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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	angstrom		ml	milliliter
cm^{-1}	reciprocal centimeter		mm	millimeter
g	gram		mo	month
g/l	gram per liter		mv	millivolt
hr	hour		NTU	nephelometric turbidity unit
µg	microgram			
			pct	percent
min	minute			
			yr	year

FLOCCULATION OF SULFIDE MINERAL FINES BY INSOLUBLE CROSS-LINKED STARCH XANTHATE

By S. C. Termes,[1] R. L. Wilfong,[1] and P. E. Richardson[2]

ABSTRACT

The Bureau of Mines conducted research on the flocculation of various minerals with insoluble cross-linked starch xanthate (ISX) to determine its potential as a beneficiation technique for low-grade, highly disseminated ores and for selective desliming. Covellite, chalcocite, pyrite, pyrrhotite, chalcopyrite, bornite, sphalerite, galena, and molybdenite fines flocculate with ISX. Floc formation, floc size, and settling rate are dependent on pH, with the pH dependence differing for each mineral. Quartz is not flocculated by ISX. Experiments to obtain selective flocculation of sulfides from quartz were attempted. Good selectivity was only obtained for the bornite-quartz system. Postflocculation separations resulted in flocculated bornite in grades as high as 92 pct. Evidence is presented that the flocculation of many of the sulfide minerals with ISX may involve covalent bonding of the xanthate group to lattice metal site(s).

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[1]Research chemist.
[2]Supervisory physicist.
Avondale Research Center, Bureau of Mines, Avondale, MD.

INTRODUCTION

Because of the increasing interest in selective flocculation as a beneficiation technique for low-grade, highly disseminated ores and for selective desliming, the Bureau of Mines has been investigating the flocculation behavior of several cross-linked starch derivatives containing chelating groups. This report discusses the flocculation of sulfide mineral fines by insoluble cross-linked starch xanthate (ISX).

Polymeric materials such as ISX, which contain a chelating group of known reactivity towards specific mineral surfaces, were first proposed by Slater, Clark, and Kitchener (1),[3] Kitchener (2), and Attia and Kitchener (3) as selective flocculants for mineral fines with particle aggregation possible through a bridging mechanism. ISX appeared to be attractive as a sulfide mineral flocculant because (1) alkyl xanthates are known to react selectively with sulfide minerals in flotation circuits by the formation of covalent bonds between the xanthate group and surface metal component(s) of the mineral (4); (2) cross-linking of starch prior to xanthation results in a high-molecular-weight polymeric backbone that generally favors floc strength; (3) ISX is prepared from easily renewable sources, and it is more stable and easier to handle than the soluble, alkali metal starch xanthates previously studied by Chang (5) and Brown (6) for the beneficiation of iron ores, and Brown and Cecil (7) for the concentration of sylvite from sylvinite ore.

The ISX reported in this paper as a flocculant for sulfide mineral fines was developed by Wing and Doane (8-9) at the U.S. Department of Agriculture, Northern Regional Research Center, Peoria, IL, for the removal of heavy metal ions from waste waters.

BACKGROUND

Starches are composed of two polysaccharide fractions, amylose and amylopectin. The ratio of these fractions is somewhat variable for each type of starch (that is, corn, potato, rice, etc.). Both amylose and amylopectin are made up

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

of D-(+)-glucose units (fig. 1A) joined in α-1,4-glycoside linkages. Amylose chains are linear (fig. 1B) while amylopectine is a branched polymer with side chains attached through α-1,6-glycoside linkages (fig. 1C). Neither of these fractions are soluble in water. Amylopectin dispersions in water are relatively stable, but amylose dispersions can be regarded as metastable.

A

B

C

a= OH
R= CH₂OH

FIGURE 1. - Components of starch. *A*, D-(+)-glucose; *B*, amylose; *C*, amylopectin.

Cross-linking in starch involves participation of the hydroxyl groups. It is a nondegradative reaction where intermolecular bridges (cross-links) are formed by reagents having multiple reactive sites such as epichlorohydrin, formaldehyde, and phosphorus oxychloride. Intermolecular bridging results in an increase in the molecular weight of the polymer.

The cross-linked starch used in the preparation of ISX is an epichlorohydrin cross-linked product that can be represented as

$$Starch \left[OCH_2-\overset{\overset{OH}{|}}{CH}-CH_2-O \right]_{DCL} Starch,$$
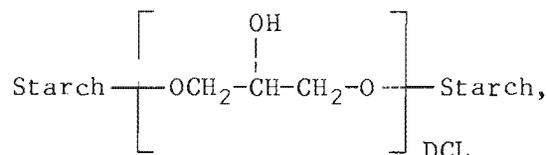
where DCL represents the degree of cross-linking.

Xanthation of starch proceeds readily in strong alkaline solutions. The primary hydroxyl group, C-6, is the principal group involved in the xanthation reaction (see figure 1). Alkali metal starch xanthates degrade rapidly in aqueous solutions, while the alkaline-earth and heavy metal salts are more stable. The magnesium derivative of cross-linked starch xanthate, which is known as ISX, was found by Wing and Doane (8-9) to produce the most desirable product in terms of room temperature stablity, effectiveness in heavy metal removal, and lower production cost.

EXPERIMENTAL

REAGENTS

Unless otherwise specified, chemicals were reagent grade and water was distilled and deionized. A commercial highly cross-linked starch (CLS) marketed as Vulca 90⁴ from the National Starch and Chemical Co. was used in preparing the xanthate derivative.

SYNTHESIS AND CHARACTERIZATION OF ISX

ISX was prepared according to the following method described by Wing (9):

$$CLS + NaOH \longrightarrow \underset{starch}{Causticized} \overset{CS_2}{\longrightarrow} \underset{\underset{(Na^+ salt)}{derivative}}{Xanthate} \overset{Mg^{2+}}{\longrightarrow} ISX.$$
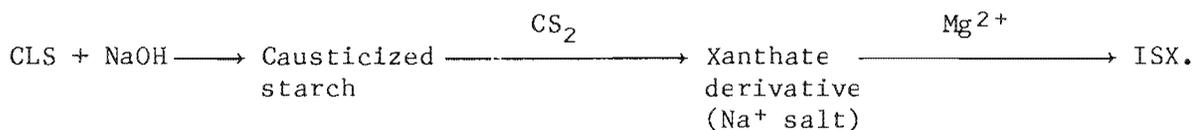
⁴Reference to specific trade names or manufacturers is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

Crude ISX is a pale orange, rather wet solid. Washing with water is necessary to remove unreacted material and impurities. Successive washings with acetone and ether leaves a pale yellow, finely powdered material stable for at least 1 yr when kept in tightly closed glass containers under refrigeration. At room temperature, the life of ISX is a few months. With aging, ISX turns dark yellow and has a foul smell. Addition of ISX to aqueous solutions produces an increase in pH. Both ISX and CLS disperse well in water at concentrations below 25 g/l.

The degree of substitution (D.S.) was determined by the acidimetric method described by Swanson and Buchanan (10). IXS with D.S. values between 0.2 and 0.4 were obtained, which is within the range recommended by Wing and Doane (8-9) for effective removal of heavy metal ions.

Chemical analysis of ISX with a D.S. of 0.4 yielded the following, in percent: sulfur, 8.27; ash, 19.6; water, 12.7; magnesium, 1.38. The infrared spectra of CLS and ISX are shown in figure 2. Xanthate-related bands are indicated in the ISX spectrum.

MINERAL PREPARATION

Mineral specimens were obtained from Ward's Natural Science Establishment, New York. Handpicked crystals were dry ground to minus 400 mesh with an agate mortar and pestle. Freshly ground minerals were used unless otherwise specified. X-ray diffraction data showed that the samples were essentially monomineralic, except for the pyrrhotite sample which also contained pentlandite. Table 1 presents analytical data and origin of the minerals.

TABLE 1. - Analytical data on mineral specimens

Mineral	Origin	Constituents	Main elements,[1] pct
Covellite, CuS....	Butte, MT............	Covellite, pyrite (minor to trace).	Cu 63.1 (66.5), Fe 1.73.
Chalcocite, Cu_2S..	Messina, Transvaal..	Chalcocite............	Cu 79.1 (79.8).
Pyrite, FeS_2......	Ambasaguas, Spain...	Pyrite................	Fe 44.2 (46.5).
Pyrrhotite, $Fe_{1-x}S$	Ontario, Canada.....	Pyrrhotite, pentlandite.	Fe 55.9,[2] Ni 6.10,[2] Co 0.3.[2]
Chalcopyrite, $(Cu,Fe)S_2$.	Messina, Transvaal..	Chalcopyrite.........	Cu 34.3 (34.6), Fe 31.9 (30.4).
Bornite, Cu_5FeS_4..	Ajo, AZ.............	Bornite, pyrite (minor to trace).	Cu 61.7 (63.3), Fe 10.3 (11.1).
Sphalerite, ZnS...	Santander, Spain....	Sphalerite, wurtzite (minor to trace).	Zn 66.1 (67.1).
Galena, PbS.......	Galena, KS..........	Galena...............	Pb 86.2 (86.4).
Molybdenite, MoS_2.	Korea..............	Molybdenite, quartz (minor to trace).	Mo 58.1 (59.9).
Quartz, SiO_2......	Brazil.............	Quartz...............	Si 45.4 (47.1).

[1]Numbers in parentheses refer to the percent of the main element, assuming a pure sample.
[2]Variable stoichiometry of Fe in pyrrhotite and of Fe, Ni, and Co in pentlandite.
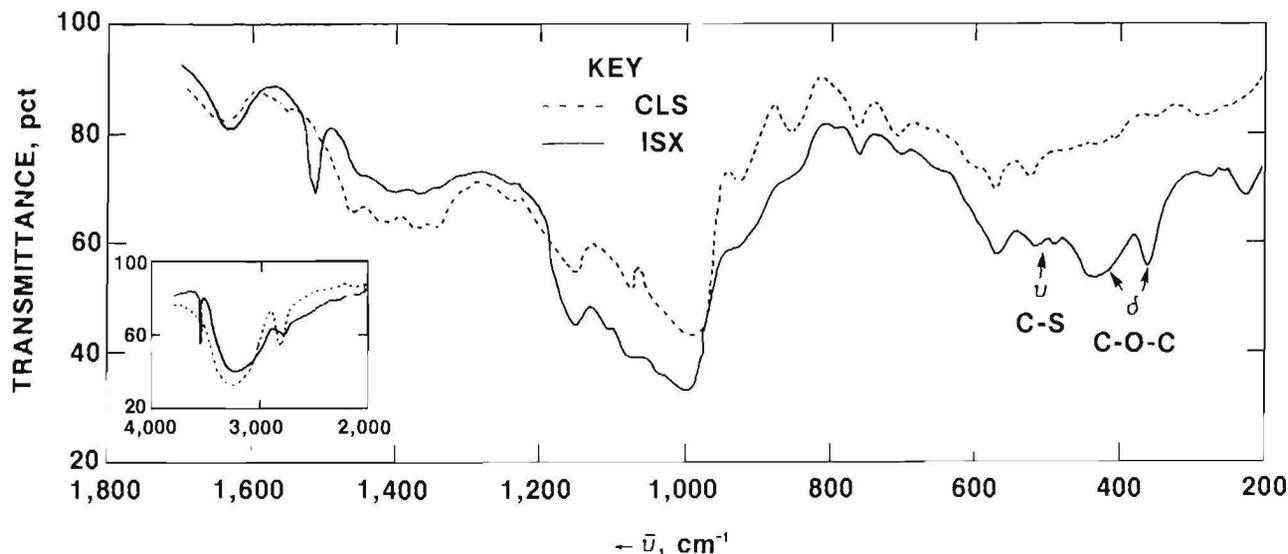
FIGURE 2. - Infrared spectra of CLS and ISX. Xanthate-related bands are indicated in the ISX spectrum.

FLOCCULATION EXPERIMENTS[5]

Flocculation tests were performed in 100-ml graduated cylinders fitted with ground glass stoppers. Unless otherwise specified, 3-g samples of each mineral were suspended in 80 ml of water. Dilute HCl and NaOH solutions (0.01M, 0.1M, and 1.0M) were used to adjust the pH to the desired values prior to flocculant addition and for any subsequent pH adjustments.

To determine the effectiveness of ISX as a flocculant, separate runs were made in the absence of any starch (acid-base additions only) and in the presence of CLS. The desired weight of CLS or ISX (0.1 or 0.2 g) was dispersed in 20 ml of water immediately before addition to the mineral pulp. Mixing was done manually by shaking and inverting the closed cylinder for 1 min, after which the cylinder was set on a bench and visible changes in the height of settled solids, clarification, and floc size were recorded at various time intervals.

To determine the selectivity of ISX, synthetic mixtures of selected sulfide minerals and quartz were prepared and the flocculation tests repeated as above.

[5]Performed by Heidi C. Triantafillou, chemist, Avondale (MD) Research Center.

Postflocculation separations were performed in two ways: (1) decantation of the suspended minerals, followed by washing of the flocs to remove nonflocculated mineral(s), and repeating the operation as necessary to clean the flocs from the nonflocculated, trapped material; and (2) by using the titled plate elutriator illustrated in figure 3. This apparatus is an adaptation of the one described by Friend, Iskra, and Kitchener (11), where washing of the flocs is performed by a counterflow of water. The unflocculated minerals are collected at the top, while the flocs are collected at the bottom.

OTHER MEASUREMENTS

Zeta potentials were measured with a commercially available zeta-meter following established procedures (12-13). Turbidities were measured with a turbidimeter. Turbidities above 200 NTU were obtained by diluting aliquots of the original sample to give turbidity values below 200 NTU and then extrapolating the results to obtain the turbidity of the original sample. Infrared spectra were recorded with a commercially available grating infrared spectrophotometer. Samples for infrared studies were prepared as KBr pellets. Photomicrographs were taken with a scanning electron microscope.

FIGURE 3. - Tilted plate elutriator. *A*, Water inlet; *B*, screen or fritted glass plate, 25 to 50 μm porosity; *C*, elutriant outlets, *D*, floc outlet; *E*, slurry inlet; *F*, flow regulators.

RESULTS

SINGLE-MINERAL PULPS

Initial tests to assess the ability of ISX to flocculate suspensions of sulfide mineral fines and quartz, and the influence of pH on flocculation behavior, involved measuring the height of settled solids. Although the height is not a quantitative measure of mineral removed from the pulp, it is a measure of floc formation and floc size.

The results are shown in figures 4 through 13 for freshly ground fines of covellite, chalcocite, pyrite, pyrrhotite, chalcopyrite, bornite, sphalerite, galena, molybdenite, and quartz as a function of pH in the presence of ISX, CLS, and for acid-base additions only. Additions of ISX and CLS were done at the natural pH (pH_n) of the mineral pulp. The pH range where good flocculation and maximum visual clarification occurred is indicated by the dashed region of the curves.
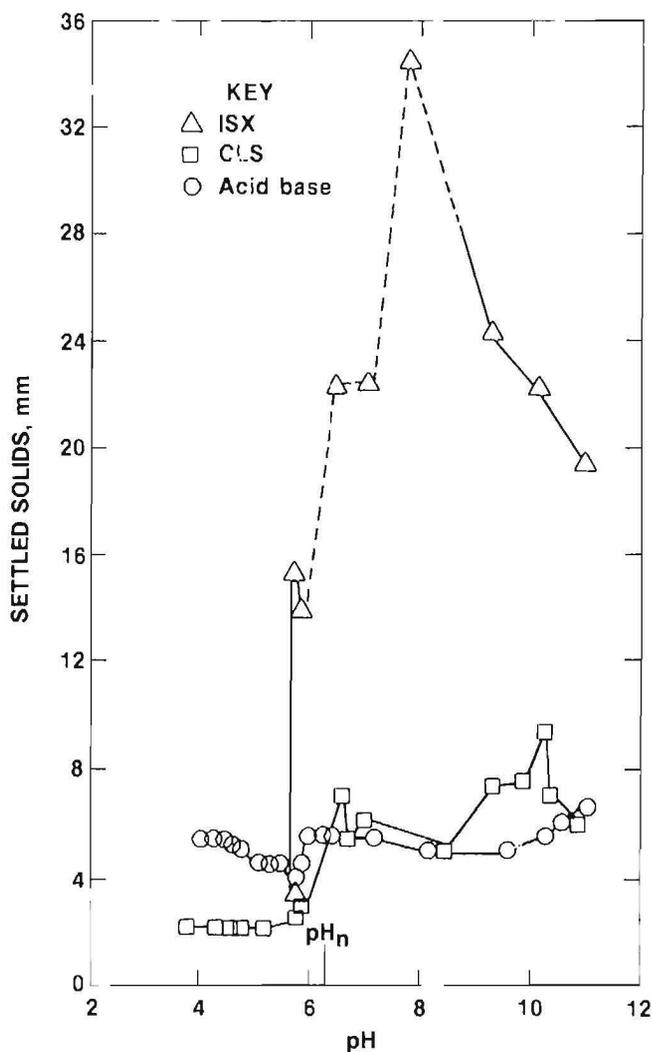
FIGURE 4. - Settling of covellite.
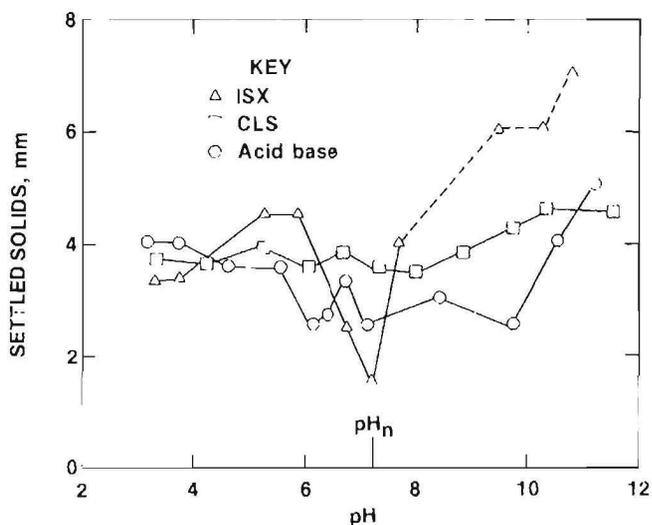
FIGURE 5. - Settling of chalcocite.

When compared with acid-base additions only or with CLS treatment, the most pronounced effect in the height of settled solids due to ISX was observed for covellite (fig. 4), bornite (fig. 9), pyrite (fig. 6), and sphalerite (fig. 10). A moderate increase in height with ISX was obtained with chalcopyrite (fig. 8) and pyrrhotite (fig. 7). Although ISX appeared to produce a negligible effect on the height of settled solid for galena (fig. 11), rapid settling was observed at pH 6 and 11 (table 2). Chalcocite (fig. 5) and molybdenite (fig. 12) formed small flocs with ISX but settling was relatively slow. No floc formation or improved settling was obtained with quartz (fig. 13). Cross-linked starch induced some floc formation on pulps of bornite and pyrite and relatively large flocs with pyrrhotite. In general, the pH range of best pulp clarification and maximum flocculation by ISX varies for each mineral.

Table 2 summarizes the results of adding ISX at pH values other than pH_n. For bornite, the pH of addition has essentially no effect upon the range where good flocculation and clarification occur, but for the other minerals the pH of addition has a slight effect on the flocculation behavior. In some instances, no ISX-induced clarification was observed, as in the case of adding ISX to chalcopyrite at pH 9.4.

The average floc size range was between 0.5 to 3 mm except for bornite. Addition of ISX at pH_n for bornite produced rapid formation of flocs in the size range of 0.5 to 1.0 mm. These small flocs further aggregated in the pulp during a presedimentation period of about 3 to 5 min, and formed floc aggregates as large as 7 to 8 mm, which then fell rapidly through the suspension. If the cylinder was slightly tilted and subjected to a gentle rotating motion, floc growth was greatly enhanced. This observation has been reported previously by Yarar (14-15) in the flocculation of mineral fines with polymers.

TABLE 2. – Effect of pH of ISX addition on flocculation

Mineral	pH at ISX addition	pH after 1st addition	pH of fastest settling and clarification
Covellite............	2.7	5.6	7- 8
	5.1	6.0	6- 7
	6.1(pH_n)	9.5	6- 9
	10.9	11.0	5- 7
Chalcocite..........	2.8	6.1	8-11
	7.2(pH_n)	10.8	9-10
	10.7	11.1	9-10
Pyrite...............	3.3	9.0	7-11
	6.5(pH_n)	10.0	6-10
	11.6	11.6	6-10
Pyrrhotite..........	2.3	3.2	7-12
	5.4(pH_n)	~10	6- 8.5
	11.9	12.0	8-11
Chalcopyrite........	3.2	10.3	5- 6
	5.6(pH_n)	11.3	≈6
	9.4	10.9	NO
Bornite.............	5.0	8.0	8-10
	6.9(pH_n)	10.0	8- 9
	10.0	11.0	8- 9
Sphalerite[1]........	3.1	10.0	NO
	6.5(pH_n)	>10	7-10
	11.3	11.3	NO
Galena..............	3.2	~7	6- 7
	5.8(pH_n)	>10.5	6, 11
	10.9	11.2	6, 11
Molybdenite[2].......	2.8(pH_n)	>10	NO
	11.8	12	NO

NO Not observed.

[1]Decomposition of ZnS and/or ISX noted at pH <4.

[2]Considerable flotation of molybdenite observed at pH >12.

An interesting feature of bornite flocs is that although they appear to break into smaller fragments upon shaking, reagglomeration into large flocs occurs continuously. More importantly, even if the flocs are separated from their supernatants (for example, by filtration) and then redispersed in water, reagglomeration into larger flocs is observed, suggesting that entrapped, nonflocculated components can be readily removed by postflocculation mechanical treatments. Flocs of the other minerals readily break apart upon shaking or washing and show little tendency to re-form.

It was observed that ISX-flocculated minerals filtered readily in ordinary vacuum and gravity filtrations, leaving clustered particles on the filter paper.
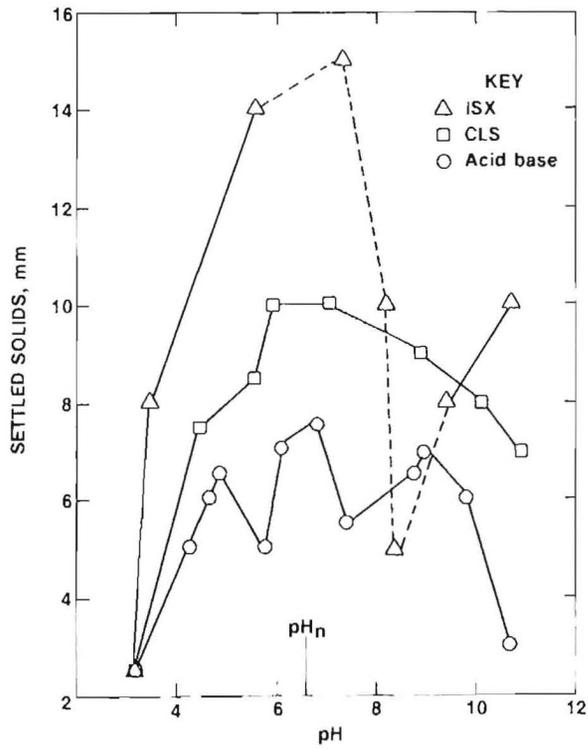
FIGURE 6. - Settling of pyrite.
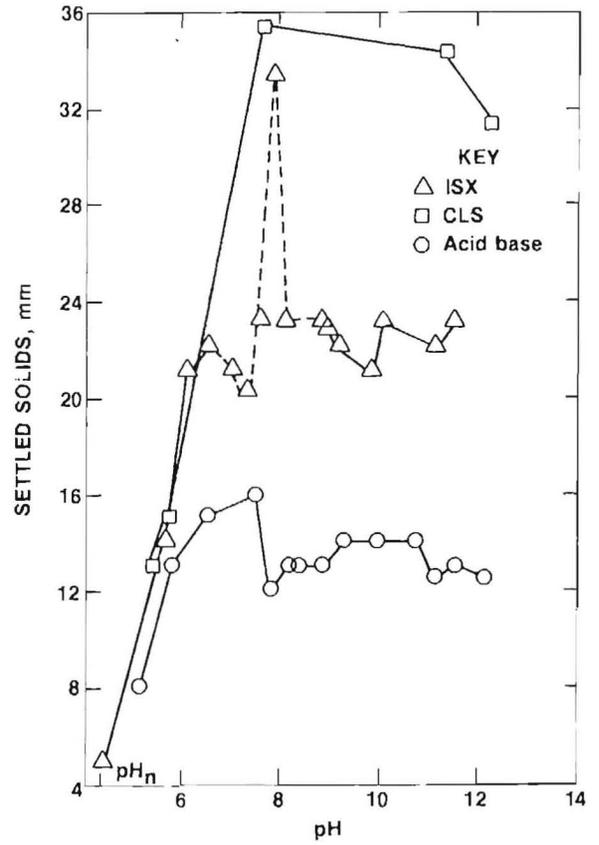
FIGURE 7 - Settling of pyrrhotite
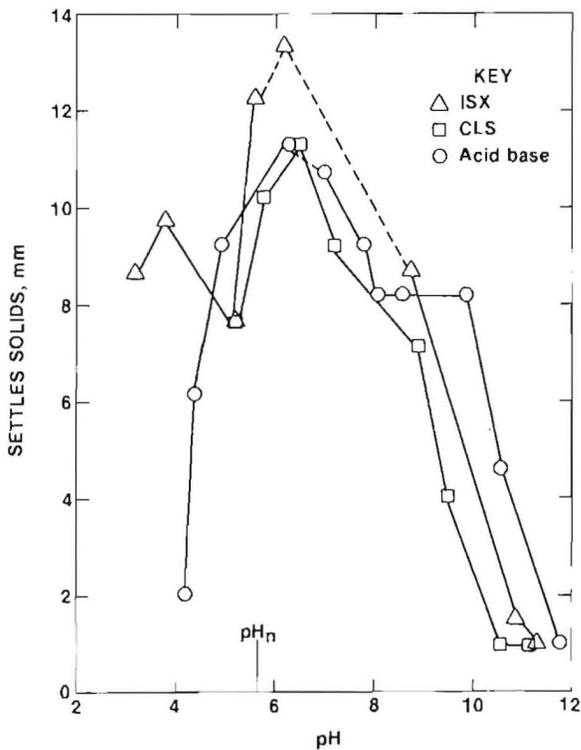
FIGURE 8. - Settling of chalcopyrite.
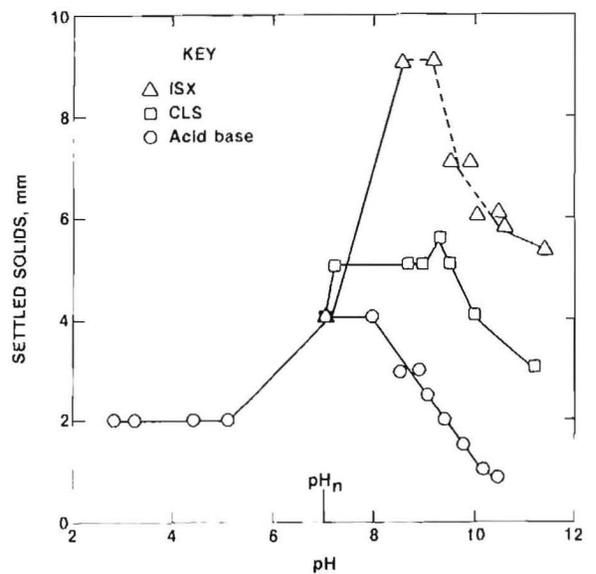
FIGURE 9. - Settling of bornite.
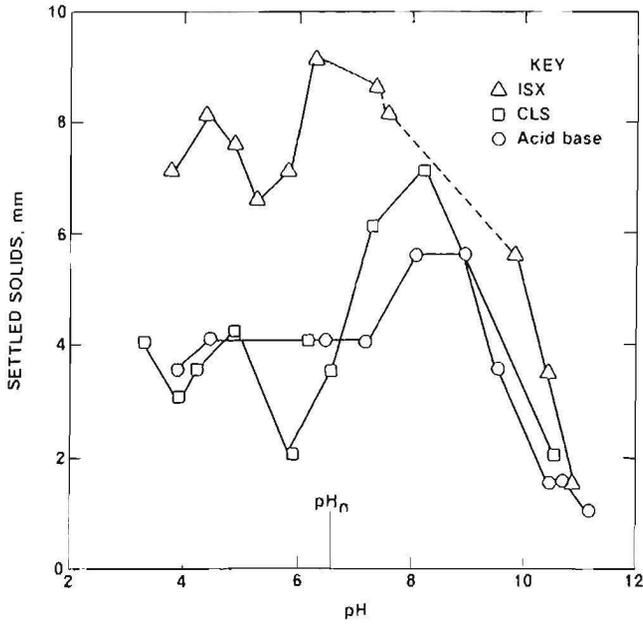
FIGURE 10. - Settling of sphalerite.
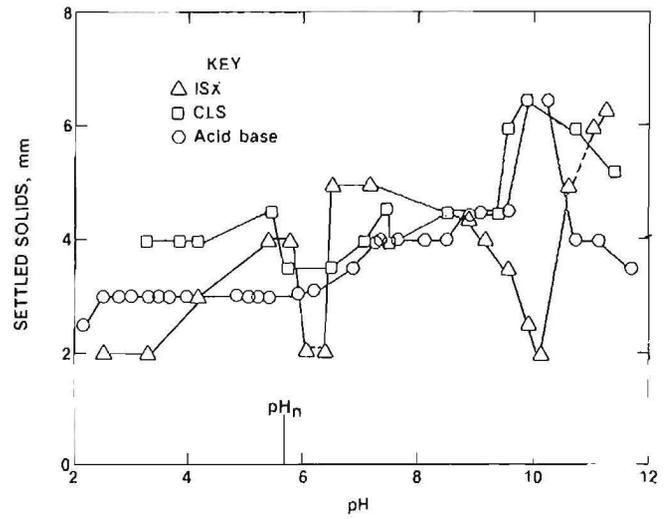
FIGURE 11. - Settling of galena.
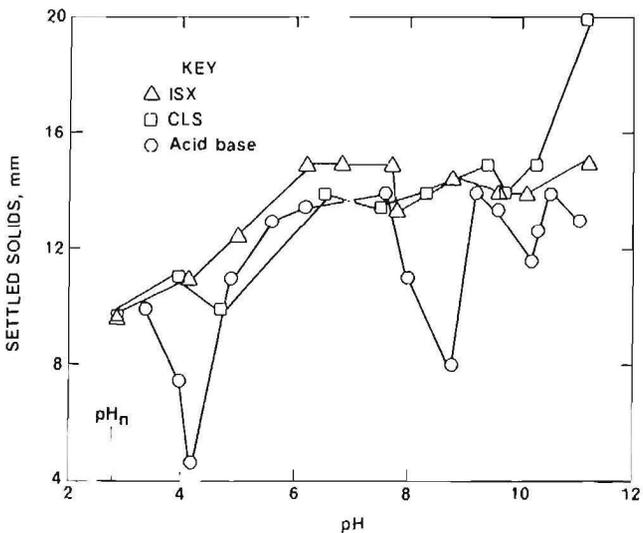
FIGURE 12. - Settling of molybdenite.
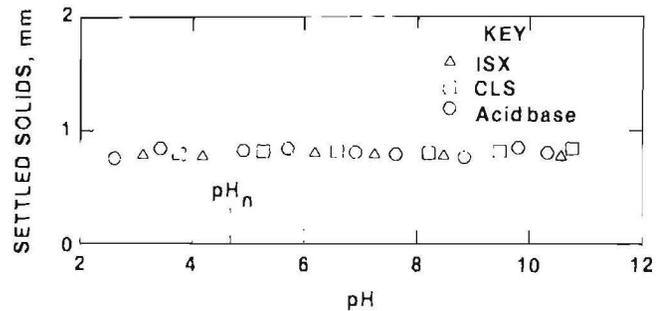
FIGURE 13. - Settling of quartz.

This is in contrast with the nontreated samples (acid-base additions only), which produce slimy residues, and with most CLS-treated samples, where the settled solids take longer to filter.

ZETA POTENTIAL MEASUREMENTS[6]

Zeta potential measurements were made to gain insight into the reaction

[6]Performed by Jeffrey A. Riehl, chemist, Avondale (MD) Research Center.

mechanisms involved in the flocculation of the sulfide minerals by ISX. Suspensions of CLS and ISX and each of the untreated, freshly ground sulfide minerals were studied. Figure 14 shows the zeta potentials of CLS and ISX in the pH range of 3 to 11. For CLS, the zeta potentials are positive, with values increasing from about +9 mv at pH 2.4 to about +25 mv at pH 9. On the other hand, ISX is negatively charged with zeta potential of ≈-8 mv, essentially independent of pH.

FIGURE 14. - Zeta potential of CLS and ISX.

FIGURE 15. · Zeta potential of freshly ground covellite and chalcocite.

The zeta potentials as function of pH for covellite and chalcocite are shown in figure 15. The point of zero charge (p.z.c.) for freshly ground chalcocite is pH 5.5 and the zeta potential is positive above this pH. Covellite (freshly ground) did not show a p.z.c.; the zeta-potential values were negative and ranged from about -35 to -65 mv.

Pyrite and pyrrhotite zeta potentials are illustrated in figure 16. Below pH 4.6 (p.z.c.) the zeta potentials of freshly ground pyrite are negative with a value of approximately -10 mv; above pH 4.6 the zeta potential becomes positive and nearly independent of pH. These results are in contrast with the zeta potential values obtained for the same ground sample which was allowed to weath-er for several months (see figure 21 and the "Effect of Weathering on Floccula-tion" section). Pyrrhotite containing some cobalt-bearing pentlandite showed a

p.z.c. at pH 4.9. Chalcopyrite and born-ite (fig. 17) exhibit a similar pattern of positive zeta potentials at pH values below their p.z.c. (4.8 to 5.0 for chal-copyrite and 6.8 to 7 for bornite) and negative above their p.z.c.

Figure 18 presents the zeta potentials of the sphalerite, galena, and molyb-denite samples. The p.z.c. of sphalerite occurred between pH 7.2 and 7.5, with maximum, positive zeta-potential values occurring between pH 4 and 5. Above pH 10 the zeta potentials were increasingly negative. Galena did not show a p.z.c.; above pH 4.8 the zeta potential was in-creasingly negative. The zeta poten-tials of freshly ground molybdenite were
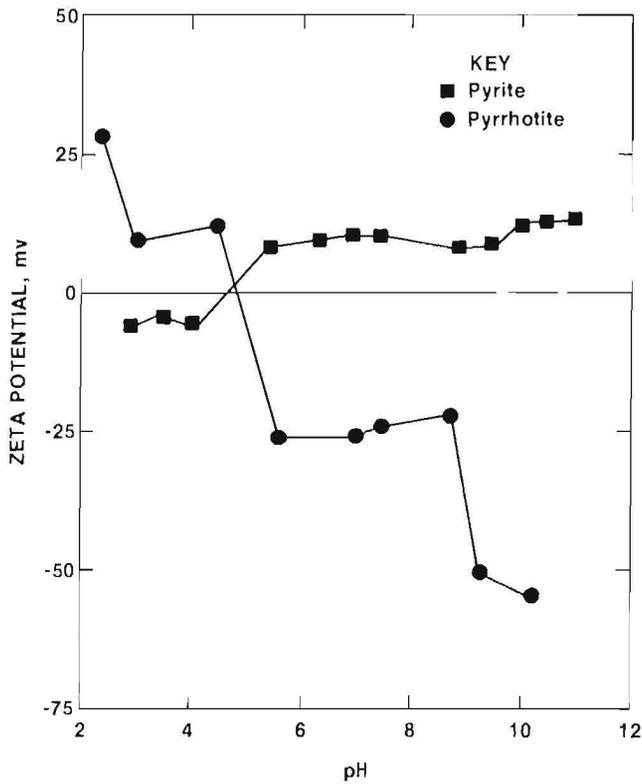
FIGURE 16. - Zeta potential of freshly ground pyrite and pyrrhotite.
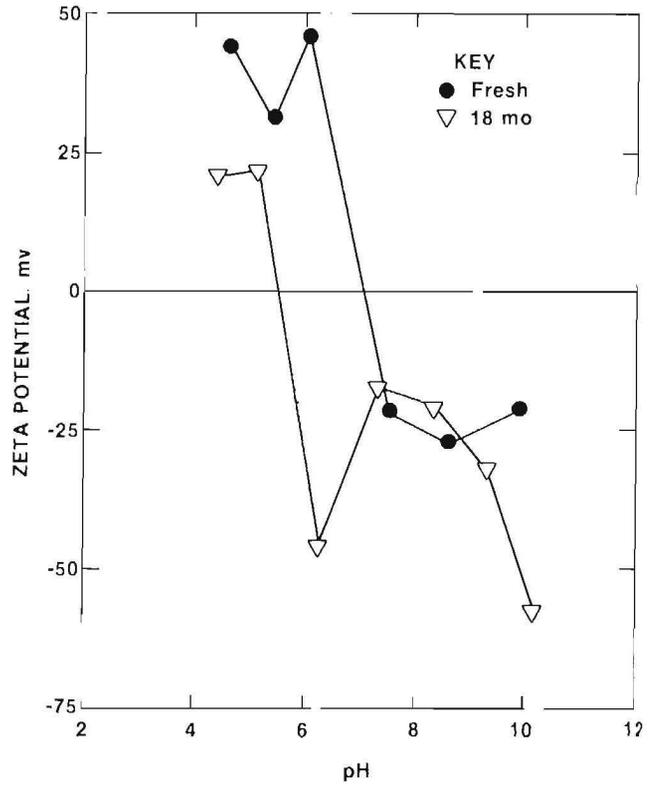
FIGURE 17. - Zeta potential of freshly ground chalcopyrite and bornite.

negative throughout the pH range of 3 to 11. The zeta potential for quartz was not measured in this study, but it is known that the p.z.c. falls in the vicinity of pH 2 (16–17) and that it has a negative zeta potential above this pH.

Table 3 lists the pH range where best flocculation by ISX was found together with the experimental zeta-potential values and p.z.c. The "Discussion" section presents an attempt to correlate the flocculation mechanism by ISX with zeta potentials, based on these results.

ISX DOSAGE AND PULP DENSITY

Since covellite formed large, rapidly settling flocs upon addition of ISX, this mineral was chosen for a study of the effect of mineral pulp concentration and ISX dosage on flocculation response. Turbidity measurements and total copper content were used to assess the extent of mineral removal.

TABLE 3. – Zeta potentials at the pH of maximum flocculation by ISX when added at pH_n

Mineral	Point of zero charge	pH of best floccula- tion	Zeta poten- tial, mv
Covellite...	NO	7- 8.5	-40
Chalcocite..	5.3-5.5	9-10	+20
Pyrite......	4.6	5- 8	+10
Pyrrhotite..	4.9	6- 8.5	-25
Chalcopyrite	4.8-5.5	6- 7	-30
Bornite.....	6.9	8-10	-25
Sphalerite..	7.2-7.5	7-10	[1]+2
			[2]-35
Galena......	NO	~6	-40
		~11	-60
Molybdenite.	NO	NO	NAp
Quartz......	[3]1.8	NAp	[4]-25

NAp Not applicable. [2]pH 10.
NO Not observed. [3]Reference 16.
[1]pH 7. [4]pH 8-10.
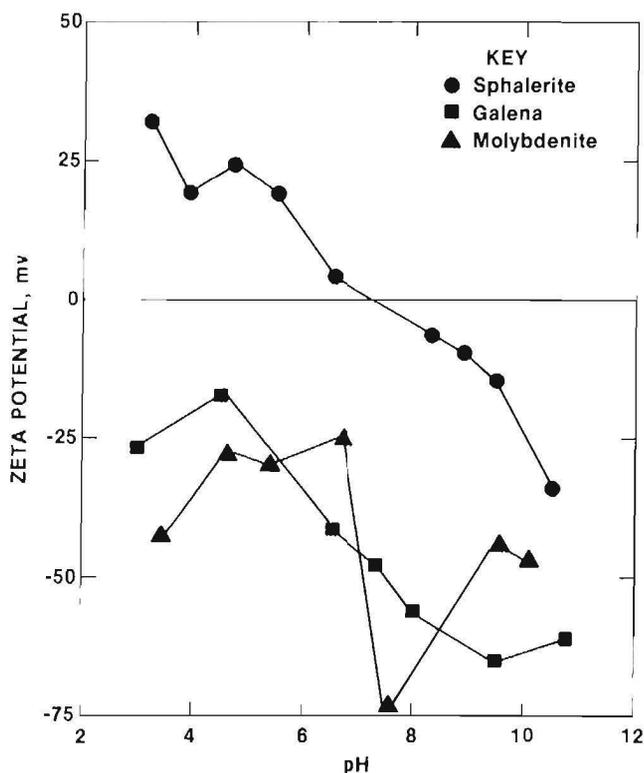
FIGURE 18. - Zeta potential of freshly ground sphalerite, galena, and molybdenite.

The desired weight of mineral was dispersed in 80 ml of water. A known amount of ISX (dispersed in 20 ml of water) was added, mixed for 1 min, then allowed to settle for 3 hr. Samples without ISX addition did not show evidence of aggregation or fast settling at pulp concentrations above 0.1 g of covellite in 100 ml of water, and the turbidity readings remained above the turbidimeter limit of 200 NTU. After 3 hr, the top 30 ml of supernatant was carefully withdrawn with a pipette, and the turbidity and total copper content were determined. The turbidity and total copper concentration of the withdrawn supernatant as a function of the weight ratio of ISX to covellite are shown in figures 19 and 20, respectively. The clearest supernatants and best mineral removal were produced at ISX-to-covellite ratios of less than 0.1. At low ISX dosages, flocs formed nearly instantaneously upon addition of the flocculant. At ratios between ≈0.1 and 0.6, both the turbidity and copper content in the supernatant increased. The

increase in turbidity may be due to dispersed ISX and/or covellite. The increase in copper content suggests that ISX may be acting as a dispersant for covellite. At ratios above 0.7, overdosage of flocculant may account for some of the decrease in turbidity and copper content. It is noteworthy that for dosages above 0.1 g of ISX flocs were not formed or were too small to be observed in the highly turbid solutions. At the higher dosages some foaming and foul odor were noted, presumably due to formation of CS_2 from decomposition of ISX.

EFFECT OF MINERAL WEATHERING ON FLOCCULATION

Pyrite fines were found to oxidize (weather) readily, even when kept dry in tight containers. Aged fines released F(III) and sulfate ions into solution and, therefore, pulps of aged pyrite exhibited lower pH_n than pulps prepared from the freshly ground mineral owing to the hydrolysis of Fe(III). Pulps of weathered pyrite treated with ISX or NaOH produced a gelatinous, rust-colored precipitate resembling hydrous iron(III) oxides, which caused rapid floc formation and nearly instantaneous settling of the mineral. Because hydrous iron(III) oxides are known to be strong flocculants and coagulants (18-19), weathering of pyrite, a common mineral in sulfide ores, and its effect on selective flocculation were studied in more detail.

In mixtures of quartz and weathered pyrite where the pH was raised to 7 and 11 with NaOH, a rusty color was detected in the collected settled fraction; this coloration was absent when fresh ground pyrite was used. X-ray diffraction analysis of the rust-colored fractions showed the presence of a poorly defined phase having broad, but not intense peaks, centered at 6.55 A (γ-FeOOH has a major d-spacing of 6.26 A). The only other peaks were those of pyrite and quartz, which suggests that the colored material may be an amorphous hydrous iron(III) oxide.
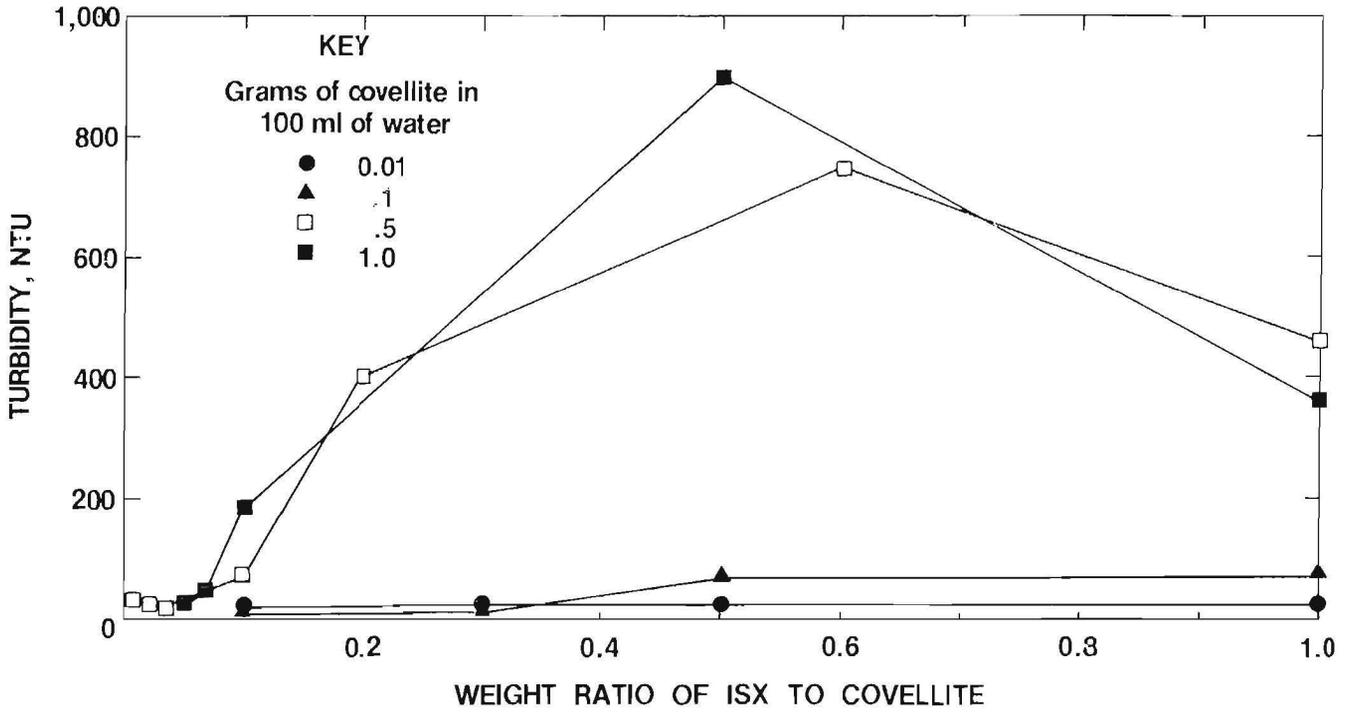
FIGURE 19. - Turbidity as a function of the weight ratio of ISX to covellite.
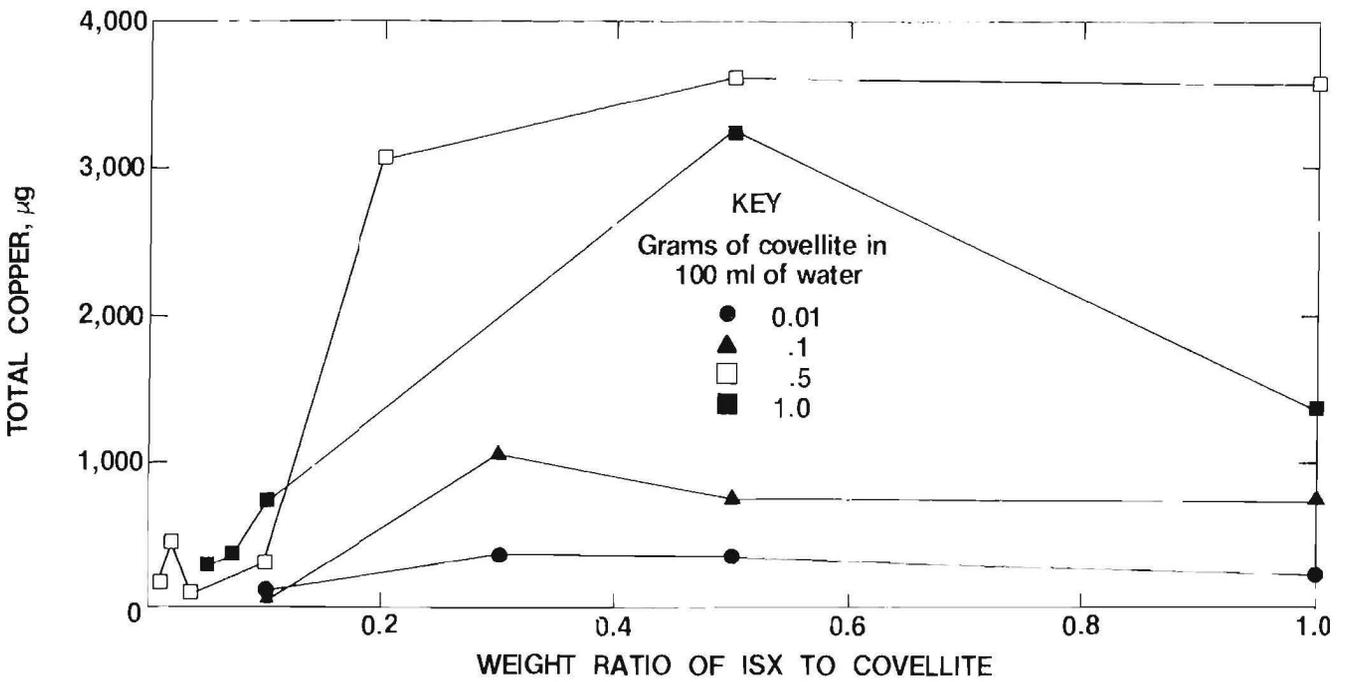
FIGURE 20. - Total copper content as a function of the weight ratio of ISX to covellite.

Selective flocculation tests were conducted with synthetic mixtures of covellite and pyrite (freshly ground and weathered) containing 0.5, 1.5, 2.5, 3.5, 5.0, and 10 pct pyrite in a total 0.1 g of mixture. The natural pH of weathered pyrite mixtures was lower and decreased with an increase in the quantity of pyrite. Addition of ISX (or NaOH) to these pulps caused rapid floc formation and settling of both minerals. Thus, the presence of weathered pyrite causes heteroflocculation and appears to inhibit selective flocculation.

The zeta potential of freshly ground pyrite differs considerably from those recorded with the same fines after air aging (fig. 21). Shifts in p.z.c. as well as charge reversal occur in going from the freshly ground to the aged mineral. The zeta potentials also become more negative at pH values above the p.z.c. with increased aging.
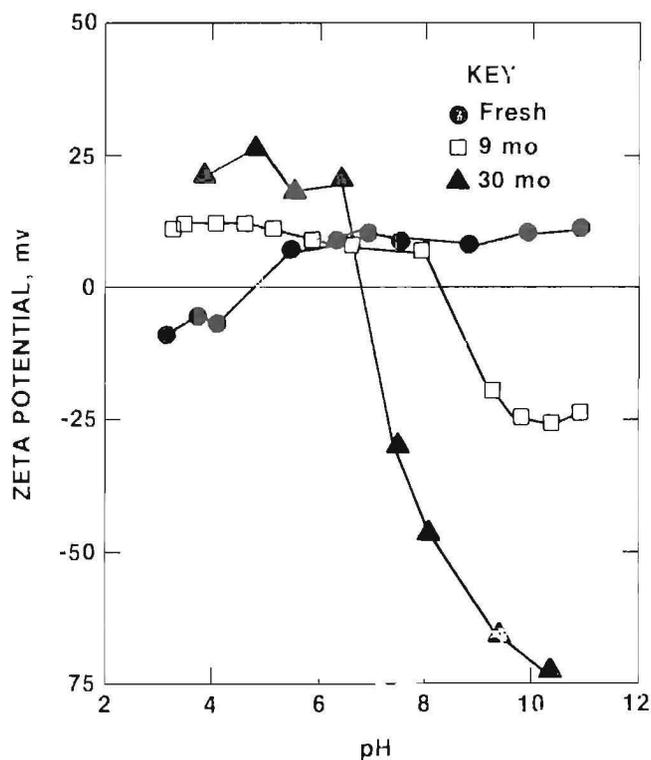
FIGURE 21. - Zeta potential of weathered pyrite.

The infrared spectrum of freshly ground pyrite (fig. 22A) shows only a sharp band at 418 cm^{-1} assigned to S-S (sulfur-sulfur) stretching vibrations (20). In the spectrum of weathered pyrite (fig. 22B), other bands of variable intensities are present besides the 418 cm^{-1} band: three bands in the 1,000- to 1,200-cm^{-1} region; one at about 990 cm^{-1}; and three between 550 and 650 cm^{-1}. These bands are in the region where S-O (sulfur-oxygen) vibrational modes in sulfate are found. The band about 990 cm^{-1} is associated with the v_1 stretching mode. Bands in the 1,000- to 1,200-cm^{-1} and in the 550- to 650-cm^{-1} regions are associated with stretching modes v_3 and v_4, respectively. These modes in a "free," that is, noncoordinated sulfate group, are degenerate because of the essentially tetrahedral symmetry of SO_4^{2-}. Bonding through oxygen causes a lowering in the symmetry of the sulfate group, and splits the degenerate modes. If only one oxygen is involved in bonding, the symmetry is reduced to C_{3v} and each v_3 and v_4 split into two bands. If two oxygens are involved, the symmetry is further reduced to C_{2v} and each v_3 and v_4 split into three bands (21). Thus, the spectrum of weathered pyrite (aged 24 mo) indicates the presence of a SO_4^{2-} where two of its four oxygens are involved in bonding. Karr and Kovach (22) had analyzed the far-infrared (50 to 200 cm^{-1}) region of surface films from pyrite-rich mine refuses and found the spectrum to be identical to that of orthorhombic, anhydrous $FeSO_4$. More recently, Brion (23) unambiguously identified the presence of SO_4^{2-} groups on weathered pyrite surfaces using X-ray photoelectron spectroscopy and suggested that the final oxidation product is $Fe_2(SO_4)_3$. Clifford, Purdy, and Miller (24) had also pointed out that pyrite ground in air showed photoelectron spectra consistent with S as SO_4^{2-}. Scanning electron microscopy (fig. 23) established that aged pyrite is extensively covered by another phase and that the surface coverage increases with aging.
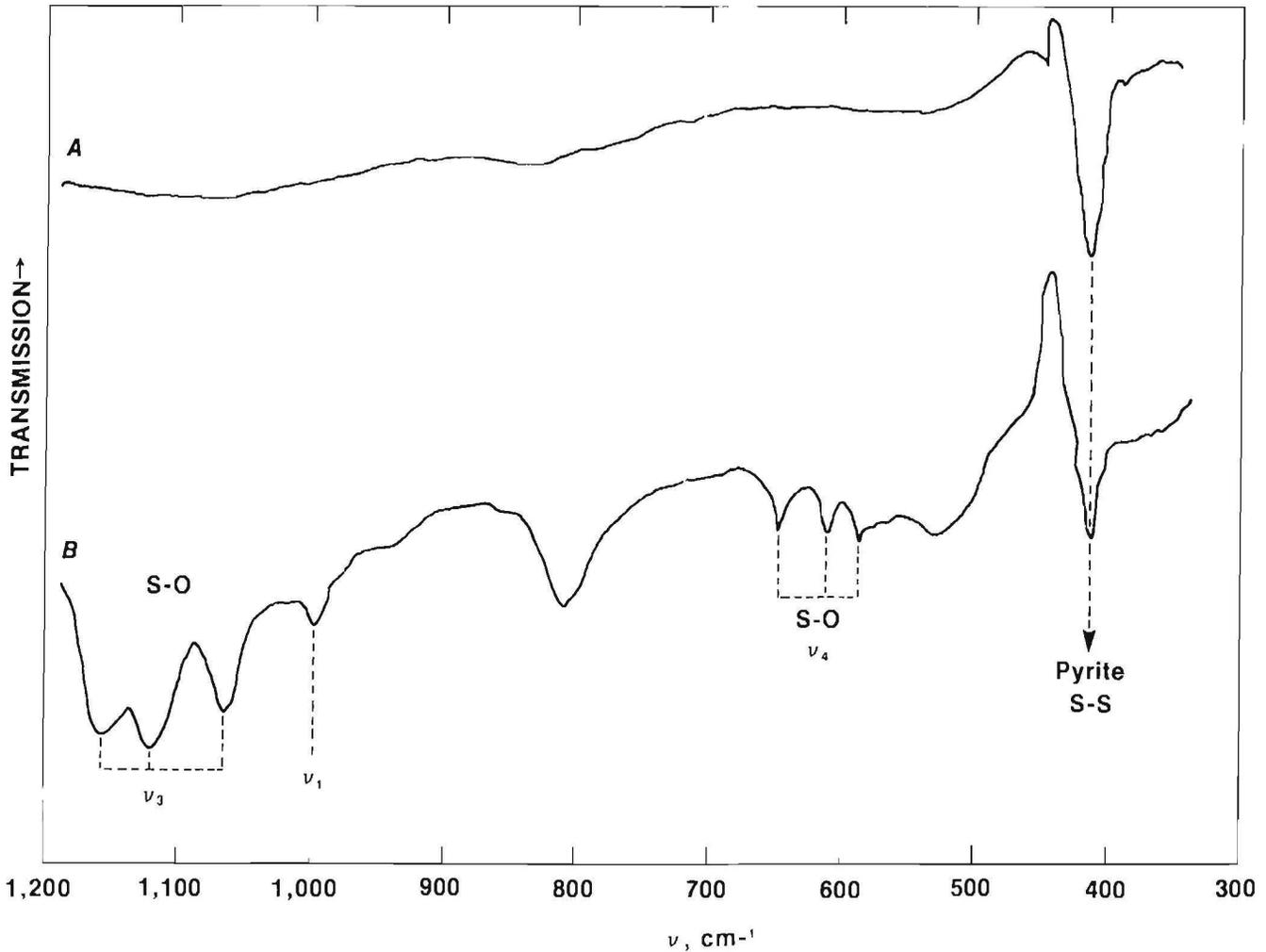
FIGURE 22. - Infrared spectra of pyrite. *A*, Freshly ground; *B*, 24 mo old.

Weathered chalcopyrite fines were also found to produce more acidic pulps than those of the freshly ground material and to form gelatinous, rusty precipitates upon addition of base or ISX. There is also a shift in the p.z.c. and a change in the magnitude of zeta potentials (fig. 24). In bornite, variations in zeta potentials and p.z.c. with aging were also found (fig. 25), but no precipitate formation was observed. Weathered pyrrhotite also produced extensive

precipitation and a shift in p.z.c. Covellite and galena samples did not show a p.z.c. when freshly ground, but exhibited p.z.c.'s at 5.5 and 5.3, respectively, when aged. Aged covellite formed rusty flocs when treated with ISX or NaOH, but this may be due to the presence of some pyrite (see table 1). The p.z.c.'s of aged sulfide minerals, together with the pH_n of their pulps, are listed in table 4.

TABLE 4. - Points of zero charge and pH_n of suspensions of aged sulfide fines

Mineral and age	Point of zero charge	pH
Covellite:		
FG...............................	NO	6.2-6.3
12 mo.........................	5.5	5.8
Chalcocite: FG.............	5.3-5.5	7.2
	~4.0	6.0
Pyrite:		
FG...............................	4.6	6.5
9 mo...........................	8.4	4.9
30 mo.........................	7.2-7.3	3.8
Pyrrhotite:		
FG...............................	4.9	5.4
30 mo.........................	7.3	5.0
Chalcopyrite:		
FG...............................	4.8-5.5	5.6
9 mo...........................	8.4-8.6	4.7
18 mo.........................	8.1	4.7
30 mo.........................	7.1-7.2	4.3
Bornite:		
FG...............................	6.9	6.9
18 mo.........................	4.8	6.3
Sphalerite:		
FG...............................	7.2-7.5	6.5
30 mo.........................	NO	5.6
Galena:		
FG...............................	NO	5.8
30 mo.........................	5.3	6.0
Molybdenite:		
FG...............................	NO	2.8-3.4
30 mo.........................	NO	4.0

FG Freshly ground.   NO Not observed.

It is interesting to note that pyrite, chalcopyrite, and pyrrhotite aged for 30 mo in air have p.z.c. values falling in the same vicinity (pH~7.2), suggesting that the dominant oxidation product(s) on the surface of the three minerals may be the same.

FLOCCULATION OF SULFIDE MINERAL-QUARTZ MIXTURES

Separations of binary mixtures of a sulfide mineral and quartz were studied to assess the capability of ISX to selectively flocculate sulfide minerals. Of particular interest were mixtures containing bornite since this mineral formed flocs with ISX, which could withstand postflocculation physical separations.

Preliminary studies using one-to-one mixtures of bornite and quartz showed that addition of ISX caused rapid formation of large, dark flocs, and a whiter supernatant, as seen in figure 26. X-ray diffraction showed that the solids collected from the supernatant were enriched in quartz while the flocs were enriched in bornite.
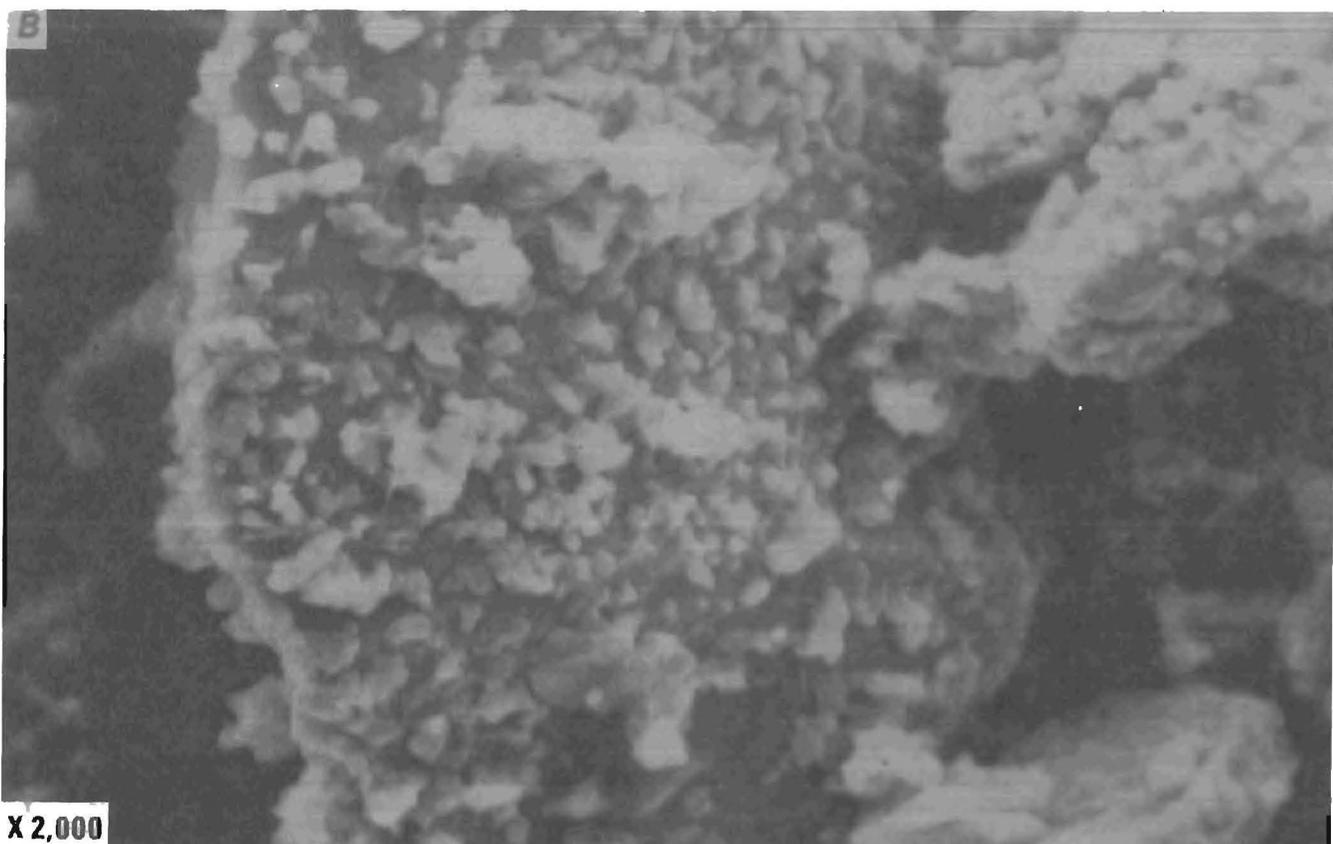
FIGURE 23. - SEM photomicrographs of pyrite fines. *A*, Aged 6 mo; *B*, aged 30 mo.
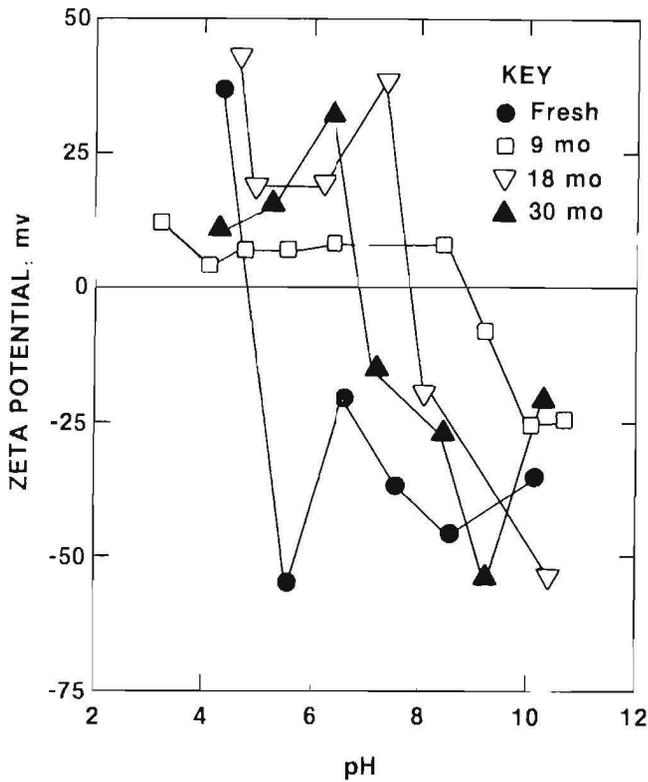
FIGURE 24. - Zeta potential of weathered chalcopyrite.

FIGURE 25. - Zeta potential of weathered bornite.

In subsequent experiments, the quartz-enriched supernatants were first decanted after flocculation with ISX. The flocs were redispersed in water and recovered by filtration. They were again redispersed in water and subjected to a swirling motion to momentarily break up the large flocs. This operation allowed the release of entrapped quartz into the supernatant, which was again decanted. This procedure was repeated twice and solids were recovered by filtration. The pH of the floc-containing fraction remained between 9 and 10 during washing of the flocs. The ISX readily flocculates bornite at this pH range.

In other experiments, the tilted plate elutriator illustrated in figure 3 was employed in postflocculation separations. In this case, flocculation was performed in a graduated cylinder and the flocculated and nonflocculated minerals were transferred to the elutriator. The counterflow of water aided in the removal of nonflocculated material from the flocs.

Nonflocculated and flocculated solids were then collected separately and recovered by filtration.

For comparison, other experiments were performed using CLS instead of ISX and without addition of any starch (only NaOH to adjust the pH to the range of 9 to 10). Settled solids were separated from the supernatant either by decantation or with the tilted plate elutriator.

The results of experiments for mixtures containing 50 pct bornite and different treatments (that is, using ISX, CLS, and no addition of starches) are summarized in table 5. All recovered solids were analyzed by X-ray diffraction for mineral identification and by chemical analyses for Cu, Fe, and Si content. Tests 1 to 3 (ISX treatment) established that the floc fractions were considerably enriched in bornite as seen from their grades (76 to 92 pct). Likewise, the grades of solids recovered from the nonflocculated fractions ranged from 83 to 87 pct
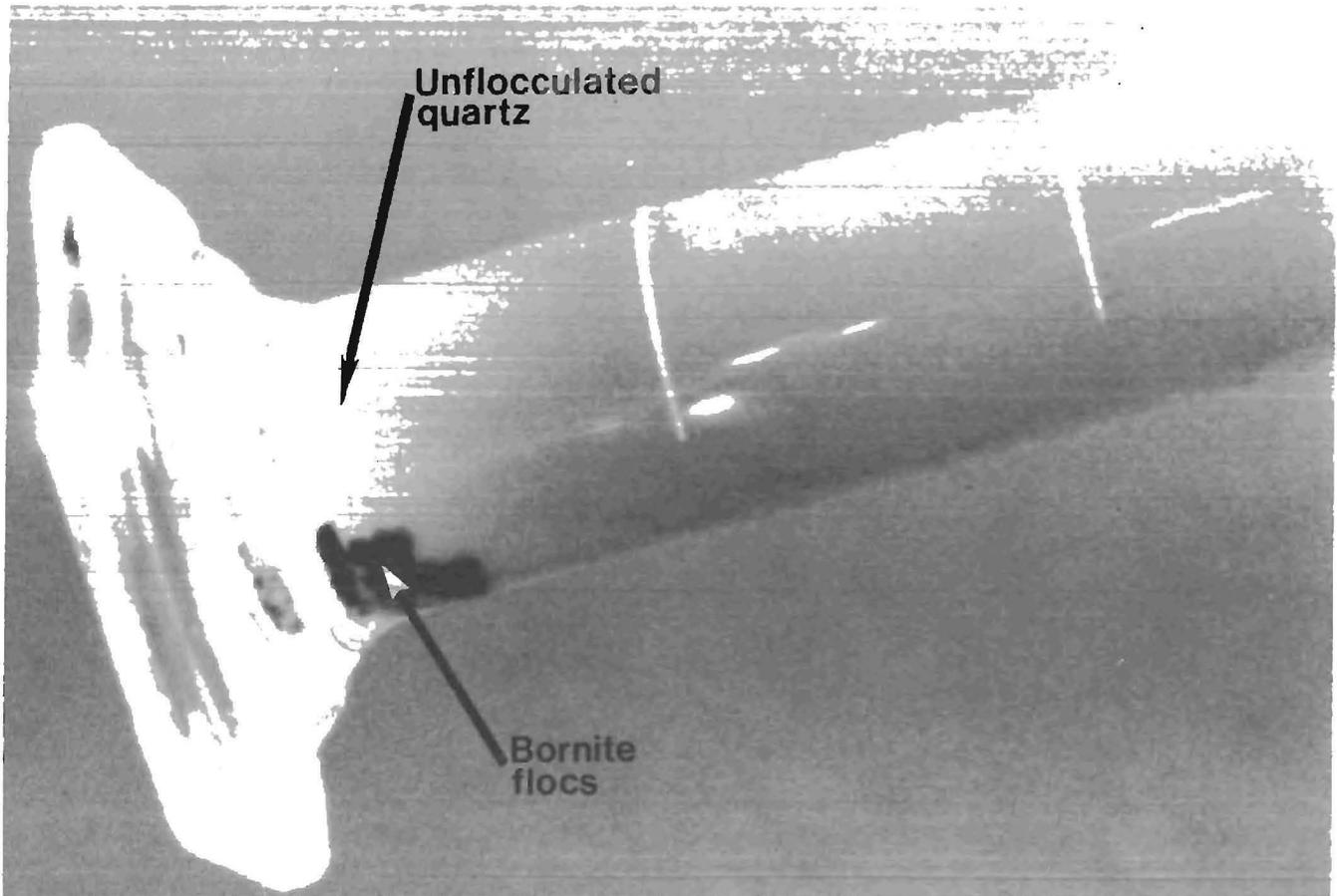
FIGURE 26. - Selective flocculation of bornite from a mixture with quartz.

TABLE 5. — Selective flocculation of bornite from quartz

Test	Reagent[1]	pH		Conditioning time, min	Fraction analyzed[2]	Recovery,[3] pct		Grade,[3] pct	
		Initial	Final			Bornite	Quartz	Bornite	Quartz
1...	ISX	8.1	10.3	150	F	65	6	92	NAp
					UF	15	71	NAp	83
2...	ISX	7.5	10.0	90	F	65	21	76	NAp
					UF	10	49	NAp	83
3...	ISX	8.0	9.0	30	F	60	11	85	NAp
					UF	13	84	NAp	87
4...	NaOH	8.1	10.0	30	Sd	72	68	51	NAp
					St	6	7	NAp	54
5...	CLS	8.0	8.1	30	Sd	70	43	62	NAp
					St	2	56	NAp	74

NAp Not applicable.

[1]1.5 g of each mineral; 0.05 g ISX.

[2]F, flocs; UF, unflocculated fractions; Sd, settled fractions; St, solids recovered by supernatants.

[3]Calculated from analytical data for Cu, Fe, and Si.

quartz. The improvement in bornite grade after treatment with ISX shows that ISX selectively flocculates bornite and that the bornite flocs are strong enough to withstand postflocculation separations. The effect of ISX can be even more clearly seen if tests 1 through 3 are compared with tests 4 and 5. In test 4, where only NaOH was used, essentially no selectivity (51 pct grade of bornite in the settled fraction) was attained and the solids in the settled fraction were slimy and difficult to filter. A slight selectivity represented by 64 pct grade of bornite in the settled fraction was found in samples treated with CLS. The flocs resulting from CLS were small, fragile, and easily resuspended, making it difficult to obtain a differential separation.

The recoveries of bornite in the ISX treated mixtures (tests 1 to 3) ranged from 60 to 65 pct and those of quartz from 49 to 84 pct. They do not total 100 pct owing to transfer losses incurred in several stages of washing, decantation, and filtration. Separation of other mixtures of sulfide minerals (covellite, chalcocite, chalcopyrite, pyrite, and pyrrhotite) with quartz were attempted. Only chalcocite and pyrrhotite formed distinct dark flocs; these flocs had the tendency to break apart during separation procedures, thus preventing postflocculation recovery.

DISCUSSION

ISX forms flocs of various strength with a number of sulfide minerals, but not with quartz. Floc strength may be related to the manner by which ISX interacts with each of the mineral surfaces.

As mentioned earlier, ISX is particularly attractive as a flocculant because the xanthate group would be expected to form covalent bonds with metal component(s) on the mineral surface, as is believed to occur in the alkyl xanthate flotation of sulfide minerals (4). In general, the larger and stronger flocs formed with ISX, when compared with those formed by cross-linked starch alone, indicates involvement of the xanthate group in the flocculation mechanism.

Table 3 lists the pH ranges of fastest settling and clarification with ISX, the corresponding zeta potential values at that range, and the experimental p.z.c. Except for sphalerite, where best flocculation was found in the vicinity of its p.z.c., best flocculation occurred at pH ranges above the p.z.c. of the minerals and, except for pyrite, at absolute values of zeta potentials greater than 14 mv. Pyrite and ISX are oppositely charged, with zeta potentials of comparable magnitude (~8 mv) in the pH range where best flocculation was observed, so that some contribution from attractive electrostatic forces may be involved in the flocculation of freshly ground pyrite by ISX (25). Contribution from attractive electrostatic forces may also be involved in the flocculation of chalcocite (zeta potential ~+20 mv, pH 9-10).

Since repulsive energy barriers between particles become more significant only at magnitudes of zeta potential above 14 mv, other contributions such as Brownian (perikinetic) and velocity gradient (orthokinetic) flocculation, and adsorption energy should be more predominant in the flocculation of covellite, pyrrhotite, chalcopyrite, bornite, and galena by ISX. For these minerals, the strength of the bond formed between ISX and lattice metal site(s) could account for their flocculation. In those instances where cross-linked starch also induced some flocculation, such as with pyrrhotite and bornite, electrostatic attraction may be one of the mechanisms involved.

The fact that bornite forms the strongest flocs with ISX also suggests that the bonding between the xanthate group and lattice metal component(s) is stronger for bornite than for the other minerals. While ISX can form strong bonds with bornite and selectively flocculate it from quartz, cellulose xanthates appear to show selectivity towards chalcopyrite (26-27). This suggests that factors

other than the nature of the chelating group, such as electronic or stereochemical contributions from the polymer backbone, may also influence flocculant selectivity as has been indicated earlier by Kitchener (2).

Weathered sulfide mineral fines, in particular pyrite, chalcopyrite, and pyrrhotite, release Fe(III) species into solution. Hydrous ion(III) oxides form, which themselves are strong flocculants and cause heteroflocculation and therefore inhibit selectivity. This may be of importance in mineral processing applications where it is not always possible to deal with freshly ground surfaces.

SUMMARY

The flocculation response of covellite, chalcocite, pyrite, pyrrhotite, chalcopyrite, bornite, sphalerite, galena, molybdenite, and quartz fines with ISX was studied. Best flocculation was observed for covellite, bornite, pyrite, and sphalerite. The pH range of flocculation is different for each mineral.

ISX selectively flocculates bornite from mixtures with quartz. The bornite flocs are strong enough to withstand separation and recovery from the unflocculated quartz. Recoveries between 60 to 65 pct of bornite and grades of 76 to 92 pct were attained using decantation and washing methods and a tilted plate elutriator as postflocculation separations.

Flocculation of sulfide minerals with ISX appears to involve covalent bond formation between the xanthate group and metal component(s) on the mineral surface, at least for freshly ground bornite, covellite, chalcopyrite, pyrrhotite, and galena.

The presence of weathered minerals, in particular pyrite, chalcopyrite, and pyrrhotite, may be detrimental to selectivity because of the release of Fe(III) species into solution, which forms hydrous iron(III) hydroxides at pH >3 and cause heteroflocculation.

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