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By S. C. Termes and R. L. Wilfong

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	mm	millimeter
keV	kilo electron volt	μm	micrometer
L	liter	mol/L	mol per liter
meq/g	milliequivalent per gram	mV	millivolt
min	minute	NTU	nephelometric turbidity unit
mL	milliliter	pct	percent
mL/min	milliliter per minute	rpm	revolution per minute

FLOCCULATION OF METAL OXIDE AND HYDROXIDE MINERALS WITH CROSS-LINKED STARCHES CONTAINING CHELATING GROUPS

By S. C. Termes[1] and R. L. Wilfong[1]

ABSTRACT

To help develop the basis for new fine-particle separation methods, the Bureau of Mines has investigated the use of cross-linked starches containing four chelating groups--carboxylate, iminodiacetate, diethanolamine, and xanthate--as flocculants for selected metal oxide and hydroxide mineral fines. It was found that those starches capable of interacting with the mineral surface by a chemisorption mechanism (as indicated by zeta potential measurements) produced the highest recoveries and grades of the metal oxide or hydroxide when flocculated from a binary mixture with quartz.

The effects of pH, dispersing agent, stirring rate, stirring time, and starch dosage on selective flocculation were studied for binary mixtures of hematite and chromite with quartz. Floc strength becomes important in achieving maximum recoveries by mechanical postflocculation separations.

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INTRODUCTION

Selective flocculation is receiving increasing attention as a potential beneficiation technique for low-grade, highly disseminated ores, and for selective desliming. Combined with flotation, it has been employed in the desliming of iron bearing ores (1-2)[2] and sylvinite ores (3). The iron system uses pearl starch as the flocculant, while the sylvinite system uses a polyacrylamide flocculant. Both of these flocculants are polymeric materials, which are believed to bridge the small, dispersed particles. The result is an aggregate of particles, which then settles faster than the nonaggregated particles. Bonding of the polymer to the mineral surface can occur by (1) electrostatic attraction, (2) hydrogen bonding, and (3) chemisorption. Flocculants capable of chemisorbing to the mineral surface are considered to be the most selective (4-5). Attia and Kitchener (6) proposed that introduction of chelating groups into the polymer backbone would enhance polymer selectivity because of the possible stronger interaction (chemical bonding) between chelating group and surface metal component(s).

It is noteworthy that the use of chelating reagents in mineral processing has generated a great deal of interest in recent years, and reagents containing chelating groups have proved to be highly selective and specific at least on a laboratory scale as flotations collectors. A few examples include the hydroxamate derivatives for hematite (7), the oxime derivatives for copper minerals (8), and the highly specific nitroso naphthol derivatives for cobalt-bearing minerals (9).

The cross-linked starch derivatives studied herein were developed by the U.S. Department of Agriculture, Northern Regional Research Center, Peoria, IL, to remove heavy metal ions from contaminated waters. These materials are epichlorohydrin cross-linked starches which have been chemically modified to incorporate the following chelating groups: (1) carboxylate, (2) iminodiacetate, (3) diethanolamine, and (4) xanthate. The xanthate derivative was investigated by Termes, Wilfong, and Richardson (10-11) as a flocculant for sulfide minerals.

The flocculation of hematite, goethite, chromite, cuprite, manganite, pyrolusite, and cassiterite induced by the above starches is reported here. To assess selectivity, mixtures of hematite, goethite, chromite, and cuprite with quartz were treated with the starches. The hematite-quartz and chromite-quartz systems were chosen to study the effect of pH, dispersing agent, method of mixing the flocculant with the pulp, and starch dosage on the recoveries and grades of the flocculated fraction.

BACKGROUND

Two types of carboxyl-containing cross-linked starches were investigated. In one of them, acrylonitrile was first grafted to the cross-linked starch (CLS) and then saponified to form a mixture of carboxamide and carboxylate groups; this derivative is labelled GC-CLS. The other carboxyl-containing derivative, C-CLS, contains carboxymethyl groups and was prepared by the reaction of monochloroacetic acid with causticized CLS. The preparation and use of GC-CLS and C-CLS are described by Rayford, Wing, and Doane (12).

The synthesis and reactivity of the iminodiacetate, IDA-CLS, and the diethanolamine, DEA-CLS, derivatives were reported by Rayford and Wing (13-14). In their work, a cross-linked starch intermediate containing 3-chloro-2-hydroxypropyl ether groups was prepared and subsequently reacted with the sodium salt of iminodiacetic acid and with diethanolamine to obtain IDA-CLS and DEA-CLS, respectively.

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

The preparation and uses of the xanthate derivative known as insoluble cross-linked starch xanthate, ISX, was reported by Wing and Doane (15-16). It is the only cross-linked starch derivative that is presently in commercial use.

The structures of the chelating groups in the cross-linked starch derivatives are shown in table 1. The arrows represent the donor atoms involved in bonding to the metal. Although xanthate and carboxylate groups are not commonly emphasized in the flotation literature as bidentate, chelating ligands, numerous examples of chelating carboxylato and xanthato complexes with metal ions are well documented in the chemical literature (17-21). Note also that in the iminodiacetate and diethanolamine groups, both oxygen and nitrogen are donor atoms. The hydroxamate, oxime, and nitroso naphthol reagents given as examples of highly selective collectors are also mixed donor chelating reagents, and their specificity has been associated with their mixed-donor nature (21).

ACKNOWLEDGMENT

TABLE 1. - Chelating groups in the cross-linked starch derivatives

Cross-linked starch derivative	Name of chelating group	Group structure
GC-CLS	Carboxylate	
	Carboxamide	
C-CLS	Carboxymethyl	
DEA-CLS	Diethanolamine	
IDA-CLS	Iminodiacetate	
ISX	Xanthate	

EXPERIMENTAL WORK

REAGENTS

Unless otherwise specified, chemicals were reagent grade and water was distilled and deionized. A highly cross-linked starch marketed as VULCA 90 by the National Starch and Chemical Co.[3] was used in the preparation of ISX and in flocculation experiments involving a non-modified cross-linked starch.

Insoluble cross-linked starch xanthate was prepared by the method described by Wing and Doane (16), and the degree of substitution was determined by the method of Swanson and Buchanan (22). The other chelating cross-linked starches were research materials synthesized and characterized by the U.S. Department of Agriculture. Analytical data on the chelating cross-linked starches are summarized as follows:

GC-CLS: Nitrogen, 4.28 pct; water, 17.64 pct; ash, 19.1 pct; capacity, 3.36 meq/g (12).

C-CLS: Water, 12.18 pct; ash, 6.12 pct; capacity, 1.43 meq metal/g (12).

IDA-CLS: Nitrogen, 2.11 pct; water, 14.22 pct; ash, 13.87 pct (13).

ISX· Sulfur, 6.1 pct; water, 14.? pct; ash, 19.8 pct; magnesium, 1.3 pct; degree of substitution, 0.2-0.3 (synthesized at Avondale Research Center).

The molecular weight of these starches is estimated to be near 1 million daltons (23).

MINERALS

Mineral specimens were obtained from Ward's Natural Science Establishment, New York. Handpicked fragments were dry-ground to minus 400 mesh with an agate mortar and pestle. The minerals were characterized by X-ray diffraction and wet-chemical analysis. Table 2 summarizes the analytical results.

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 2. - Analytical data on mineral specimens

Mineral	Origin	Constituents	Main elements, wt pct
Hematite, α-Fe_2O_3, red, massive.	Ironton, MN.....	Hematite (major).............	Fe 66.9
Goethite, α-FeO·OH......	Biwabik, MN.....	Goethite (major), quartz minor to trace).	Fe 51 Si 6.8
Chromite, (Mg,Fe)Cr_2O_4..	Nye, MT.........	Chromite (major), serpentine (minor).	Cr 27.6 Fe 10.3 Mg 10.9 Al 13.1 Si 1.74
Cuprite, Cu_2O...........	Bisbee AZ.......	Cuprite (major), quartz (major), feldspar (minor).	Cu 29.0 Si 25.6
Manganite, γ-MnO·OH.....	Cuyuna Range, MN	Manganite (major), groutite, α-MnO·OH minor.	Mn 61.1
Pyrolosite, β-MnO_2......	Brazil.........	Pyrolusite (major).........	Mn 50.3
Cassiterite, SnO_2.......	Bolivia.........	Cassiterite (major), quartz (trace).	Sn 77.2

OTHER MEASUREMENTS

Zeta potentials were measured with a zeta meter following established procedures (24-25). The values reported at each pH represent the average for 10 particles. Turbidities were measured with a ratio turbidimeter. Photomicrographs were taken with an AMRAY model 1400 scanning electron microscope; the energy dispersive mode was used for element mapping.

SELECTIVE FLOCCULATION STUDIES

Selective flocculation studies were done with synthetic binary mixtures of a metal oxide or hydroxide mineral with quartz. Unless otherwise specified, the composition of the mixture was 30 pct in metal oxide or hydroxide and the total weight of the mixture was 3 g; the total volume of the pulp was 250 mL, and the starch dosage was 0.05 g. The starches were added at the natural pH of the pulp (pH_n); that is, the pH without acid-base adjustments. Since the use of small quantities of materials can lead to large errors in recovery, multiple runs were performed at the beginning of these studies, which showed that the maximum variation in recoveries was ≈ 10 pct.

The experiments were carried out in two steps: (1) dispersion of minerals and mixing of the flocculant into the pulp and (2) separation of flocs from unflocculated mineral.

Dispersion of Minerals and Mixing of Flocculant

Two methods of dispersing the minerals and mixing the flocculant into the pulp were employed. In one method, the dispersion and mixing were done in 250-mL glass-stoppered cylinders, where the mineral was introduced first and the cylinder then filled to the 210-mL mark with water. The cylinder was placed for 5 min in an ultrasonic bath, after which the flocculant was added. The flocculant was dispersed in 30 mL of water and sonicated for 1 min just before addition to the pulp. To avoid flocculant loss, the container was immediately washed with 10 mL of water and the wash was also added to the pulp. The mixture was handshaken for 1 min, initially hard to distribute any settled solids and then in such a manner as to produce a gentle back and forth flow from end to end of the cylinder. The cylinder was allowed to stand for 5 min, after which the contents were transferred to the elutriation column (fig. 1) to separate the flocs from the unflocculated material.

The second method consisted of performing both dispersion of the mineral and mixing of the flocculant with the pulp in the elutriation column. The pulp was stirred with a cone-drive stirring motor fitted with a two-blade, glass, propeller-type sitrrer. With each rotation, a small magnet reed switch attached to the upper portion of the stirrer triggered an electronic counter, which permitted an accurate measure of the stirring rate.

In the standard procedure with the stirrer, the minerals were dispersed in 210 mL of water and stirred at 200 rpm for 5 min. Stirring continued while the flocculant (dispersed in the same manner as described above) was added and for 5 min thereafter. Stirring was then stopped, and a 5-min settling time was allowed before elutriation.

Separation of Flocs

Separation of the flocs from the unflocculated material was performed in the elutriating column presented in figure 1, which provided a standard, reproducible method of performing the separation. Stoke's law (26) was applied to determine the upward flow rate necessary to retain in the column all material larger than 40 μm (flocculated). An initial flow rate of 225 mL/min, which passed 2 L of water, and a final flow rate between 420 and 500 mL/min, which passed 3 L of water, were employed. Elutriating time was 15 to 16 min. Solids in both the elutriated and floc fraction were collected by conventional vacuum filtration and analyzed.
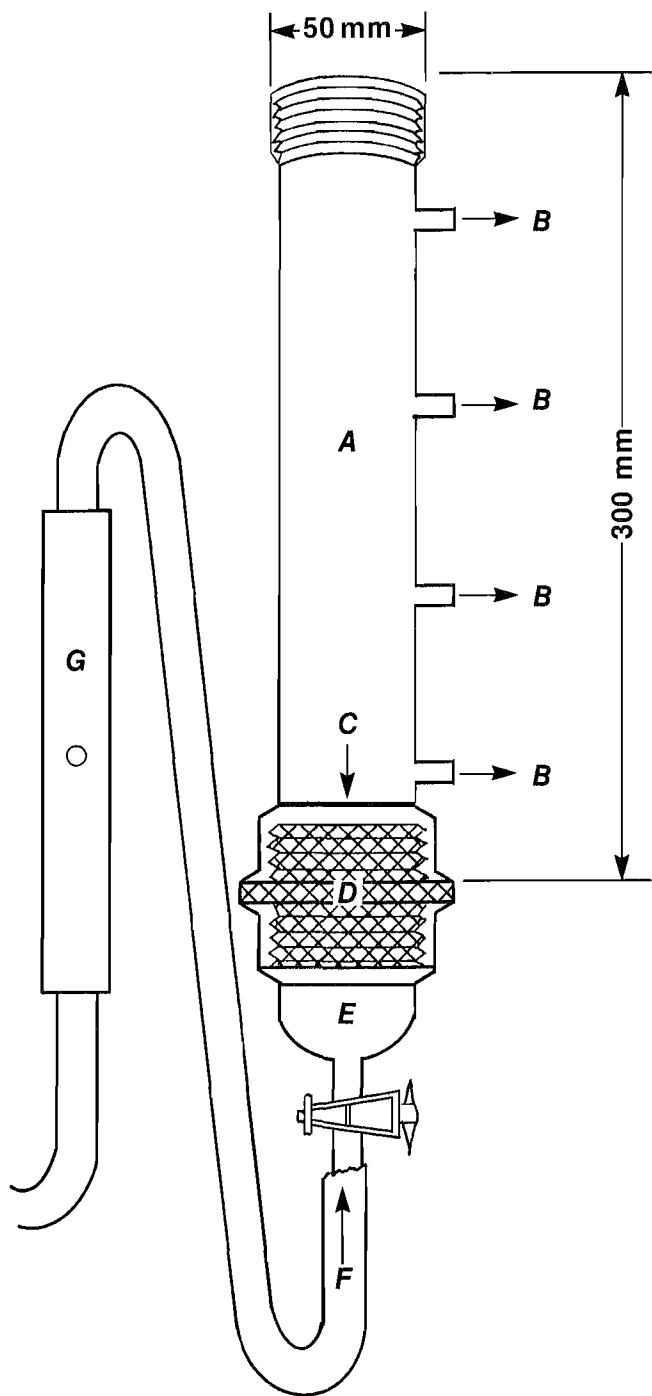
FIGURE 1. - Column elutriator. A, Threaded chromatographic column (Ace No. 5820B-48); B, water outlets; C, glass frit, 25- to 50-μm pore size; D, Teflon coupling (Ace No. 5840-51); E, bottom drip adapter (threaded) with Teflon stopcock (Ace No. 5835B-20); F, water inlet; G, flowmeter.

TABLE 3. - Flocculation response of single-mineral pulps

Mineral and cross-linked starch derivative	pH of flocculation	Av floc size, mm
Hematite, pH_n 7.6:		
GC-CLS..............	8.2	4- 7
C-CLS..............	7.9	3- 4
DEA-CLS.............	7.2	1- 2
IDA-CLS.............	10.2	1
ISX................	10.0-10.5	<1
Goethite, pH_n 6.4:		
GC-CLS..............	8.6	10
C-CLS..............	8.3	1
DEA-CLS.............	6.4	2
IDA-CLS.............	10.2	2
ISX................	10.0-10.5	<1
Chromite, pH_n 8.4:		
GC-CLS..............	9.1	6
C-CLS..............	9.0	3
DEA-CLS.............	7.9	1
IDA-CLS.............	9.8	<1
ISX................	10.0-10.5	<1
Cuprite, pH_n 6.8:		
GC-CLS..............	8.9	10
C-CLS..............	8.4	1
DEA-CLS.............	6.6	4
IDA-CLS.............	10.3	<1
ISX................	10.0-10.5	<1
Manganite, pH_n 8.9:		
GC-CLS..............	9.1	5
C-CLS..............	7.7	2
DEA-CLS.............	9.3	1
IDA-CLS.............	NO	NO
ISX................	10.0-10.5	<1
Pyrolusite, pH_n 7.1:		
GC-CLS..............	8.7	5
C-CLS..............	7.5	2
DEA-CLS.............	7.6	1
IDA-CLS.............	10.2	<1
ISX................	10.0-10.5	<1
Cassiterite, pH_n 6.2:		
GC-CLS..............	8.9	NO
C-CLS..............	7.5	NO
DEA-CLS.............	6.2	2- 3
IDA-CLS.............	10.1	NO
ISX................	10.0-10.5	NO

NO Not observed.

RESULTS

FLOCCULATION OF SINGLE-MINERAL PULPS

Table 3 summarizes the flocculation response of each mineral towards the different starches (solid content 1 g per 100 mL and starch dosage 0.01 g). This table includes the average size of the flocs, the pH_n of the mixture, and the pH after the addition of starch, where flocculation was observed.

The zeta[4] of the starches in the pH range 3 to 11 are shown in figure 2. Only CLS exhibited positive values of zeta potential throughout this range. A point of zero charge (p.z.c.) at pH 8.7

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[4]Zeta potential measurements were provided by J. A. Riehl, chemist, Avondale Research Center (now with U.S. Marine Corps).
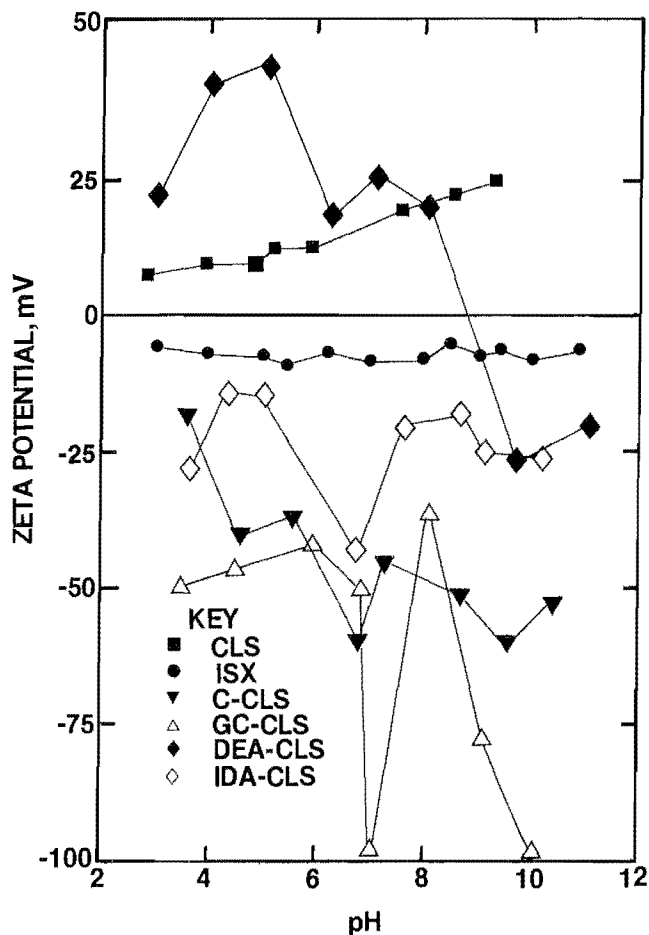
was found for DEA-CLS, with positive values below this pH. The other derivatives had negative zeta potentials, of which ISX was the least negative and GC-CLS the most negative. Figure 3 shows the zeta potentials of hematite, goethite, chromite, and cuprite, and figure 4 shows the zeta potentials of manganite, pyrolusite, and cassiterite. Because all of the minerals that formed flocs with GC-CLS, C-CLS, and IDA-CLS had negative zeta potential values of magnitude >14 mV, the repulsive electrostatic forces should be large enough to suggest that chemisorption is involved in the flocculation mechanism (27). It is probable that chemisorption involves the surface metal component(s) of the mineral and the chelating group, similar to the behavior of ISX which sulfide minerals (10-11). Note
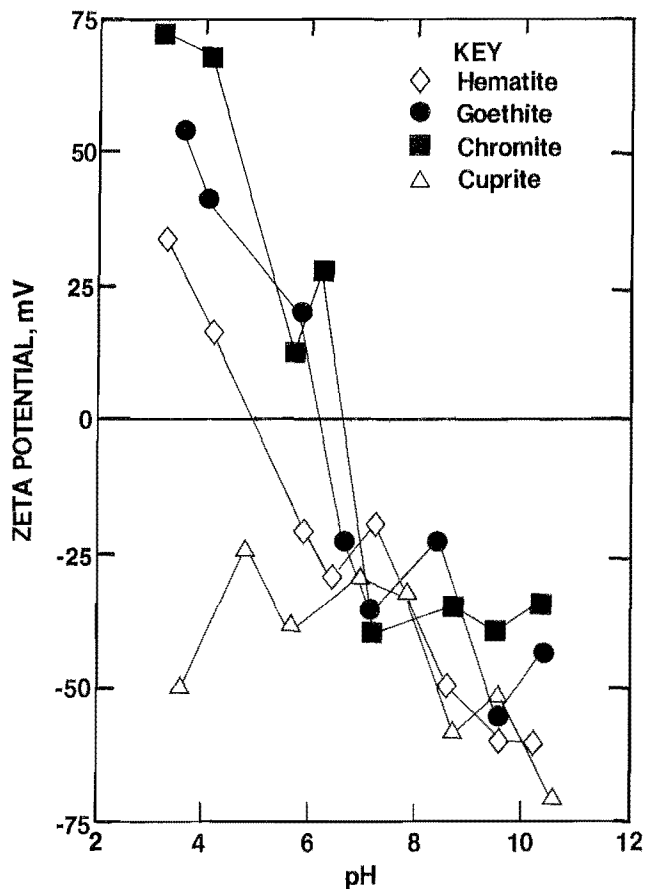

FIGURE 2. - Zeta potential of starches.

FIGURE 3. - Zeta potential of hematite, goethite, chromite, and cuprite.
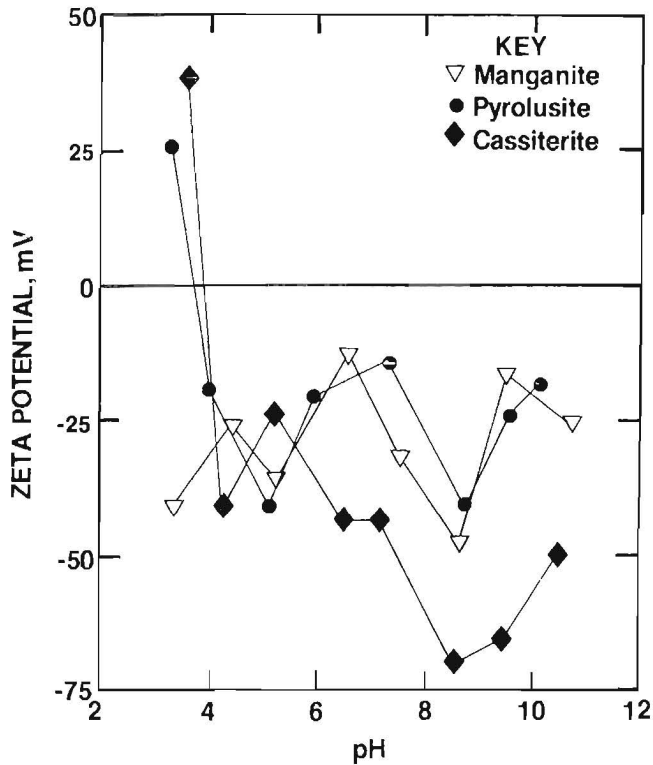
FIGURE 4. - Zeta potential of manganite, pyro-lusite, and cassiterite.

FIGURE 5. - Clarification of hematite, suspensions by different starches.

that with DEA-CLS, adsorption may occur by electrostatic attraction at pH values below its p.z.c. (8.7). However, an additional contribution from chemisorption is also likely, particularly above pH 8.7.

For most minerals, the largest and strongest flocs were produced by GC-CLS; these large flocs could be redispersed but re-formed readily. The only starch derivative that flocculated quartz was DEA-CLS, and this was to a slight extent.

Although turbidity measurements were made at the beginning of the investigation as a way of evaluating the ability of each starch to flocculate the minerals, the results were misleading in predicting starch selectivity. A good example is the better clarification of hematite suspensions by DEA-CLS, as evidenced from the faster decrease in turbidity, than by GC-CLS (fig. 5). However, in selective flocculation experiments, higher recoveries and grades of hematite were obtained with GC-CLS than
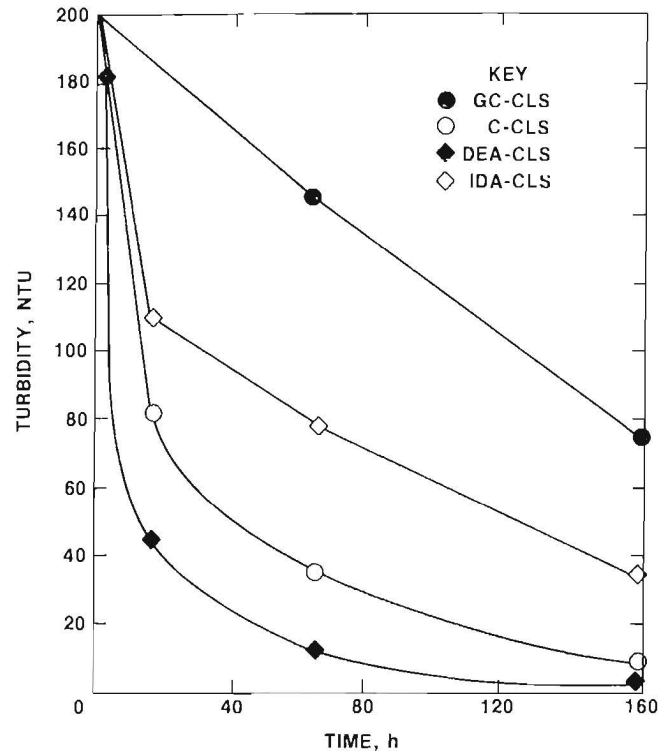
with DEA-CLS (figs. 6-7). For this reason, turbidity measurements were abandoned and starch selectivity was determined in terms of the recovery and grade of the metal oxide or hydroxide mineral from a quartz mixture. The recovery of the mineral is expressed as

$$\frac{\text{weight of mineral in flocs}}{\text{weight of mineral in mixture}} \times 100; \text{ the}$$

grade of the flocs is the weight percent of the metal oxide or hydroxide in the flocs.

SELECTIVE FLOCCULATION

To evaluate the ability of each starch to selectively flocculate a metal oxide or hydroxide mineral from a mixture with quartz, the following minerals were selected: (1) hematite, (2) goethite, (3) chromite, and (4) cuprite. The mixtures contained 0.9 g of the selected mineral and 2.1 g of quartz. Mixing of the
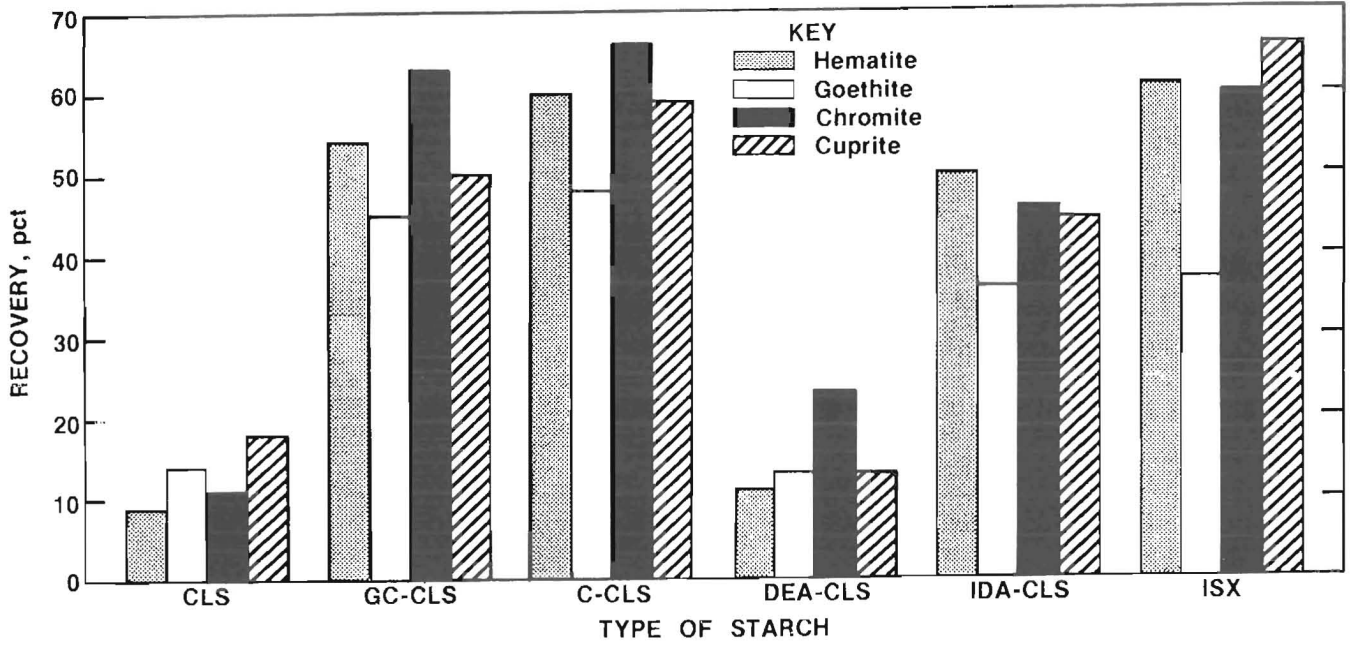
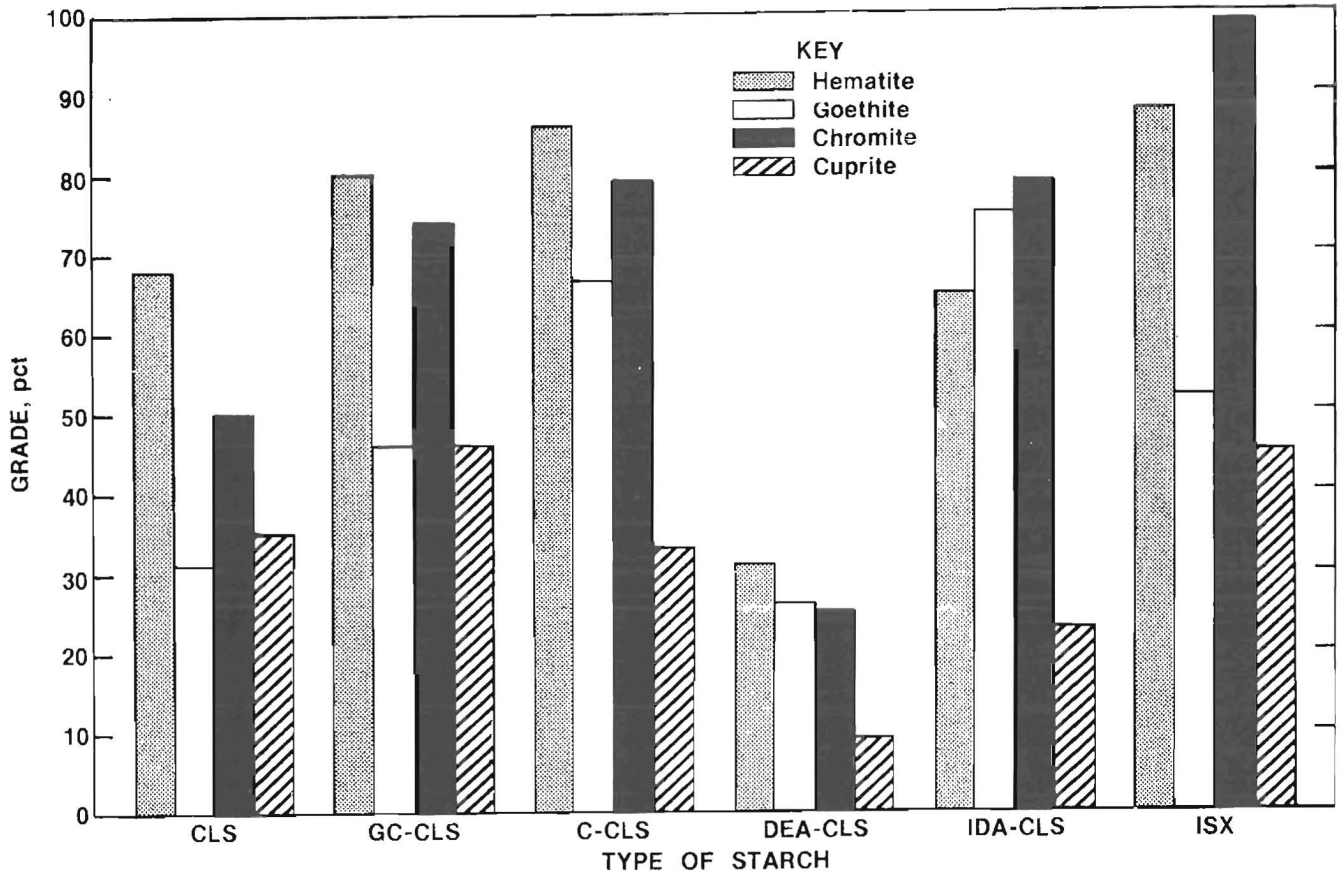FIGURE 6. - Recovery of metal oxide or hydroxide from quartz.

FIGURE 7. - Grade of flocs.

flocculant with the pulp was performed with the motor-driven stirrer following the standard procedure. Grades of chromite are represented by the percent of chromia (Cr_2O_3) in the flocs with respect to the maximum Cr_2O_3 content in the chromite mineral (40.3 pct).

From figure 6 it can be seen that higher recoveries were obtained with the negatively charged starches GC-CLS, C-CLS, IDA-CLS, and ISX than with the positively charged CLS and DEA-CLS. The grades (fig. 7) were also higher with the negatively charged starches, except for CLS and cuprite. Recoveries and grades were the lowest with DEA-CLS. It is interesting to note from table 4 that the pH_n of the mixtures and the pH after addition of DEA-CLS were below 8.7, the p.z.c. of this starch (fig. 2). Therefore, an electrostatic attraction mechanism rather than one involving chemisorption may account, in part, for the poorer selectivity of DEA-CLS. With GC-CLS, C-CLS, IDA-CLS, and ISX, flocculation occurred at pH regions where both the minerals and the starches were expected to be highly negative (fig. 2). The fact that selective flocculation was observed with these starches provides further evidence for a chemisorption mechanism.

Effect of Pulp pH and of Dispersing Agents

To evaluate the effect of pulp pH and the dispersing agents sodium metasilicate and sodium metaphosphate, the starches CLS, GC-CLS, and ISX were added at the pH_n of the pulp and at pH 11 in the absence and in the presence of the dispersing agent. The concentration of dispersing agent was 1×10^{-4} mol/L, and mixing of the flocculant with pulp was carried out in the cylinders as described in the "Experimental Work" section. Results are presented in table 5 for hematite and in table 6 for chromite.

TABLE 4. - Pulp pH before and after starch addition in selective flocculation experiments[1]

Mineral mixture	pH_n	pH after addition of--					
		CLS	GC-CLS	C-CLS	DEA-CLS	IDA-CLS	ISX
Hematite-quartz.....	6.9	7.1	9.5	9.2	6.8	10.6	10.6
Goethite-quartz.....	6.5	6.8	8.7	9.3	6.0	10.3	10.4
Chromite-quartz.....	8.4	8.2	9.4	9.1	7.2	10.2	10.7
Cuprite-quartz......	7.6	7.4	8.1	8.2	7.1	10.1	10.2

[1]Mixing performed at 200 rpm.

TABLE 5. - Effect of pulp pH and of dispersing agents on the flocculation of hematite from quartz, percent

Starch	Dispersing agent					
	None		Sodium metasilicate		Sodium metaphosphate	
	Recovery	Grade	Recovery	Grade	Recovery	Grade
At $pH_n \sim 7$:						
CLS..........	25	67	45	82	8	61
GC-CLS......	65	79	65	86	26	80
ISX..........	64	82	52	85	13	65
At pH 11:						
CLS..........	48	73	42	79	36	78
GC-CLS......	59	84	50	86	27	81
ISX..........	55	84	32	83	15	61

TABLE 6. Effect of pulp pH and of dispersing agents on the
flocculation of chromite (11.6 pct Cr_2O_3) from quartz,
percent

Starch	Dispersing agent					
	None		Sodium metasilicate		Sodium metaphosphate	
	Re-covery	Grade[1]	Re-covery	Grade[1]	Re-covery	Grade[1]
At pH_n~8.2:						
CLS........	13	21 (52)	25	28 (69)	16	21 (52)
GC-CLS.....	69	33 (82)	45	22 (55)	27	33 (82)
ISX........	68	40 (99)	49	39 (97)	15	23 (57)
At pH 11:						
CLS........	15	24 (60)	30	31 (77)	18	28 (69)
GC-CLS.....	70	34 (84)	55	20 (72)	30	35 (87)
ISX........	53	39 (97)	43	39 (97)	34	40 (99)

[1]Numbers in parentheses refer to the percent of Cr_2O_3 in flocs
relative to the maximum Cr_2O_3 content (40.3 pct) in the chromite
mineral.

A marked decrease in recovery was ob-
served for both hematite and chromite
treated with GC-CLS and ISX when sodium
metaphosphate was used as the dispersing
agent, but no further experiemental work
was undertaken to determine the cause.
It is possible that sodium metaphosphate
may interact with either the mineral sur-
face or the starch (or both), thus hin-
dering the attachment of the starch to
the mineral and subsequent floc
formation.

For hematite (table 5), the recoveries
with GC-CLS and ISX were higher at pH 7
than at 11, in the presence or absence of
sodium metasilicate, but the grades were
nearly the same. For chromite (table 6),
the recoveries and grades with GC-CLS
were nearly independent of pH in the ab-
sence of sodium metasilicate, but were
higher at pH 11 in the presence of the
metasilicate. With ISX, the grades were
independent of pH, but the recoveries
were lower at the higher pH as well as in
the presence of sodium metasilicate.

The X-ray spectra of hematite flocs
with GC-CLS showed the presence of some
Si (corresponding to less than 10 pct

quartz) as a result of either coflocula-
tion or entrapment of the quartz parti-
cles. However, SEM photomicrographs and
mapping of Fe and Si indicated that the
quartz was not clustered, but was present
as isolated particles (fig. 8), which
suggested that it was entrapped in the
floc rather than coflocculated.

Effect of Mixing Method and Settling Time Prior to Elutriation

A comparison between the two standard
methods used to mix the flocculant into
the pulp--manually and with a motor-
driven stirrer--is presented in table 7
for hematite and in table 8 for chromite.
The mineral mixture contained 0.9 g of
the oxide mineral and 2.1 g of quartz,
and the starches (0.05 g) were added at
the pH_n of the pulp. The recoveries were
lower, but the grades were essentially
unvariable, when the motor-driven stirrer
was used. The exceptions were for chro-
mite treated with C-CLS, where both the
recovery and grade increased, with GC-CLS
and chromite (grade decreased), and with
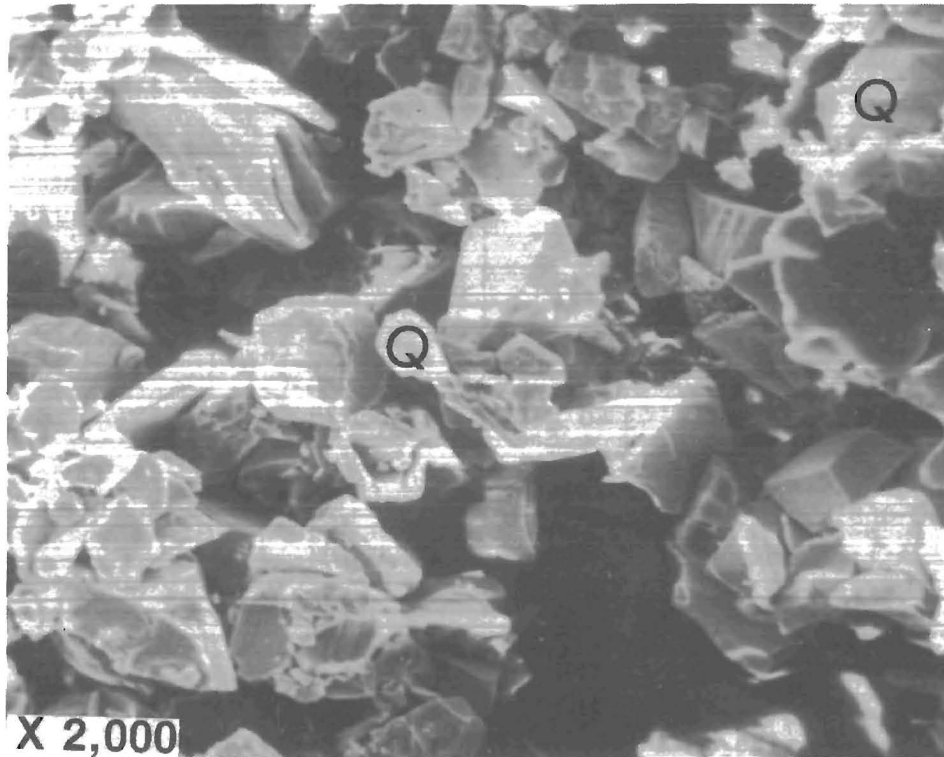IDA-CLS and hematite (grade decreased).

FIGURE 8. - SEM photomicrograph of hematite flocs; Q denotes quartz.

TABLE 7. - Comparison between the two mixing methods used in the flocculation of hematite from quartz, percent

Starch	Manual mixing		Motor-driven stirrer, 200 rpm	
	Re-covery	Grade	Re-covery	Grade
GC-CLS.....	65	79	54	80
C-CLS......	74	87	60	86
IDA-CLS....	67	84	50	65
ISX........	64	82	61	78

Higher stirring rates (300 and 400 rpm), as shown in figure 9, increased the grades of hematite when ISX and GC-CLS were used, but recoveries were not significantly increased. Longer stirring times at a constant stirring rate of 200 rpm (fig. 10) increased the recoveries, but grades were lower at 5 min than at 1 or 15 min of stirring. Longer settling periods prior to elutriation (fig. 11) exerted less influence on recoveries and grades with GC-CLS than with ISX.

TABLE 8. - Comparison between the two mixing methods used in the flocculation of chromite from quartz, percent

Starch	Manual mixing		Motor-driven stirrer, 200 rpm	
	Re-covery	Grade[1]	Re-covery	Grade[1]
GC-CLS..	87	37 (92)	63	31 (77)
C-CLS ..	54	28 (69)	66	32 (79)
IDA-CLS.	68	33 (82)	46	32 (79)
ISX.....	73	40 (99)	60	40 (99)

[1]Numbers in parentheses refer to the percent of Cr_2O_3 in flocs relative to the maximum Cr_2O_3 content (40.3 pct) in the chromite mineral.

For chromite, higher stirring rates (fig. 12) increased the recovery with GC-CLS and decreased it with ISX; grades were higher at 400 rpm for GC-CLS. It was observed that higher stirring rates did not appear to break flocs of chromite with GC-CLS; however, flocs formed by ISX did break with stronger stirring. It was
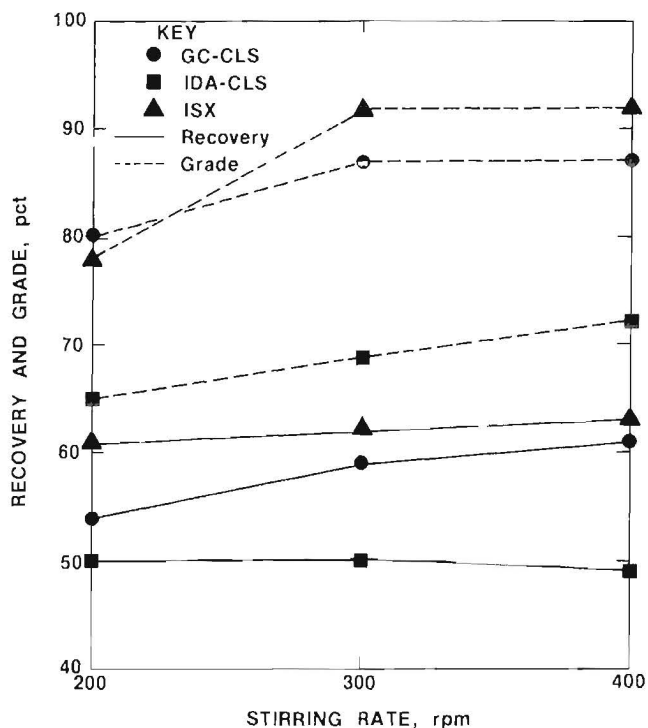
FIGURE 9. - Effect of stirring rate on the selective flocculation of hematite.

FIGURE 10. - Effect of stirring time on the selective flocculation of hematite.

also observed that broken ISX-chromite flocs were carried away with the unflocculated material during elutriation but were re-formed in the collecting vessel, which accounts for the decrease in recovery. Longer stirring times (fig. 13) increased the recovery with both GC-CLS and ISX. With ISX, grades decreased with stirring time.

Note that in the experiments at variable stirring times, elutriation started 1 min after stopping the stirring, compared to a 5-min period allowed in experiments at variable stirring rates. At 200 rpm and 5-min settling time (fig. 12), recoveries were higher than at 200
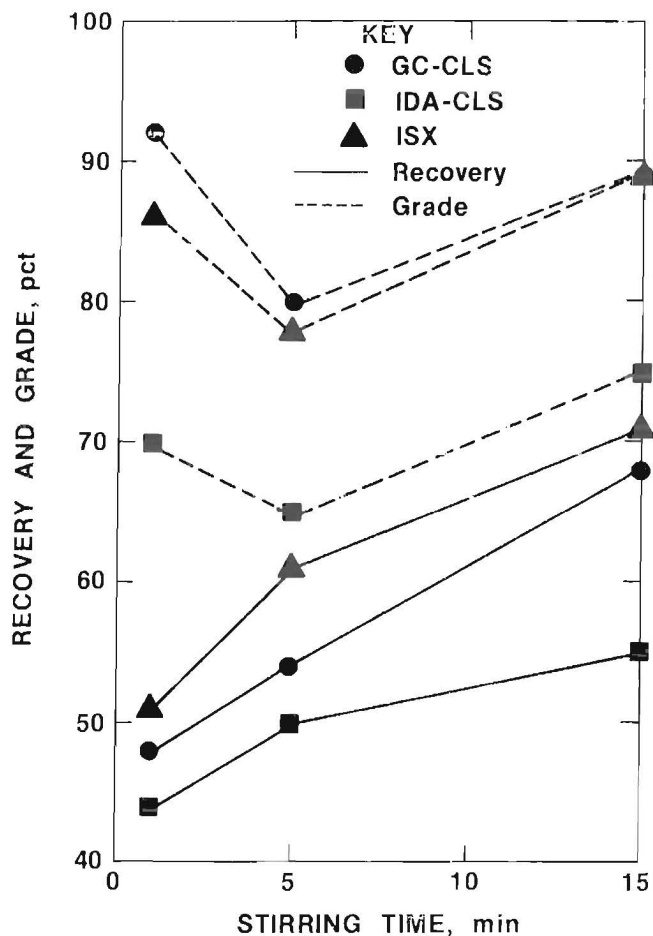
rpm and 1-min settling time (fig. 13), the difference being more pronounced with ISX. This may be due to further floc formation or floc growth during longer settling periods.

Effect of Flocculant Dosage

The recoveries and grades of hematite as a function of the weight of starch are shown in figure 14. The lowest recoveries, not exceeding 30 pct, were obtained with CLS. For the starches, the grades were essentially independent of dosage, while the recoveries were sensitive only at low ($\leq$0.1-g) dosages.

DISCUSSION

The *effectiveness* of separating mineral fines by selective flocculation may be

envisioned as the contribution of at least two factors: (1) the formation of
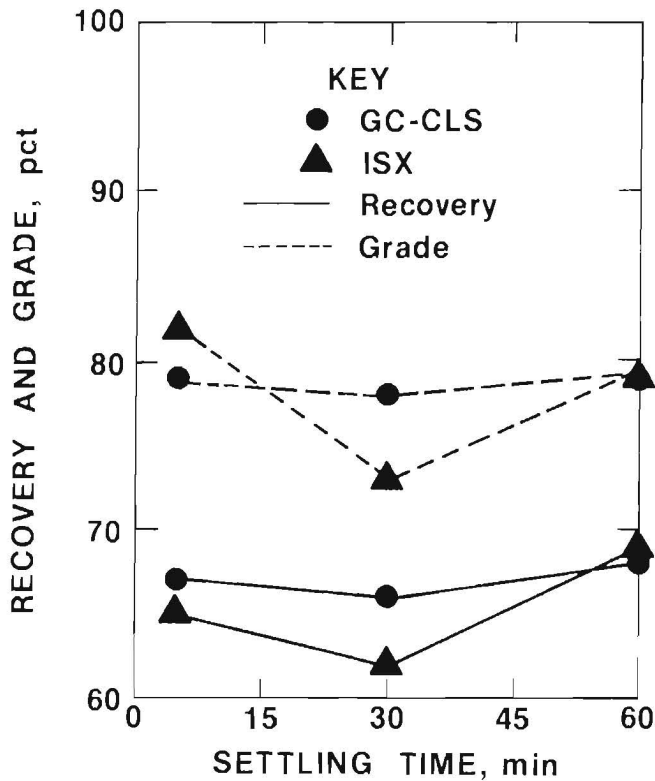
FIGURE 11. - Effect of settling time prior to elutriation on the selective flocculation of hematite.
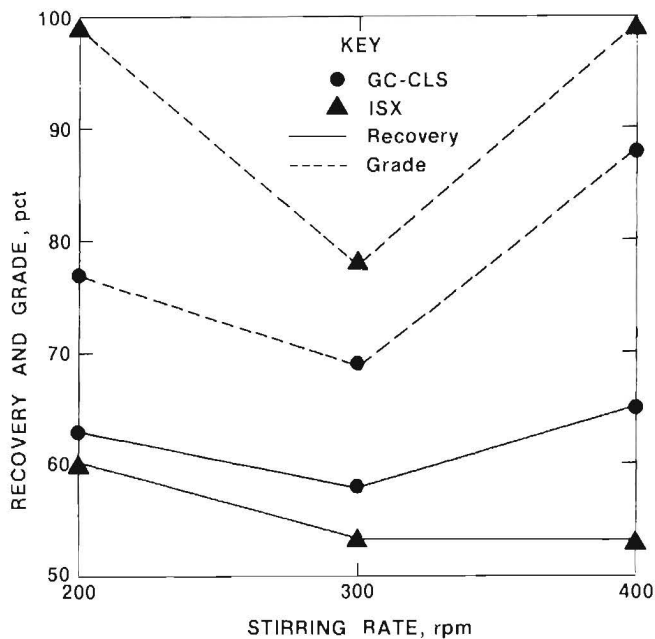

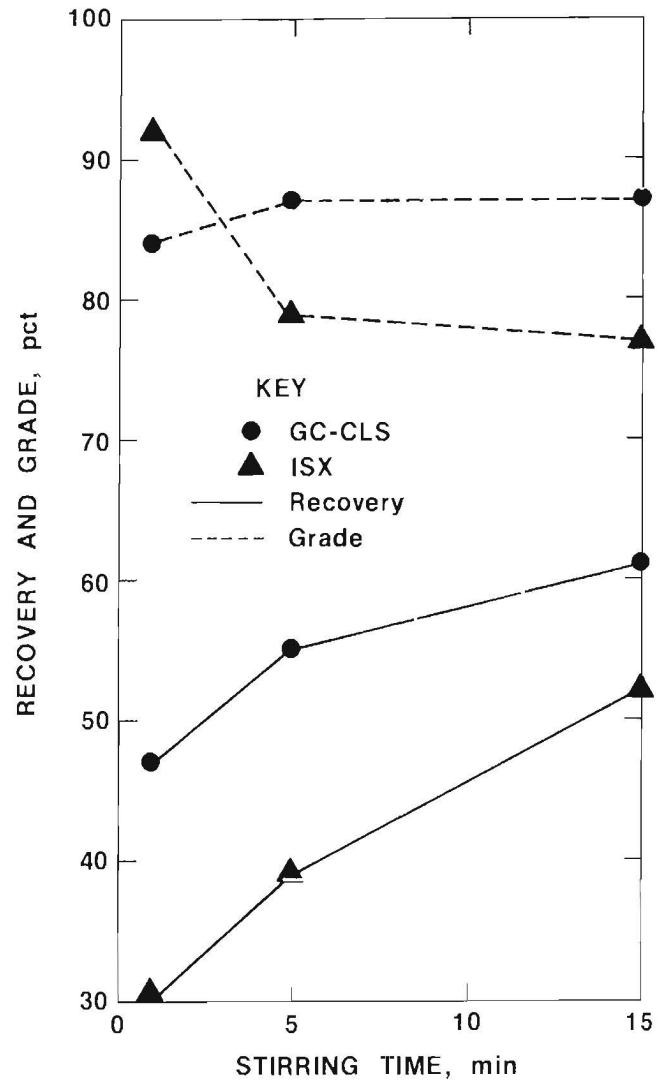FIGURE 12. - Effect of stirring rate on the selective flocculation of chromite.

FIGURE 13. - Effect of stirring time on the selective flocculation of chromite.

a strong, covalent bond between groups in the polymer and surface metal components in the mineral and (2) the strength of the resulting floc, which may be associated with the arrangement of particles in the flocs (that is, floc morphology). While the first factor is predominantly chemical in nature and, therefore, dependent on the type of flocculant and functional group, metal entity, and chemical environment, the second factor could be affected not only by the chemical environment but also to a great extent by mechanical constraint imposed during mixing and elutriation.

For example, the high grades of chromite flocs with ISX, which approach 99 pct of Cr_2O_3 content in the chromite mineral, indicate that ISX showed high selectivity towards this mineral, at least under the experimental conditions reported here. This high selectivity for chromite may be related to a stronger surface metal-sulfur bond with Cr than with any of the metal components of the other minerals. While the grades were high and nearly constant when ISX was used as a flocculant for chromite, the recoveries (table 6) depended on the medium (pH, dispersing agent) and mixing methods (table 8). The fact that chromite ISX flocs were observed to break upon vigorous stirring, thus resulting in lower recoveries, is evidence of the role floc strength may play in the effectiveness of selective flocculation as a separation method. Unfortunately, no systematic studies directly relating morphology to floc strength are known at the present time, probably due to the experimental difficulties involved in preserving floc structures away from their aqueous medium.

The flocculation of the negatively charged minerals by the negatively charged cross-linked starch particles (keeping in mind the colloidal nature of the starches) may resemble the flocculation of particulate dispersions with small particles of opposite sign, where it has been found that the small particles bridge between the large particles by an electrostatic interaction (28-31), except that in our case the bridging is likely to occur by a covalent interaction. Although we have some indication, from scanning electron microscopy, of the
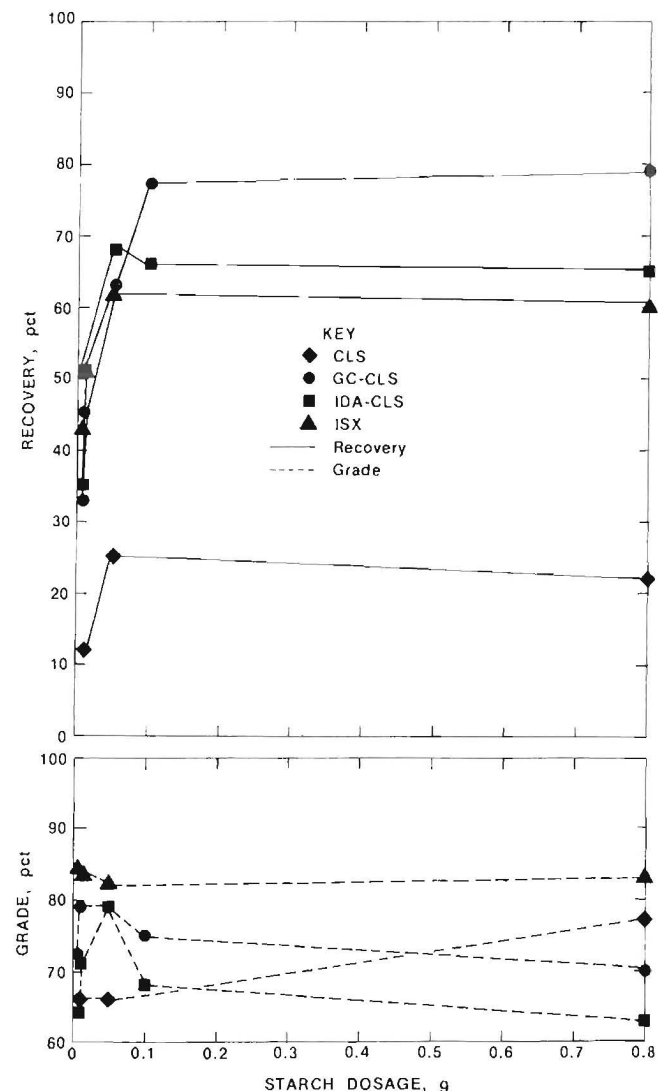

FIGURE 14. - Effect of starch dosage on the selective flocculation of hematite.

presence of starch particles on flocculated mineral surfaces, further studies would be required to establish a particle bridging mechanism.

CONCLUSIONS

The separation of metal oxide and hydroxide mineral fines from mixtures with quartz by selective flocculation was found to improve with the use of cross-linked starch derivatives capable of undergoing chemisorption.

Although it is extremely difficult to establish experimentally that a covalent bond forms between metal sites on the mineral surface and the chelating groups in the starches because of the low density of surface bonds, zeta potential measurements have provided some evidence that chemisorption rather than electrostatic attraction is involved in the flocculation by the carboxylate, iminodiacetate, and xanthate derivatives.

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