all values of pH, but the surface becomes more negative below about pH 6 (Fig. 11). Furthermore, the concentration of collector ions is becoming smaller as the pH is reduced due to hydrolysis. It seems likely that both of these phenomena may contribute to the complete depression observed in acid media.

The surface charges of apatite and fluorite, on the other hand, are positive in acid media, and the fact that fluorite still responds to flotation at pH 3, while apatite is depressed, is probably then due to the differences in mineral solubility. The concentration of oleate ion will be small at pH 3, and the mineral with the greater solubility will be depressed sooner due to precipitation of the collector as calcium oleate.

The role that sodium silicate assumes in these systems is varied and is especially significant in calcite flotation. Sodium silicate is a complex mixture, which can be seen from the general dissolution scheme presented by Harmon,⁶



Breakdown of the complex silicate ions probably occurs as the solution is diluted, or



The brackets are used to designate colloidal compounds. Hydrolysis of silicate anions to HSiO_3^- and H_2SiO_3 will occur, the first and second dissociation constants of H_2SiO_3 being 4.2×10^{-10} and 5.1×10^{-17} respectively.⁶ As a result, any dilute solution of sodium silicate can probably be assumed to contain SiO_3^- , HSiO_3^- , and the complex $(m\text{SiO}_3 \cdot n\text{SiO}_2)^{=m}$ anions; dissolved $\text{H}_2\text{SiO}_3(aq)$; and colloidal SiO_2 and $\text{Na}_2\text{O} \cdot r\text{SiO}_2$.

In Fig. 6, it can be noted that complete depression is obtained with 5×10^{-4} mole per liter sodium silicate in which the ratio of SiO_2 to Na_2O is 1.6 to 1. No colloidal silica will be present in this system,⁶ and depression can be attributed to silicate anion adsorption. That this adsorption is probably chemical in nature, can be seen from the fact that depression is effected even at pH 12 where the calcite surface is negatively charged.

When the ratio of SiO_2 to Na_2O is greater than 2 to 1, colloidal silica is present in the sodium silicate, and this content increases as the ratio of SiO_2 to Na_2O increases.⁶ Since depression is obtained at lower values of pH with sodium silicates containing greater quantities of colloidal silica, it seems likely that the adsorption of colloidal silica is responsible for this action. In view of the fact that quartz and most silicates have zero-points-of-charge in the vicinity of pH 3,^{12, 13} colloidal silica particles should be negatively charged above about pH 3, and adsorption can occur on positively charged surfaces. The data in Figs. 5 and 8 show this phenomenon well in that the surface of calcite is positively charged from about pH 6 to 11, and depression is obtained in this range. Above pH 11 the calcite surface is negatively charged, and apparently the formation of surface calcium oleate is preferred to the formation of surface calcium silicate with these additions. The fact that complete flotation is effected at pH 6 is probably due to the high ionic strength of the solution which resulted from the dissolution of the calcite. The zeta potential will be approximately zero under these conditions.

The addition of relatively high quantities of sodium silicate has little or no effect on the flotation responses of apatite and scheelite. It seems reasonable to assume that the bonds between surface calcium and oleate ions will vary from one calcium mineral to another because oleate ions chemisorb by replacing surface anions of each mineral. Apparently, the surface calcium oleates of apatite and scheelite are of such a stability that neither colloidal silica nor silicate anion is able to affect the adsorption of the collector and the formation of surface calcium oleate with these levels of addition.

In the case of fluorite, however, the formation of calcium oleate is preferred to the adsorption of colloidal silica but not to the formation of surface calcium silicate (Figs. 3 and 10).

Since colloidal silica is apparently the species principally responsible for the depression of calcite in a moderately basic medium, acidifying the sodium silicate solution before adding the silicate should increase the depressing action because acidification will result in an increase in the colloidal silica content of the sodium silicate. This phenomenon may be seen from Eqs. 1 and 2; as the pH is reduced, hydrolysis of SiO_3^- will result and more of the complex

ion, $(m\text{SiO}_3 \cdot n\text{SiO}_2)^{-m}$ will dissociate. Furthermore, as the concentrations of $(m\text{SiO}_3 \cdot n\text{SiO}_2)^{-m}$ and SiO_3^- are reduced, more $\text{Na}_2\text{O} \cdot \text{RSiO}_2$ will dissolve. The data presented in Figs. 6 and 7 show this premise to be correct. This conclusion is in agreement with that of others.¹⁴

Under equilibrium conditions the quantity and type of silicate species would be independent of the initial pH of the silicate solution at a specific value of pH for flotation. In view of the fact that the silicate solutions of different initial pH values provide different flotation responses at the same pH, the reverse reactions given in Eqs. 1 and 2 must be slow.

ACKNOWLEDGMENTS

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INTERFACIAL FRICTION, MOISTURE AND COAL PILLAR STRENGTH

by Charles T. Holland and David A. Olsen

Considerable work has resulted in the development of a formula by which the strength of coal pillars for an L to T ratio of up to 12 may be estimated. One of the factors involved in this formula is the coefficient of friction between the coal pillar and the adjacent rock with which it is in contact. This paper presents the results of studies on sandstone, limestone, shale and coal and the coefficient of friction between coal and the other three under wet and dry conditions. With the coefficients of friction thus determined and the use of results obtained earlier by Meikle and Holland, it seems probable that coal pillar strength may be more closely estimated.

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Several investigators¹⁻³ have found that the compressive strength of cubical coal specimens can be correlated by an equation such as

$$S = \frac{K}{D^{1/n}} \quad [1]$$

where D = edge dimension in inches

K = a coefficient depending upon the coal used and other factors

S = strength in psi

and $1/n$ has a value somewhat less than $1/2$. Holland^{4,5} has found that for model coal pillars the results of compressive strength tests can be correlated by an equation such as

$$S = C \sqrt{L/T} \quad [2]$$

where C = a coefficient depending upon the coal used and other factors

S = strength of specimen in psi

L = least width of model pillar in inches

T = thickness of pillar in inches