

METAL ION ACTIVATION IN XANTHATE FLOTATION OF QUARTZ

by M. C. Fuerstenau, J. D. Miller, R. E. Pray and B. F. Perinne

Quartz cannot be floated with potassium amyl xanthate as collector at any pH. Complete flotation is achieved with certain minimal additions of amyl xanthate and Pb^{++} from pH 5.8 to 8.5 and with amyl xanthate and Zn^{++} from pH 7.5 to 8.1. The active species of these metal ions responsible for activation are shown to be $PbOH^+$ and $ZnOH^+$. No flotation was effected when Cu^{++} and Mg^{++} were added as activators.

Previous work^{1,2,3,4,5,6,7} has shown that quartz may be floated in the presence of sulfonate or soap when the following two criteria are met:

- 1) some portion of the added metal ion has hydrolyzed to its first hydroxy complex, and
 - 2) a precipitate of the metal-collector has formed.
- Since sulfonate and soap, two substantially different anionic collectors, conform to these criteria, this phenomenon may well be expected to be of a general nature. In this view then, it would appear that any anionic collector, including xanthates, should also float quartz when these two criteria are met.

The object of this paper is to demonstrate the conditions under which quartz will respond to flotation in the presence of potassium amyl xanthate.

EXPERIMENTAL MATERIALS AND TECHNIQUES

Quartz was prepared by leaching the sized sample (48×150 mesh) with HCl until no iron could be detected in the leach liquor. Conductivity water, made by passing distilled water through an ion exchange column, was used in the investigation. Potassium amyl xanthate was selected as collector. Purification of this reagent was effected with the following method:

- 1) a laboratory sample of potassium amyl xanthate was dissolved to saturation in hot ethyl alcohol and filtered several times while still hot,
- 2) the filtrate was cooled, during which time potassium amyl xanthate crystallized out of solution; the

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xanthate was then separated from the solution by filtration,

- 3) the amyl xanthate was dissolved in fresh hot ethyl alcohol and filtered,

- 4) step (2) was repeated,

- 5) the crystalline potassium amyl xanthate was washed with ethyl ether five times, and

- 6) the xanthate was dried for 24 hours under continuous vacuum.

Inorganic impurities are insoluble in hot ethyl alcohol whereas dixanthogen is soluble in ethyl ether.

Five-gram charges of 48×150 mesh quartz were conditioned for 3 min in 125 cc of solution containing the reagents and were floated with the small-scale cell and procedure described in previous papers.^{4,8} Reagent grade HCl and NaOH were used for pH adjustment, while reagent n-amyl alcohol was added as frother. Frother addition is necessary with this technique, but it should be mentioned that data, similar to those shown in Fig. 2 for 1×10^{-4} mole per liter Pb^{++} and 1×10^{-4} mole per liter AX^- , were also obtained with a Hallimond cell in the absence of frother.

EXPERIMENTAL RESULTS

Clean quartz could not be floated with amyl xanthate at any pH. Flotation was achieved under certain conditions, however, when various metal ions were added to the system. The activating ions used were lead, zinc, copper and magnesium, added as reagent grade chloride salts.

Lead as Activator: The effect of Pb^{++} as activator was examined at five different additions of amyl xanthate (Fig. 1, 2 and 3). When 1×10^{-5} mole per liter xanthate was added in the presence of 1×10^{-4} mole per liter Pb^{++} , no flotation was obtained at pH 6.5 or below, while a recovery of about 60% was effected at pH 7. When the pH was increased to 7.8, no flotation was again obtained. Complete depression was noted from pH 7.8 to about 10, at which point a recovery of about 30% was achieved. At about pH 11, the precipitate of lead amyl xanthate which was present below this pH dissolved and complete depression occurred.

When 2.5×10^{-5} mole per liter xanthate was added with the same lead addition, no flotation was obtained at pH 5.8 and below, whereas a recovery of

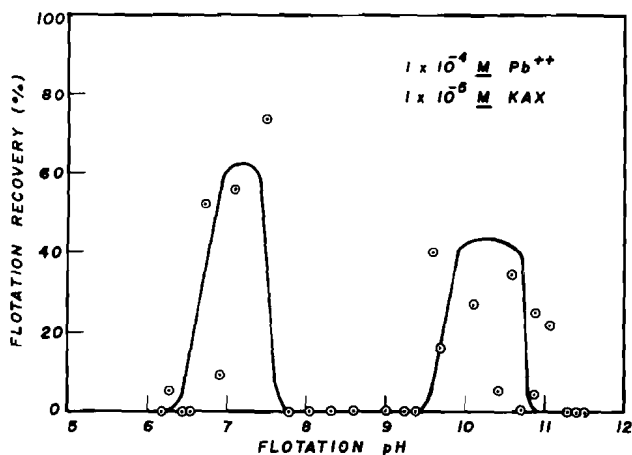


Fig. 1 - Relationship between flotation recovery and pH with constant Pb^{++} and amyln xanthate additions (separate experiments).

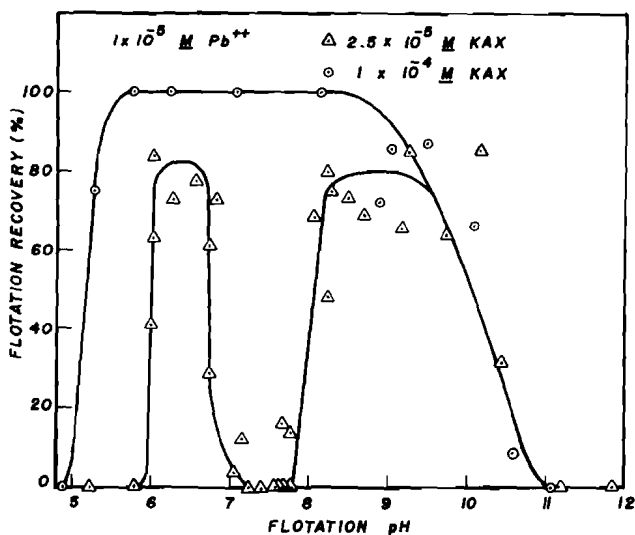


Fig. 2 - Relationship between flotation recovery and pH with constant Pb^{++} and various amyln xanthate additions (separate experiments).

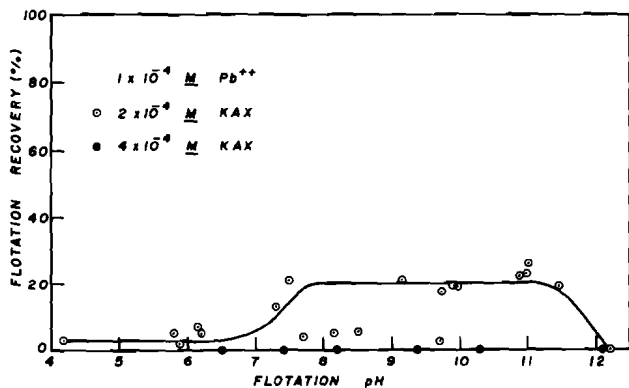


Fig. 3 - Relationship between flotation recovery and pH with constant Pb^{++} and various amyln xanthate additions (separate experiments).

80% was achieved at pH 6.0. The intermediate region of complete depression was reduced both in extent and in magnitude of pH under these conditions. When the pH was increased above 8, good flotation was obtained, while complete depression was noted again at pH 11 and above.

When the same molar additions of lead and amyln xanthate were involved, complete flotation was obtained from pH 5.8 to 8.5 and the intermediate region of depression was absent. When twice as much xanthate as lead was added, a maximal recovery of 20% was obtained; and finally when the system contained four times more xanthate than lead, no flotation was obtained at any pH.

Zinc as Activator: The first series of experiments involving zinc as activator were conducted with constant additions of 1×10^{-4} mole per liter Zn^{++} and 1×10^{-4} mole per liter amyln xanthate. No flotation was obtained at any pH under these conditions.

The experimental results obtained when 5×10^{-4} mole per liter Zn^{++} was added together with five different additions of xanthate are shown in Fig. 4 and 5. Maximum recoveries of about 30, 80 and 90% were obtained when 5×10^{-5} , 7.5×10^{-5} and 1×10^{-4} mole per liter xanthate, respectively, were added. The data also show that the effective pH region in which flotation is possible is broadened with increased additions of xanthate, while the pH at which complete depression is obtained (about pH 8) is independent of these xanthate additions.

Fig. 5 shows data obtained with additions of 2.5×10^{-4} and 5×10^{-4} mole per liter amyln xanthate in the presence of 5×10^{-4} mole per liter Zn^{++} . Flotation was obtained at slightly higher values of pH than when lower additions of xanthate were involved.

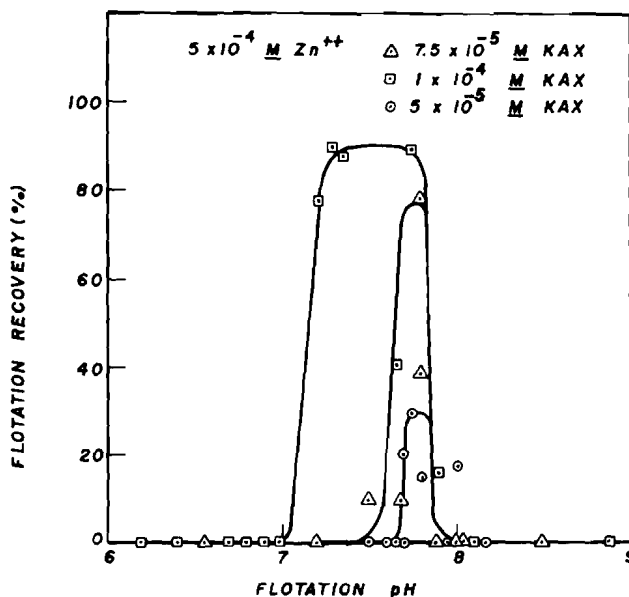


Fig. 4 - Relationship between flotation recovery and pH with constant Zn^{++} and various amyln xanthate additions (separate experiments).

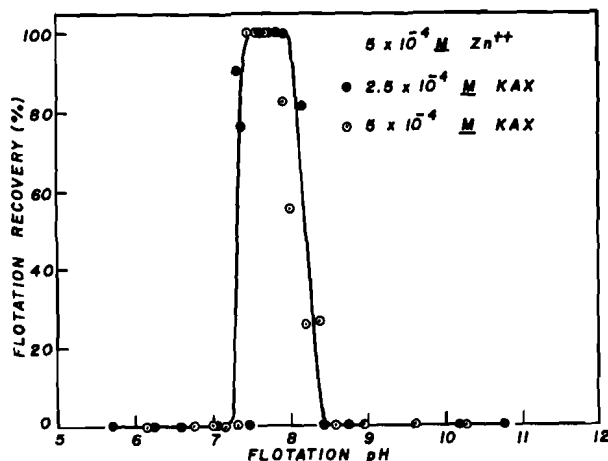


Fig. 5 - Relationship between flotation recovery and pH with constant Zn^{++} and various amyl xanthate additions (separate experiments).

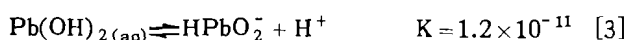
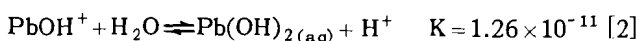
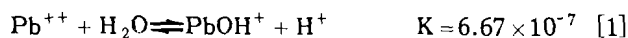
Copper and Magnesium as Activators: Experiments were conducted with three levels of addition of Cu^{++} ion (1×10^{-4} , 5×10^{-4} and 1×10^{-3} mole per liter) at a constant addition of 1×10^{-4} mole per liter amyl xanthate. No flotation was obtained from pH 3.8 to 11.1.

Similarly, no flotation was obtained with Mg^{++} at any pH from pH 9.5 to 11.6. Experiments were performed with three levels of addition of Mg^{++} ion (2×10^{-4} , 1×10^{-3} and 2×10^{-3} mole per liter) at 1×10^{-4} mole per liter amyl xanthate.

Lead as Activator (Fagergren Cell): An experiment was also conducted with a Fagergren cell to determine if the intense action produced by this cell would affect the flotation response of quartz in the presence of lead and amyl xanthate. One hundred grams of quartz were conditioned for 3 min in 2600 cc of solution containing 1×10^{-4} mole per liter Pb^{++} and 1×10^{-4} mole per liter KAX at pH 7. Two drops of n-amyl alcohol were used for frother. A recovery of 57% was obtained under these conditions.

DISCUSSION OF RESULTS

Similarly to the sulfonate-quartz and oleate-quartz systems, the added metal ions function as activators only in the pH regions in which some portion of the added metal ion has hydrolyzed to its first hydroxy complex. This fact can be seen from the hydrolysis schemes of the various metal ions. In the case of lead,⁹



The concentration of the various species of lead for an addition of 1×10^{-4} mole per liter $PbCl_2$ to water is shown in Fig. 6. As the solubility product of $Pb(OH)_2(s)$ is given as 4×10^{-15} , it is assumed that

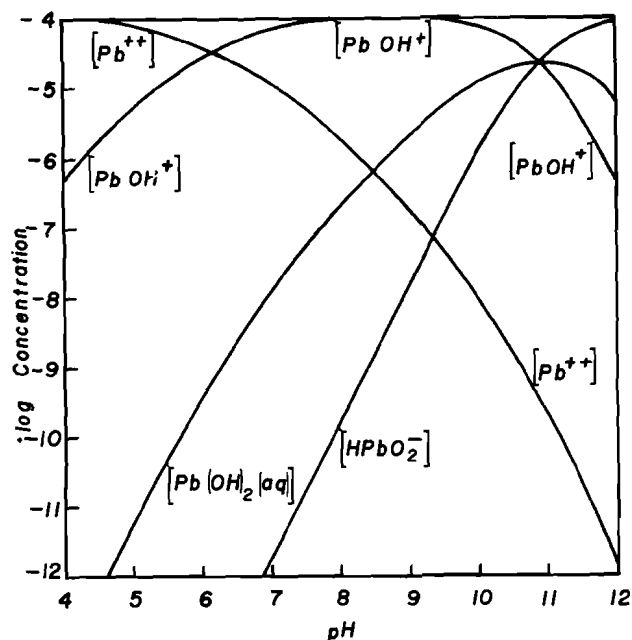
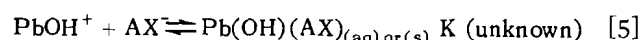
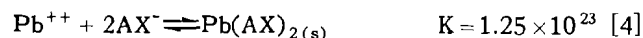


Fig. 6 - Logarithmic concentration diagram for an addition of 1×10^{-4} molar lead chloride to water.

the system is unsaturated with respect to lead hydroxide at all values of pH.⁹

Correlation of metal ion species with flotation response shows that $PbOH^+$ is the species of lead that is probably responsible for activation. Pb^{++} ion could not be functioning as activator, since flotation does not occur at pH 4 to 5 where it is the predominate species of lead ion, but does occur at pH 10 where it is vanishingly small.

In the presence of amyl xanthate, the following additional equilibria will be present:¹⁰

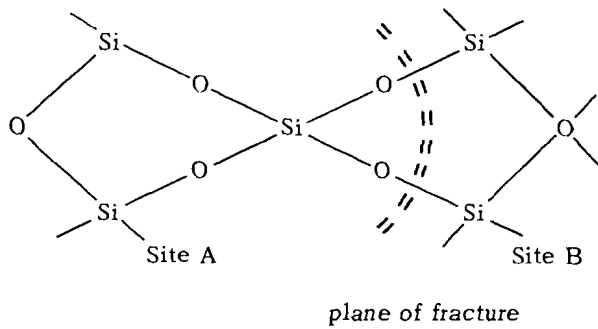


It is conceivable that either or both an aqueous lead hydroxy xanthate or a precipitate of basic lead xanthate may be present in these systems.

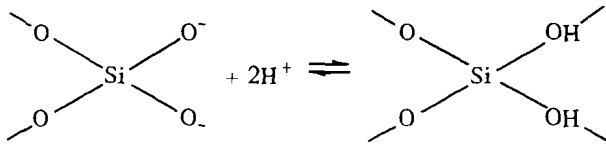
Calculation shows that the solubility product of lead amyl xanthate was exceeded by many orders of magnitude under all of the conditions employed. For example, when complete flotation was effected with 1×10^{-4} mole per liter Pb^{++} and 1×10^{-4} mole per liter AX^- , very little free xanthate was present in the system, while 5×10^{-5} mole per liter free lead (mainly $PbOH^+$ above pH 7) was present.

One possible mechanism of adsorption and hence flotation that has been presented previously in the case of the lead-sulfonate-quartz system, is that colloidal $Pb(OH)(RSO_3)_{(s)}$ may be functioning as the collector. Other mechanisms can also be presented. There may be an aqueous basic lead sulfonate, or in this system a basic lead xanthate complex, (analogous to $Fe(OH)_3(aq)$ in a saturated ferric hydroxide system) that is adsorbing on the surface.

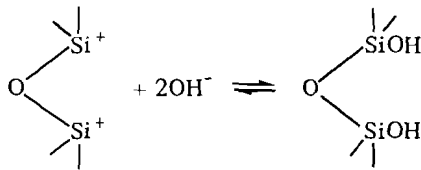
Representing the following reactions as happening to freshly fractured quartz,¹¹



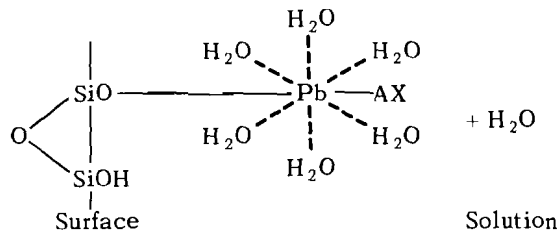
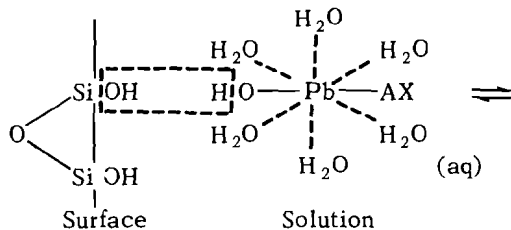
hydrogen ion can adsorb on Site A,



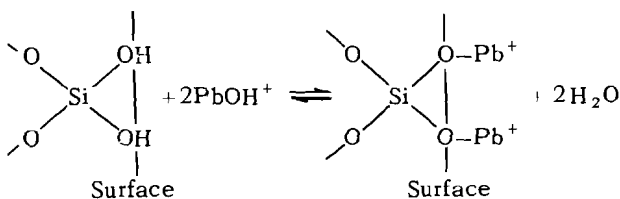
and hydroxyl on Site B



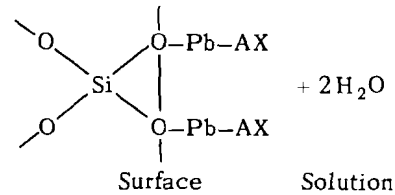
With Site B, adsorption may occur by splitting out water as follows:



Another possible adsorption mechanism could occur with Site A,



followed by the adsorption of xanthate ion,



The same basic lead xanthate would be present at the solid-liquid interface, and the splitting out of water would be involved by either route. With the latter mechanism though, the necessity for the precipitation of lead amyl xanthate is not as apparent as with the basic complexes.

Intermediate regions of flotation depression occur when there is a large excess of free Pb^{++} and $PbOH^+$ and essentially no free xanthate ion in solution. The reasons for collection, depression and then collection as the pH is increased is not clear at the present time. Additional work will have to be done to clarify this phenomenon.

At the other extreme, when twice as much xanthate as lead is added, a maximal recovery of about 20% is obtained; and when the xanthate addition is much in excess, the system is completely depressed. These phenomena can probably be explained by the fact that essentially all of the added lead will have been precipitated as lead amyl xanthate, with the result that essentially no $PbOH^+$ ion will be present in the system.

The flotation depression observed at pH 11 and above in all cases can be attributed to the formation and stability of plumbite ion ($HPbO_2^-$).

The experiments conducted with Zn^{++} as activator showed that flotation results only when some of the Zn^{++} has hydrolyzed to the first hydroxy complex. This can be seen by comparing the flotation data with the calculated concentrations of zinc species listed in Table I as a function of pH for an addition of 1×10^{-4} mole per liter $ZnCl_2$ to water.

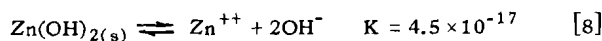
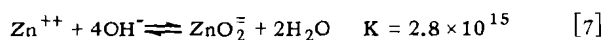
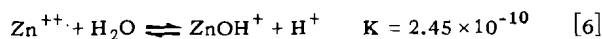
As shown, a critical concentration of about 4×10^{-7} mole per liter $ZnOH^+$ is necessary for flotation. Again, Zn^{++} cannot be responsible for flotation because no recovery is obtained in the pH region where it is the most abundant species. Depression occurs at pH 8 and above, due probably to the formation and stability $Zn(OH)_2(s)$. Zincate ion, $ZnO_2^{=}$, is vanishingly small below pH 10 under these conditions.

The second criterion for activation in non-metallic flotation, i.e. the necessity for metal-collector precipitation, is demonstrated clearly in this system. The solubility product of $Zn(AX)_2$ is given¹³ as 1.55×10^{-12} . When 1×10^{-4} mole per liter Zn^{++} and 1×10^{-4} mole per liter AX^- were used, no precipitation of $Zn(AX)_2$ was observed and no flotation was effected at any pH. When 5×10^{-4} mole per liter Zn^{++} and 5×10^{-5} mole per liter AX^- were used, a recovery of about 30% was obtained at pH of 7.7. This is a

Table I. Concentrations of Various Zn⁺⁺ Ion Species as a Function of pH for a Nominal Addition of 1 × 10⁻⁴ Molar ZnCl₂ to Water

pH	Zn ⁺⁺	Species			Zn(OH) _{2(s)}
		ZnOH ⁺	ZnO ₂ ⁼		
6.0	1.0 × 10 ⁻⁴	2.4 × 10 ⁻⁸	2.8 × 10 ⁻²¹		0
7.0	1.0 × 10 ⁻⁴	2.4 × 10 ⁻⁷	2.8 × 10 ⁻¹⁷		0
7.2	1.0 × 10 ⁻⁴	3.9 × 10 ⁻⁷	1.8 × 10 ⁻¹⁶		0
7.5	1.0 × 10 ⁻⁴	7.8 × 10 ⁻⁷	2.8 × 10 ⁻¹⁵		0
8.0	4.5 × 10 ⁻⁵	1.4 × 10 ⁻⁶	1.0 × 10 ⁻¹³	5.4 × 10 ⁻⁵	
8.5	4.5 × 10 ⁻⁶	3.5 × 10 ⁻⁷	1.0 × 10 ⁻¹²	9.6 × 10 ⁻⁵	
9.0	4.5 × 10 ⁻⁷	1.4 × 10 ⁻⁷	1.0 × 10 ⁻¹¹	9.9 × 10 ⁻⁵	
10.0	4.5 × 10 ⁻⁹	1.4 × 10 ⁻⁸	1.0 × 10 ⁻⁹	1.0 × 10 ⁻⁴	
10.5	4.5 × 10 ⁻¹⁰	4.4 × 10 ⁻⁹	1.0 × 10 ⁻⁸	1.0 × 10 ⁻⁴	
11.0	4.5 × 10 ⁻¹¹	1.4 × 10 ⁻⁹	1.0 × 10 ⁻⁷	1.0 × 10 ⁻⁴	

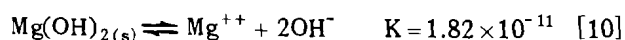
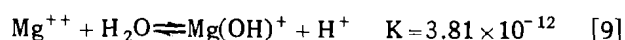
These calculations were made utilizing the following equilibria:¹²



concentration product of 1.25 × 10⁻¹² or, in other words, just under the solubility product of Zn(AX)₂. When 5 × 10⁻⁴ mole per liter Zn⁺⁺ and 7.5 × 10⁻⁵ mole per liter AX⁻ were involved, a recovery of about 80% was obtained at pH 7.7. This is a concentration product of 2.8 × 10⁻¹², which exceeds the solubility product, and the precipitate of Zn(AX)₂ was observed.

When the solubility product was exceeded by an even larger margin, 90% recovery was achieved for nearly a complete unit of pH.

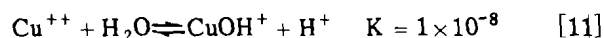
The data obtained with Mg⁺⁺ and Cu⁺⁺ ions as activators add support to the conditions required for quartz flotation with anionic collectors. When Mg⁺⁺ was used as an activator, no precipitation of Mg(AX)₂ occurred and no flotation was obtained, even in the pH region (above pH 10) where some Mg⁺⁺ hydrolyzes to MgOH⁺. Complete hydrolysis of Mg⁺⁺ to Mg(OH)_{2(s)} occurs at pH 11 to 11.5. These phenomena may be seen from the following equilibria:¹⁴



Both quartz and beryl have been shown to float well from pH 10.5 to 11.5 with Mg⁺⁺ as activator and sulfonate as collector. In these cases the solubility product of Mg(RSO₃)_{2(s)} had been exceeded; such was not true in the case of magnesium amyl xanthate.

If the first hydroxy complex of metal ions is the species responsible for flotation, Cu⁺⁺ ion would be expected to function as an activator above about

pH 6. That is, about 1% of the cupric ion in solution will have hydrolyzed to CuOH⁺ at pH 6.¹⁵



In fact, Gaudin¹⁶ has shown that complete flotation of quartz occurs from pH 6 to 10.5 in the presence of cupric nitrate and sodium oleate. A recovery of about 4% was obtained at pH 5.8.

Conversely, cuprous ion will not be expected to function as an activator, since even if it is capable of hydrolyzing to a first hydroxy complex, there would not be a valence site available for the collector ion.

In the presence of xanthate, Cu⁺⁺ ion is reduced to Cu⁺, and xanthate is oxidized to dixanthogen. Cu⁺ ion then combines with AX⁻ to form CuAX_(s). Because of these phenomena, quartz flotation could not be effected with Cu⁺⁺ ion as activator and amyl xanthate as collector.

Finally, an experiment was conducted with a Fagergren flotation cell to determine whether the intense action produced by this cell would account for the fact that xanthates have been reported as being incapable of functioning as collectors for quartz and silicates, even in the presence of heavy metal salts.¹⁷ Compared with performance in the small-scale cell, flotation recovery was somewhat reduced when the Fagergren cell was used, but still a good flotation response was obtained. As the experimental conditions employed by Sutherland and Wark were not listed, it is not possible to delineate reasons for the reported lack of response by quartz to amyl xanthate flotation in the presence of suitable activating metal ions. The experimental results contained in the present work show clearly the conditions under which quartz can be floated with amyl xanthate as collector and also lend support to the two criteria necessary for activation in nonmetallic flotation systems.

ACKNOWLEDGMENTS

The authors wish to thank Mr. F. W. Bloecher, Jr., of Cyanamid International, Wayne, New Jersey for supplying the potassium amyl xanthate and the technique for its purification.

The authors also wish to acknowledge the financial support provided by the Institute for Extractive Metallurgy, Bethlehem Steel Co. and the Colorado School of Mines Foundation, Inc.

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STARCHES AND STARCH PRODUCTS AS DEPRESSANTS IN SOAP FLOTATION OF ACTIVATED SILICA FROM IRON ORES

by I. Iwasaki and R. W. Lai

Some physical as well as chemical aspects of the methods of dispersion of various corn starches and their derivatives are investigated and their effects as depressants in anionic silica flotation of iron ores ascertained. The adsorption behavior of starches on hematite and quartz is strongly affected by their molecular sizes as inferred from viscosity measurements. The implication of this behavior on flotation and flocculation is discussed. Mechanical treatment of causticized starch solutions is shown to reduce the starch requirements in flotation appreciably.

Starches and starch products have been used as depressants for iron oxides both in amine flotation of siliceous gangue and in soap flotation of activated silica from iron ores. Cooke and his associates^{1,2,3,4} extensively studied the effects of certain starches and their derivatives in the amine flotation of iron ores at near-neutral pH and found that although most starches were good flocculants for hematite and de-

pressed that mineral more or less selectively^{1,3} they did not flocculate quartz suspensions. Further, that replacement of active groups in corn starch modified its behavior as a flocculant for hematite or quartz suspensions¹ and as an iron oxide depressant.⁴ Schulz and Cooke² showed that many starches and their derivatives, except aminoethyl starch, were abstracted more effectively by Brazilian hematite than by quartz and that the adsorption of a starch product was strongly dependent on pH and on the presence of calcium ion. In soap flotation of calcium-activated quartz, certain starches and their products have been used to depress iron oxides.^{5,6} The behavior of these substances in flotation appears at times to be at variance with those previously reported and especially with results obtained in the Mines Experiment Station laboratories. This is attributed, at least in part, to differences in flotation procedure and flowsheets and in the method of preparing the depressant. Most of the investigators referred to above, solubilized the starch products by autoclaving at 120°C. Others have used acid,⁷ alkali⁸ or oxidizing agents.⁹

In view of the limited knowledge of the depressing action of starches and their derivatives in iron ore flotation, particularly in soap flotation of calcium-activated silica at high alkalinity, an extensive study

I. IWASAKI and R. W. LAI are respectively Associate Professor and Research Assistant, Mines Experiment Station, University of Minnesota, Minneapolis, Minn. TP 65B102. Manuscript, Feb. 25, 1965. Chicago Meeting, February 1965. Discussion of this paper, submitted in duplicate prior to Mar. 15, 1966, will appear in *SME Transactions*, June 1966, and *AIME Transactions*, 1966, vol. 235.