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Dispersion-Selective Flocculation-Desliming Characteristics of Oxidized Taconites

By R. E. Green and A. F. Colombo



UNITED STATES DEPARTMENT OF THE INTERIOR

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BUREAU OF MINES

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Library of Congress Cataloging in Publication Data:

Green, R. E. (Robert E.), 1925-

Dispersion-selective flocculation-desliming characteristics of oxidized taconites.

(Report of investigations ; 8867)

Bibliography: p. 17-18.

Supt. of Docs. no.: I 28.23:8867.

1. Ore-dressing. 2. Taconite. 3. Slimes (Metallurgy). 4. Flocculation. I. Colombo, A. F. (Arthur F.), II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 8867.

TN23.U43 [TN538.I7] 622s [622'.341] 83-600302

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree centigrade	mg/L	milligram per liter
cm ² /g	centimeter squared per gram	min	minute
cm/min	centimeter per minute	mL	milliliter
cp	centipoise	μm	micrometer
g	gram	μmho/cm	micromho per centimeter
L	liter	pct	percent
lb	pound	psi	pound per square inch
lb/ft ³	pound per cubic foot	vol pct	volume percent
lb/ton	pound per ton	wt pct	weight percent
mg	milligram		

DISPERSION-SELECTIVE FLOCCULATION-DESLIMING CHARACTERISTICS OF OXIDIZED TACONITES

By R. E. Green¹ and A. F. Colombo²

ABSTRACT

The Bureau of Mines undertook a bench-scale study of three different types of oxidized taconites³ from the Lake Superior district to improve the dispersion-selective flocculation-desliming process for beneficiating these materials. The response-surface contours of the effects of dissolved ionic species in the water and of three dispersion systems on the selective flocculation process were studied. Results of metallurgical data and chemical analyses of the aqueous phase showed that the water quality affects the performance of the selective flocculation process.

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³"Oxidized" refers to iron oxides that are not recovered by a drum-type magnetic separator.

INTRODUCTION

During the past 20 years, the Bureau of Mines has studied iron ore flotation with the objective of increasing the domestic iron supply through the use of low-grade oxidized taconites. Flotation processes are applicable to beneficiation of substantial tonnage (5, 21);⁴ most recent research was devoted to the selective flocculation and gangue flotation processes. These processes were evaluated on oxidized materials from Minnesota and Michigan, and yielded concentrates with less than 5 pct silica and accompanying iron recoveries of more than 80 pct.

The slime content of ore slurries has been recognized as detrimental to these flotation processes. Gaudin (8) lists several causes for this: (1) low probability of encounter with air bubbles, (2) chemical and physical characteristics of slime particles, and (3) dissolved species in the water surrounding particles and bubbles. The presence of silica slime in an iron ore can increase the collector consumption and slows the flotation of the silica gangues (7, 11). Desliming usually results in high iron losses. Selective flocculation followed by desliming is an attractive technique because a lower iron content in the slime can be rejected and the reagent consumption is lower.

Using the Haseman system for selective flocculation of slime phosphate in the presence of clay (9) as a starting point, the Bureau of Mines developed a method for treating finely ground iron ores (4-6). The process has three steps: (1) dispersion of the ore ground with sodium hydroxide for pH control and sodium silicate and/or sodium tripolyphosphate as dispersants, (2) selective flocculation of the iron oxide particles with a starch, and (3) separation of the

supernatant slime from the settled sands. The alkaline reagents increase the negativity of the mineral particles so that the forces of repulsion acting between them prevent natural flocculation and settling. Corn starch, which is slightly negative due to the presence of the carboxylate group, is preferentially adsorbed on the iron oxides (1) which are selectively flocculated. The deslimed sand or pulp is an excellent feed for the flotation of the gangue minerals in a cationic or calcium-activated system. A successful selective flocculation-desliming separation depends on the electrokinetic properties of the minerals, both the dissolved species in the water and the mineral constituents of the ore. Minerals that are soluble in alkaline slurries will release inorganic ions which are adsorbed on the mineral particles and influence the magnitude and sign of the zeta potential of the mineral particles. Hydrolyzed metal ions can reverse the charge of an anionic colloidal substrate (13-14, 16-17). Since the selective flocculation-desliming flotation process is a very complex physicochemical system, it is important to evaluate the effects of different metal ions on the dispersion of siliceous gangue minerals. The ionic species selected for this study were chosen for the following reasons: Natural and processed water usually contains dissolved calcium and magnesium ions. If an iron ore deposit contains pyrite, pyrrhotite, and similar mineral gangue, they are a source of dissolved ions. For example, the reaction of air on alkaline pyrite pulp yields sulfide, thiosulfate, sulfate, and iron cations. Ferrous ions will be oxidized to the ferric state and will form a complex amorphous iron hydroxide in the alkaline medium. The precipitate formed may become the flocculant for the dispersed mineral particles. Three types of iron ores were studied to better understand the selective flocculation mechanisms involved.

⁴Underlined numbers in parentheses refer to the list of references preceding the appendix.

MATERIALS

PREPARATION OF SAMPLES

Three samples--one from the Mesabi (MN), Marquette (MI), and Menoninee (WI) ranges--were evaluated. Each sample weighed approximately 1,500 lb. The ores were crushed through 8 mesh, blended six times by coning and quartering, and divided in half with a riffle splitter. One half of each sample was stored, and the other half was split into 600-g charges to insure uniform samples throughout the research program. Chemical analyses of randomly selected head samples are summarized in table 1. Their estimated mineral distributions were calculated from the chemical analysis of the iron and the silica content in the sample and the petrographic identification and are given in table 2.

MINERALOGY OF SAMPLES

Sample A, MN

The iron minerals found in sample A were hematite and goethite. Some magnetite, siderite, and iron silicates were also present. Most magnetite was unaltered, but some had been partly replaced by hematite, leaving a magnetic core. Hematite was present in a slightly greater proportion than goethite. Most of the goethite was present in irregularly shaped pieces and had no crystal outline. The grain size of both hematite and magnetite ranged from 30 to 300 μm and averaged approximately 100 μm . The goethite ranged from a few to 1,500 μm and averaged about 40 μm . The quartz matrix was friable.

Sample B, MI

Sample B consisted primarily of hematite, although some magnetite was present in the middle areas of the larger grains. The hematite was a pseudomorphic replacement of magnetite and occurred as polycrystalline aggregates retaining the original shapes of the magnetite crystals. The size range of the iron oxides was broad. Less than 1 pct of the

hematite was smaller than 10 μm and was not readily liberated. Locked hematite-quartz grains were liberated at minus 20 μm . The average grain size of the hematite was about 50 μm , but clusters of several grains were up to 500 μm in diameter.

TABLE 1. - Partial chemical analysis of samples, percent

Analysis	A	B	C
Fe (total).....	¹ 35.7	² 35.3	³ 30.5
Fe (ferrous).....	2.0	1.0	6.6
SiO ₂	¹ 43.5	² 47.5	³ 43.1
MgO.....	.2	.1	3.5
CaO.....	.4	.5	2.4
Al ₂ O ₃4	.4	1.5
P.....	<.1	<.1	<.1
LOI (400° C).....	2.6	.3	<.1
LOI (1,000° C).....	2.9	.6	2.4

¹Average of 45 analyses.

²Average of 36 analyses.

³Average of 16 analyses.

TABLE 2. - Estimated mineral distribution, percent

Mineral	A	B	C
Quartz.....	45	48	43
Hematite.....	26	46	20
Goethite.....	23	2	NAp
Magnetite.....	4	4	25
Siderite.....	2	NAp	NAp
Calcite.....	NAp	NAp	5
Chlorite.....	NAP	NAP	4
Tremolite.....	NAp	NAp	2
Feldspar.....	NAP	NAP	1
Iron silicate ¹	<1	NAP	NAP
Total.....	100	100	100

NAP Not applicable.

¹The silicate mineral was not identified.

Sample C, WI

Magnetite and hematite occurred in approximately equal amounts. Most of the iron oxides were liberated in the 38- to 53- μm range. Fine iron oxide particles ranging in size from 1 to 11 μm and averaging 5 μm were disseminated throughout the larger quartz grains and some of the feldspar and amphibole grains.

EXPERIMENTAL PROCEDURES

STANDARDIZED SELECTIVE FLOCCULATION TESTS

A 600-g ore charge and a total of 600 mL of pH 9.0 distilled demineralized water containing 8 mg Ca^{2+} /L (test water) and the reagents needed by the individual tests were added to a batch rod mill. All the reagents added were pipetted. The pulp was ground at approximately 50-pct solids for 25 min. The size distribution and surface area of the ground ores are given in table 3. Blaine and Fisher apparatus were used to determine surface area.⁵

The ground slurry was washed from the rod mill into a 4-L beaker and diluted to 3 L. Test water was used for both washing and dilution. The solids in the pulp were approximately 17.5 pct, or 5.9 vol pct. The pulp was thoroughly mixed for 2 min and then baffled.⁶ The settling characteristics of the unflocculated materials were observed for 3 min. The pulp was remixed, and 3 mL of 2.5-pct pearl starch solution was pipetted into

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

⁶The term "baffled" indicates stopping the mixing motion of the slurry to quiescent state by use of a wide spatula.

the pulp to induce selective flocculation of the iron oxides. After the starch addition, the slurry was mixed for 1 min, baffled, and permitted to settle for 1 min. During this period, the floccules and their settling characteristics were observed. After the desired settling time had elapsed, the slime product was siphoned off, starting at the 3,000-mL line and stopping at the 1,000-mL level of a 4-L beaker. However, in a few tests, the floccules were so large that their settled bed did not permit removal of 2,000 mL of slime slurry. The slime withdrawal rate was approximately 10 cm/min. The pH of the slime was determined, and a 15-mL sample was taken when a starch analysis was made. Most starch analyses were baseline, and were not performed routinely but were made periodically to check on the carbohydrate levels.

A pressure filter with two ordinary paper towels as the filtering medium was rinsed thoroughly with distilled demineralized water. The undiluted slime slurry was poured into the filter, and about 100 psi pressure was applied. The filtrate was allowed to run into the drain until it was visibly clear. At this point, water samples were collected for SiO_2 , Ca^{2+} , Mg^{2+} , SO_4^{2-} , amine, and phosphorus

TABLE 3. - Size distribution and surface area of feed¹

Size fraction, μm	Sample A		Sample B		Sample C	
	Wt, pct	Cumulative pct	Wt, pct	Cumulative pct	Wt, pct	Cumulative pct
+44.....	1.8	1.8	2.1	2.1	3.6	3.6
-44 +34.....	3.3	5.1	2.5	4.6	7.0	10.6
-34 +24.....	12.3	17.4	11.1	15.7	17.4	28.0
-24 +16.....	21.7	39.1	24.1	39.8	23.9	51.9
-16 +11.....	12.5	51.6	15.4	55.2	12.0	63.9
-11.....	48.4	100.0	44.8	100.0	36.1	100.0
Surface area ² ..cm ² /g..	2,900		2,700		2,400	

¹Samples were ground in the rod mill at 50 pct solids for 25 min. Size distribution was obtained from the cyclosizer, Warman International PTY. Ltd, Australia.

²The surface area of the ground sample was obtained by an air permeability method.

as sodium tripolyphosphate (STPP) analyses (19-20). After a sufficient volume was obtained for analysis, the slime remaining was washed into the filter, filtered, dried, weighed, and analyzed for Fe and SiO₂. The sand slurry, which had a volume of approximately 1,000 mL, was filtered, dried, weighed, and analyzed for Fe and SiO₂.

The inorganic ions released by the samples were evaluated by grinding 600 g of ore for 25 min in a rod mill with 600 mL of distilled water and no reagent added. The ground ore was washed from the mill with distilled water into a 4-L beaker, and enough water was added to make the final volume 3 L. The slurry was mixed for 2 min and then filtered in a pressure filter. The filtrate was analyzed for pH, calcium, specific conductivity, sulfate, soluble silica, sodium, and total alkalinity. A summary of the averaged results is given in table 4. The low dissolved ionic species leached from the ore samples assures that the selective flocculation procedure can be applied.

ANALYTICAL EQUIPMENT AND METHODOLOGY

A spectrophotometer analyzed the liquid fraction of the slime slurries for soluble silicates, phosphorus as STPP, sulfate, and amine. The ethylenediaminetetraacetic acid (EDTA) complexometric procedure analyzed the calcium and magnesium ions. Reagents used in the chemical analyses were analytical reagent (AR) grade unless stated otherwise.

CHEMICAL REAGENTS

Sodium Silicate

The sodium silicate had a SiO₂:Na₂O weight ratio equal to 3.22, a silica content of 28.7 pct, a Baumé of 41.0°, and a viscosity of 180 cp. A 5-pct silicate solution was used.

Sodium Tripolyphosphate

Granular anhydrous STPP (Na₅P₃O₁₀) with a P₂O₅ content of 57 pct and a bulk density of 60 lb/ft³ was used. One percent STPP solution was made in 1-L batches and gave analyses in the 2,500-mg P/L-range. The theoretical addition was 2,526 mg P/L.

Arosurf MG-98A

MG-98A, an alkyl ether amine acetate, has a chemical formula equal to R-O-(CH₂)₃NH₃⁺acetate, where R = a mixture of C₈H₁₇ and C₁₀H₂₁ groups. A 0.3-pct solution was used.

Pearl Starch

A Douglas pearl starch was used. Fresh starch dispersion was made every 2 weeks. The percent solids of the thoroughly mixed starch solution was checked with an American Optical T/C refractometer. The readings obtained varied between 2.2 and 2.3 pct solids; theoretically, it should have been 2.5 pct.

TABLE 4. - Partial chemical analysis of the aqueous phase¹

Sample	pH	Specific conductance, μ mho/cm	Calcium, mg/L	Sodium, mg/L	Sulfate, mg/L	Soluble silica, mg/L	Total alkalinity, mg/L
A.....	8.1	128	11	10	31	4	21
B.....	8.3	65	5	7	10	4	22
C.....	9.4	124	7	9	7	10	39

¹No reagent addition.

Water

Distilled and demineralized water, containing less than 0.1 mg salt/L as NaCl per liter, was used to prepare analytical solutions and the test water.

HEXAGONAL DESIGNED EXPERIMENTS

Hexagonal designed experiments were run to evaluate the responses of the three

different ore types. The data obtained were analyzed by a response-surface technique (2-3) using the mathematical model

$$\hat{Y} = B_0 + B_1(X_1) + B_2(X_2) + B_3(X_1)^2 + B_4(X_2)^2 + B_5(X_1)(X_2).$$

Coefficients for the response-surface diagrams for the statistical analysis of the results are given in the appendix.

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

In a selective flocculation separation, a sand and a slime product are obtained.

These products are dependent on each other. Therefore, only one of them needs

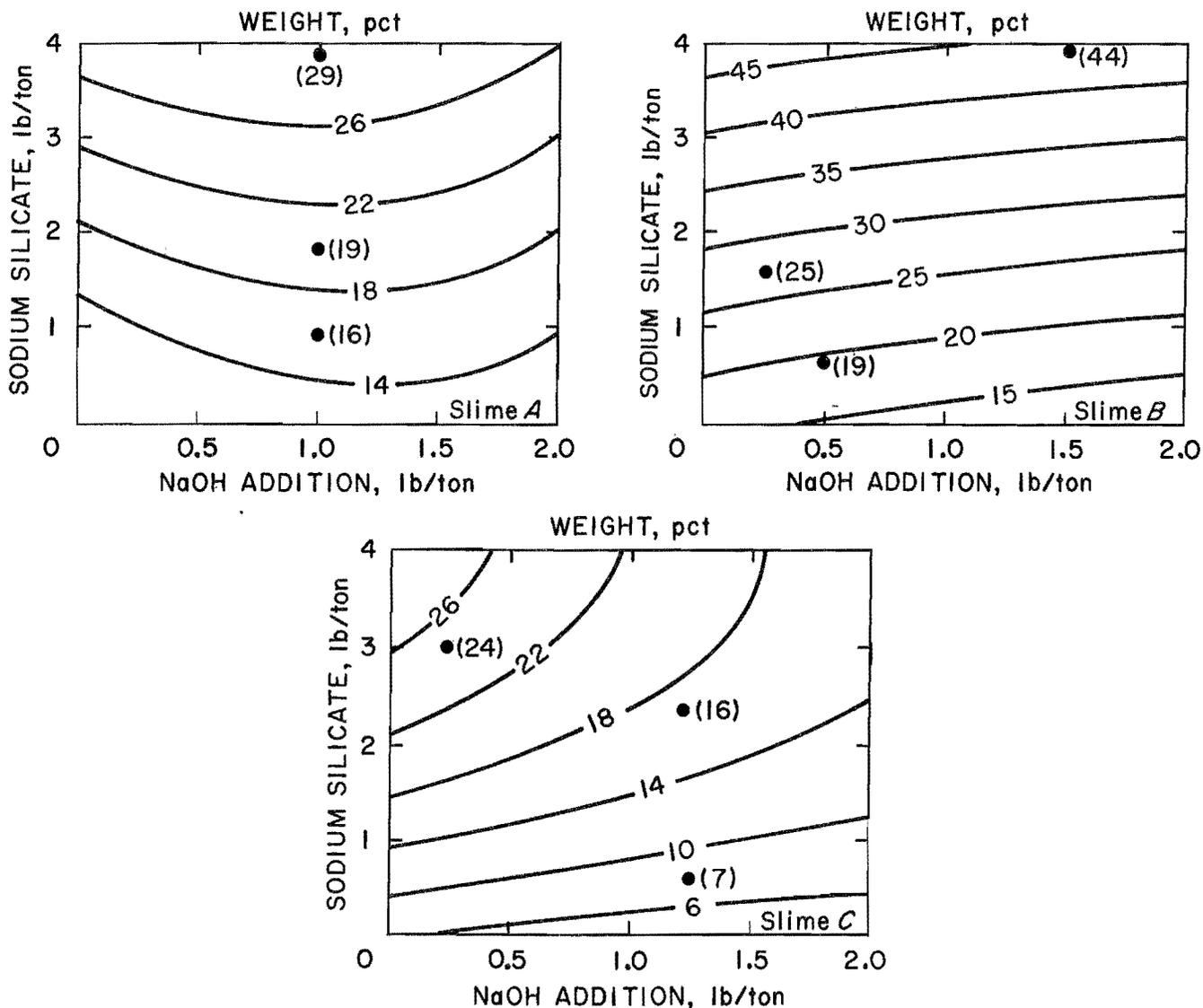


FIGURE 1. - Response-surface diagrams, silicate-hydroxide system, for percent weight of slimes A, B, and C.

to be analyzed. Whenever selective flocculation data are presented or tests are compared, the slime products will be given primary emphasis. This choice was made because the slime slurry is the primary indicator of the state of dispersion and flocculation caused by the reagents being evaluated.

The results of the experiment determined the parameters of the response-surface contours. The figures include two or more test data (parenthesized), which are marked by the solid circles on the figures.

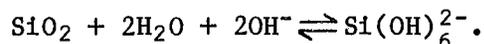
INFLUENCE OF SODIUM SILICATE AND SODIUM HYDROXIDE DISPERSION SYSTEM ON SELECTIVE FLOCCULATION

Sodium silicate addition between 0 and 4 lb/ton and sodium hydroxide addition from 0 to 2 lb/ton of ore were evaluated.⁷ The starch addition was maintained constant at 0.25 lb/ton for samples A and B. Sample C was selectively flocculated with 0.15 lb/ton of starch; the amount of starch was decreased because all of the mineral suspension including the silica and carbonate gangue flocculated. Figure 1 shows the response-surface diagrams of weight percent of slime obtained from the three types of iron ore: goethite-hematite (A), hematite (B), and magnetite-hematite (C). All the samples evaluated showed an increase in the weight of slime with increased silicate addition. The more highly dispersed slurries were the result of higher electronegativity of the siliceous gangue and the iron oxide minerals, which increased the coulombic dispersion forces among the mineral particles. At constant silicate addition, samples B and C showed a decrease in slime weight with increased hydroxide addition. In

slurry A, when the hydroxide addition was 1 lb, the slime weight increased; it decreased at additions greater than 1 lb.

The iron assay of the slime from slurry A (fig. 2) decreased with increased silicate addition up to 2 lb/ton and then increased with silicate addition above this level. Slurry B (fig. 2) gave an increase in the iron assay with more silicate addition. However, the iron lost to the slime product can be regained through the increased addition of starch flocculants. As shown in figure 2, slime iron content of the magnetic-hematite sample C was increased by increasing the silicate. Ore C gave the lowest slime iron content of the three samples. This may be because magnetite is chemically inert to silicate and hydroxide ions and can form a magnetic floccule.

The pH profile reported in figure 3 applied to all three slurries. The soluble silicate isograms in figure 3 were similar to those for the other two except that approximately twice the amount of silicate ions was present. In figure 3 at constant silicate addition, silicate ion content increased with increased sodium hydroxide addition because the fine siliceous gangue particles react with the alkaline water according to the following simplified reaction (10):



INTERACTION OF CALCIUM IONS AND SODIUM SILICATE

The relationship between calcium ions and sodium silicate was evaluated in the ranges of 0 to 28 mg Ca^{2+} ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) per liter and 0 to 4 lb sodium silicate per ton of ore. The sodium hydroxide addition was constant at 1.0 lb/ton. The

⁷The ton referred to in this paper is the short ton or 2,000 lb.

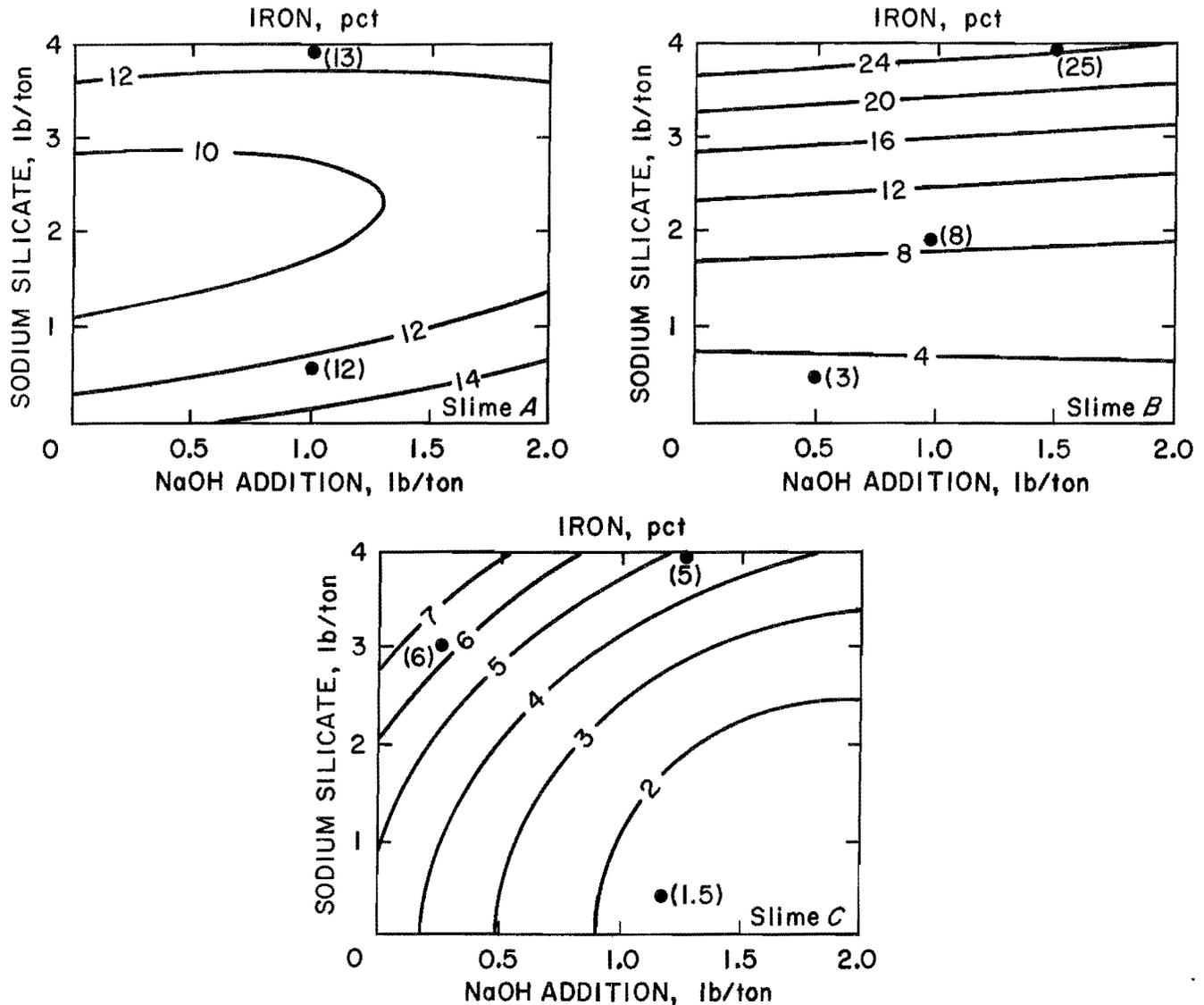


FIGURE 2. - Response-surface diagrams, silicate-hydroxide system, for percent iron in slimes A, B, and C.

starch addition was maintained constant at 0.25 lb/ton for samples A and B. Sample C was selectively flocculated with 0.15 lb/ton of starch. The pH of samples containing goethite-hematite (A), hematite (B), and magnetite-hematite (C) ranged from 10.1 to 10.4, 10.7 to 10.9, and 11.1 to 11.3, respectively. The hydroxide addition that maintained the pH level depended on the surface area and on the soluble salts contained in the ore. Sample A had the greatest surface area of the three samples, and its slurries had the highest sulfate ion concentrations,

which were related to the contained pyrite (tables 3 and 4). Approximate chemical analyses for the carbonate-bicarbonate content in the slurries were determined by potentiometric acid titration to pH 4.5. Slurries A, B and C contained approximately 170, 150, and 2,400 mg CaCO_3 per 100 g ore, respectively. The high alkalinity value of slurry C was caused by the presence of the carbonate gangue. The data in table 4 are the baseline results for the research reported in this paper.

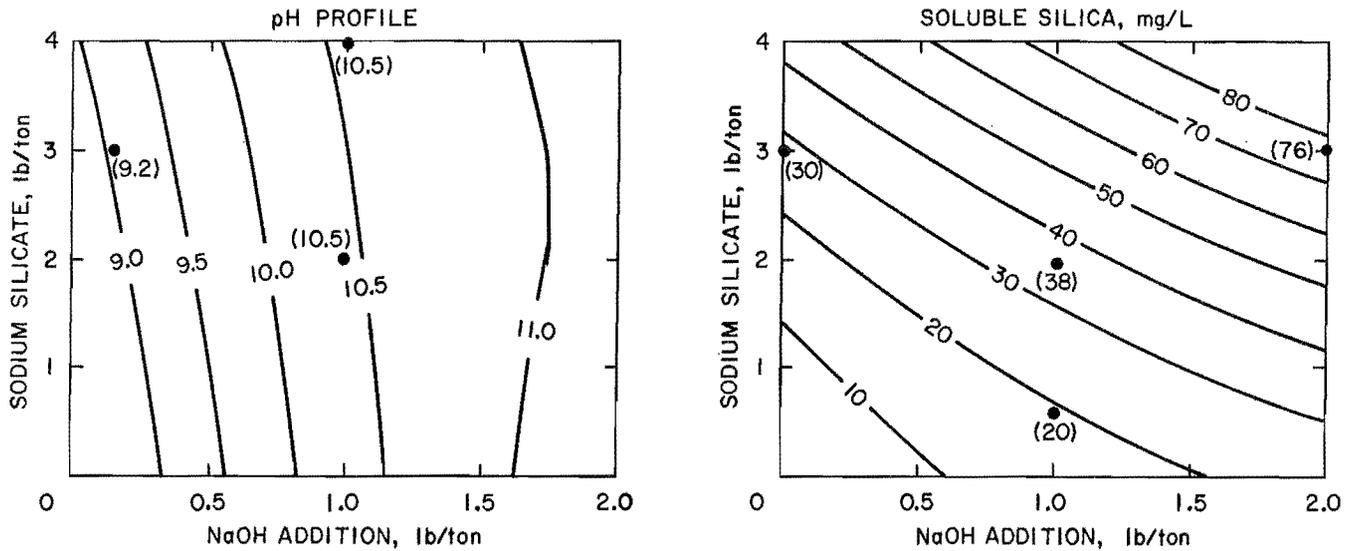


FIGURE 3. - Response-surface diagrams, silicate-hydroxide system, for pH profile and soluble silica in slurry A.

Adding more silicate to sample A slurry increased the slime weight (fig. 4). With silicate constant at less than 2 lb/ton, an increase in the calcium decreased the slime weight and increased the iron assay (fig. 4). The calcium ions were coagulating the siliceous gangue. With silicate above 2 lb/ton, increasing the calcium addition up to 14 mg/L increased both the slime weight and the iron assay. Analysis of the aqueous phase of sample A slurries for soluble silica indicated a small interaction between calcium and silicate ions. Increasing the silicate decreased the size of the flocule, increased the settling rate of the flocculated particles, and increased the dispersion of both siliceous gangue and iron oxide particles to a level where selective flocculation of the iron minerals was difficult to obtain even with more starch flocculant.

Increasing the silicate addition to slurries of sample B increased the slime weight fraction. With constant silicate, an increase in calcium addition decreased the slime weight. The iron assays for slime B (fig. 4) show that increasing the calcium ion addition decreased the slime

iron content to a minimum, an area bounded by isogram 4. At a calcium addition of more than 16 mg/L, the slime iron content increased. At a constant addition of 15 mg Ca^{2+}/L , increasing the silicate to 1.5 lb decreased the iron lost in the slime. At higher additions of silicate more of the hematite particles were lost in the slime.

As shown in figure 4, the magnetite-hematite slime weight of sample C was increased by increasing the silicate addition. With constant silicate, increasing the calcium ion up to 14 mg/L increased the slime weight. The MgO and CaO analyses of the slimes indicated that in the area bounded by isogram 18 the MgO-CaO rejected in the slime increased. Compared to samples A and B, slurries of sample C required more sodium silicate and fewer calcium ions to maintain an acceptable slime weight rejection and a minimum amount of iron lost in the slime. The iron silicate and magnetite minerals were unaffected by the reagent additions. The magnetite particles were observed to form tightly bound magnetic flocules, which entrapped the hematite and siliceous materials.

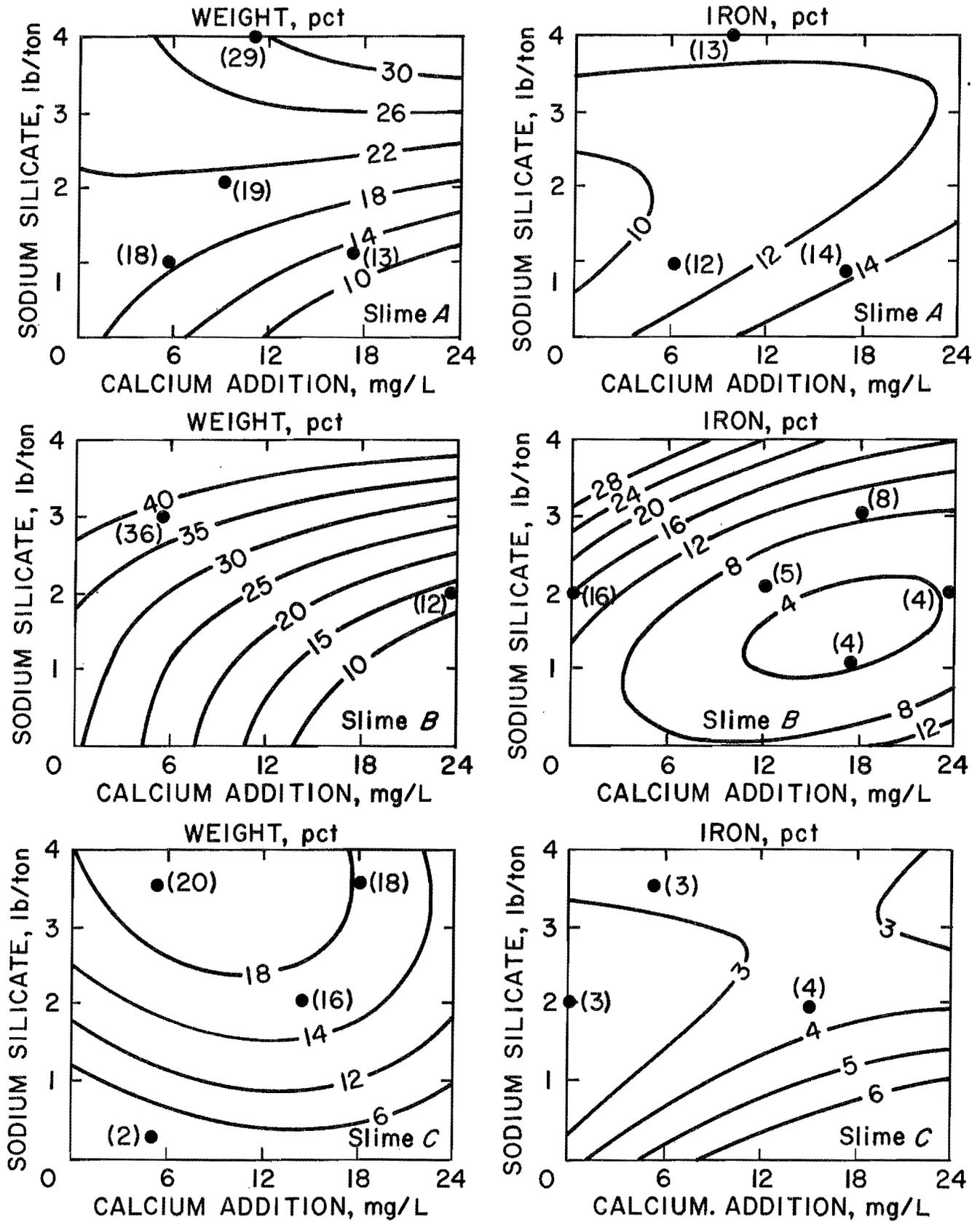


FIGURE 4. - Response-surface diagrams, silicate-calcium system, for percent weight and percent iron in slimes A, B, and C.

INTERACTION OF CALCIUM AND AMINE COLLECTOR

The effects of flocculation by the calcium and amine additions were evaluated for samples A and B in the range of 0 to 20 mg Ca^{2+} /L and 0 to 20 ppm Arosurf MG-98A. The dispersion system employed 1.0 lb NaOH and 2.0 lb sodium silicate per ton of ore. The pH of slurries A and B ranged from 10.1 to 10.5 and 10.8 to 11.0, respectively. The slime weight rejection for the goethite-hematite slurry A and for the hematite slurry B was independent of the amine addition and strongly dependent on the calcium ion addition. Chemical analyses of solutions containing amine-calcium and amine-silicate mixtures, which were adjusted to pH 11.5, showed that no

interaction had occurred between these components.

When more calcium was added, the slime weights for both slurries A and B decreased, indicating that adsorbed Ca^{2+} caused coagulation of the iron oxides and siliceous gangue. Chemical analyses of the filtrates from both samples indicated that some calcium ions reacted with the silicate ions in the pulp and suppressed the equilibrium condition for the dissolution of siliceous gangue. Slurry B pulp showed more silicate ions because of its more alkaline environment. The residual amine in both pulps was less than 1 mg/L. The amine adsorptive capacities of samples A and B at pH 11.5 were 47 and 35 mg per 100 g of sample, respectively.

INFLUENCE OF SODIUM TRIPOLYPHOSPHATE (STPP) AND SODIUM HYDROXIDE DISPERSION SYSTEM ON SELECTIVE FLOCCULATION

The sodium hydroxide and sodium tripolyphosphate dispersion system was evaluated for ranges from 0 to 2.0 lb NaOH and from 0 to 1.0 lb STPP per ton of ore. For the goethite-hematite slime (A) in figure 5, increasing the STPP increased the slime weight. At constant STPP addition, increasing the hydroxide decreased the slime weight. The iron assays in figure 5 showed a different trend from that obtained from the slime weight analysis; in general, the iron content of the slime products decreased with increasing reagents.

In the system evaluated, the silicate ions produced from the caustic dissolution of the siliceous gangue increase with increased NaOH addition, and also the pH increases from 9.0 to 11.4 (fig. 5). When the NaOH additions were above 1.5 lb/ton, the pH ranged from 11.0 to 11.4 and the soluble silica level ranged from 25 to 30 mg/L.

In many types of water treatment, phosphate and tripolyphosphate compounds are used to prevent calcium carbonate deposition. The phosphate anions are also

removed from the water by alumina, kaolinites, montmorillonite, and freshly precipitated ferric and aluminum hydroxides (18). Analyzing the pulp aqueous phase for soluble phosphorus showed a trend of increasing STPP adsorption with increased slime weight. The phrase "STPP adsorption" is used because the STPP ions could be adsorbed as a complex on the mineral surface or removed from solution as a precipitate. Increasing the sodium ion concentration increased the dissociation of the STPP-metal complex and decreased the STPP adsorption. Increased slime weight and lower iron analyses occurred at high STPP adsorptions and were indications of selective separation of the iron oxide and gangue minerals.

EFFECT OF CALCIUM ION AND STPP

The relationship between Ca^{2+} ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and STPP was evaluated for addition limits from 0 to 1.0 lb STPP/ton and from 0 to 28 mg calcium/L. The NaOH addition was kept at 1.0 lb/ton of ore. The pH of the tests ranged from 9.8 to 10.6 for goethite-hematite slurries.

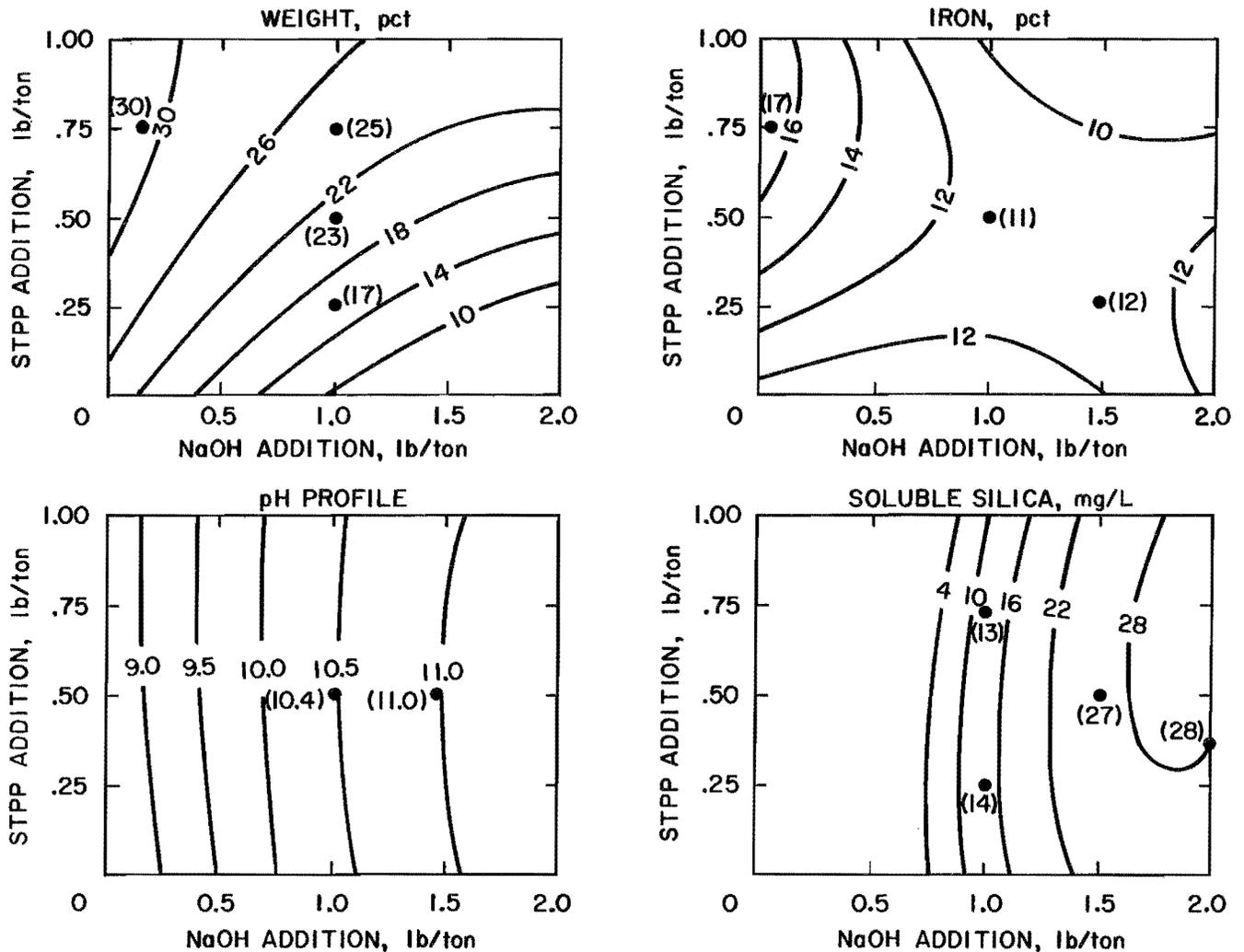


FIGURE 5. - Response-surface diagrams, STPP-hydroxide system, for percent weight, percent iron, pH profile, and soluble silica in slurry A.

The percent slime weight rejected increased with increasing STPP (fig. 6). At 10 mg Ca^{2+}/L and STPP additions up to 0.5 lb (fig. 6) the iron content of the slime products and the silicate ion content in the aqueous phase of the pulp decreased. At an STPP addition of more than 0.5 lb/ton of feed, the iron lost to the slime fraction and the silicate ion level in the pulp increased. Removal of the silicate ions by the calcium ions

probably decreased the pH of the pulp and formed a calcium silicate precipitate, which may have coated the mineral surface and inhibited the dissolution of the silica gangue. A reasonable weight rejection and iron loss in the slime product depends on the balanced addition of STPP and calcium ions. Too much of either resulted in more iron being lost to the slime fraction or a decreased slime weight.

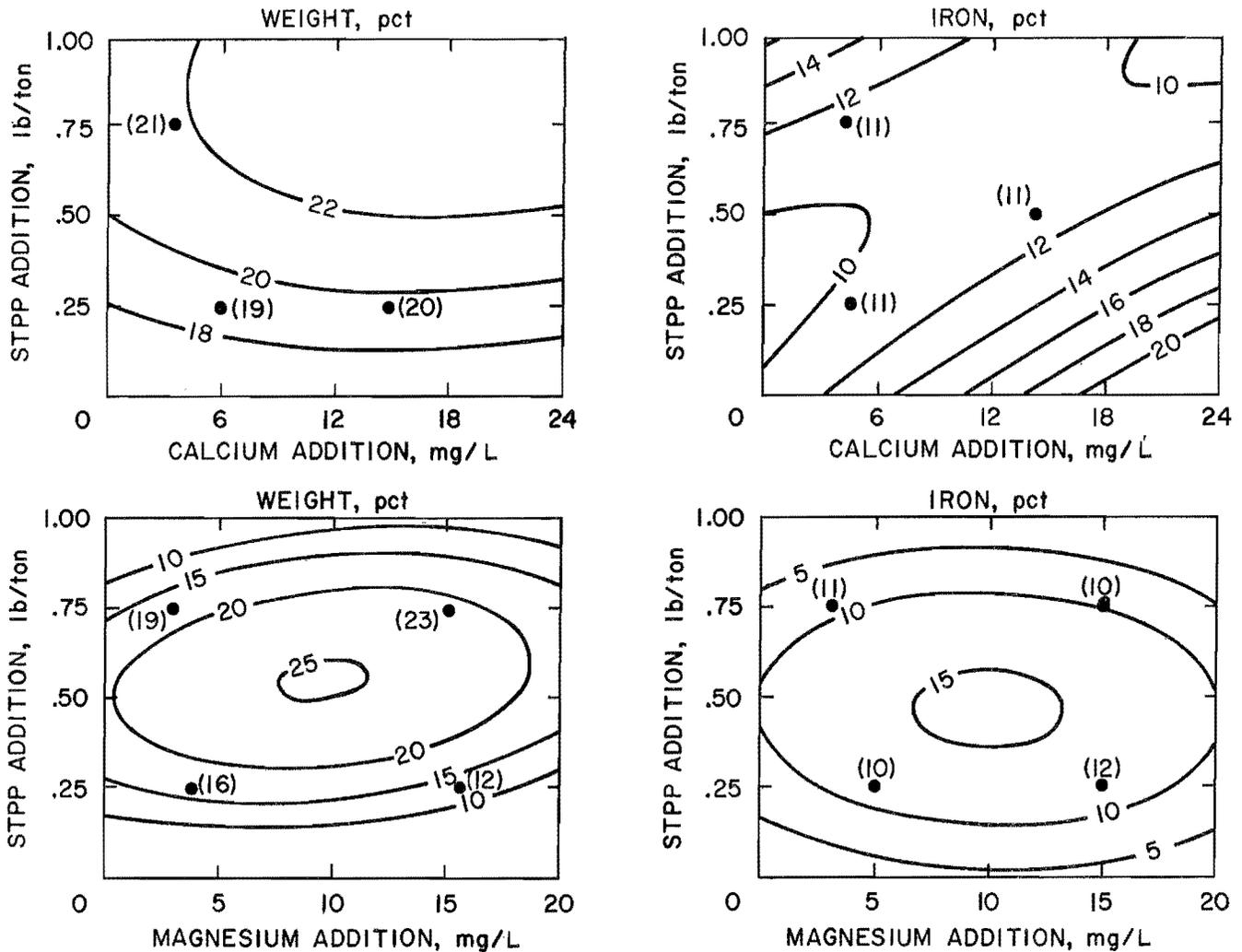


FIGURE 6. - Response-surface diagrams, STPP- Ca^{2+} and STPP- Mg^{2+} system, for percent weight and percent iron in slime A.

EFFECT OF MAGNESIUM ION AND STPP

An experiment was made with Mg^{2+} ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the range of 0 to 24 mg/L and STPP addition from 0.25 to 1.0 lb/ton. Sodium hydroxide was maintained at 1.0 lb/ton ore A. When magnesium ions reacted with the hydroxyl ions in solution, the pulp pH decreased from 10.8 to 10.0. Since STPP is a sequestering agent for magnesium, the magnesium ion would also chelate with STPP to form a precipitate, $\text{Na}_3\text{MgP}_3\text{O}_{10} \cdot 13\text{H}_2\text{O}$ (20).

At 0.5 lb STPP and 10 mg Mg^{2+} /L, the slime weight and iron content were at maximums 25 and 15 pct, respectively

(fig. 6) with a minimum silicate ion level of less than 2 mg/L. The aqueous phase of the pulp showed no magnesium ions except at low STPP and high Mg^{2+} addition. The decreased silicate ion concentration in the pulp is probably caused by the removal of silicate by the magnesium.

The diagrams in figure 6 suggest that at constant STPP and Mg^{2+} addition above 10 mg/L, the mineral particles were non-selectively coagulated. At a 10 mg Mg^{2+} /L, increasing the STPP addition above 0.5 lb put a coating of Mg-STPP complex on the mineral surface. The coating decreased the electronegativity

of the mineral particle and subsequently decreased the slime weight rejections.

EFFECT OF FERROUS ION AND STPP

An experiment was made with Fe^{2+} ($FeSO_4 \cdot 7H_2O$) in the range from 0 to 30 mg/L and STPP addition from 0 to 1.0 lb/ton ore. The sodium hydroxide addition was maintained at 1.0 lb/ton sample A. Because of the high pH of slurry A, the ferrous ions reacted with the hydroxyl ions in solution and the pH of pulp decreased from 10.5 to 9.8 as the ferrous salt went up. STPP is a sequestering agent for the ferrous ion and should form a precipitate, $Na_3FeP_3O_{10} \cdot 11.5H_2O$ (20).

Since ferrous ions are easily air-oxidized to their ferric form when dissolved in an alkaline medium, hydrous amorphous iron oxide precipitate was probably the ultimate product of the ferrous ion addition. A precipitate similar to this type of hydrous amorphous iron oxide was observed.

The weight of slime product (fig. 7) with STPP below 0.5 lb/ton decreased with increasing ferrous ion; whereas with STPP above 0.5 lb/ton, increasing the ferrous addition increased the slime product. Iron analyses of the slime (fig. 7) showed a minimum of 10 pct at 0.5-lb/ton STPP addition. Analysis of

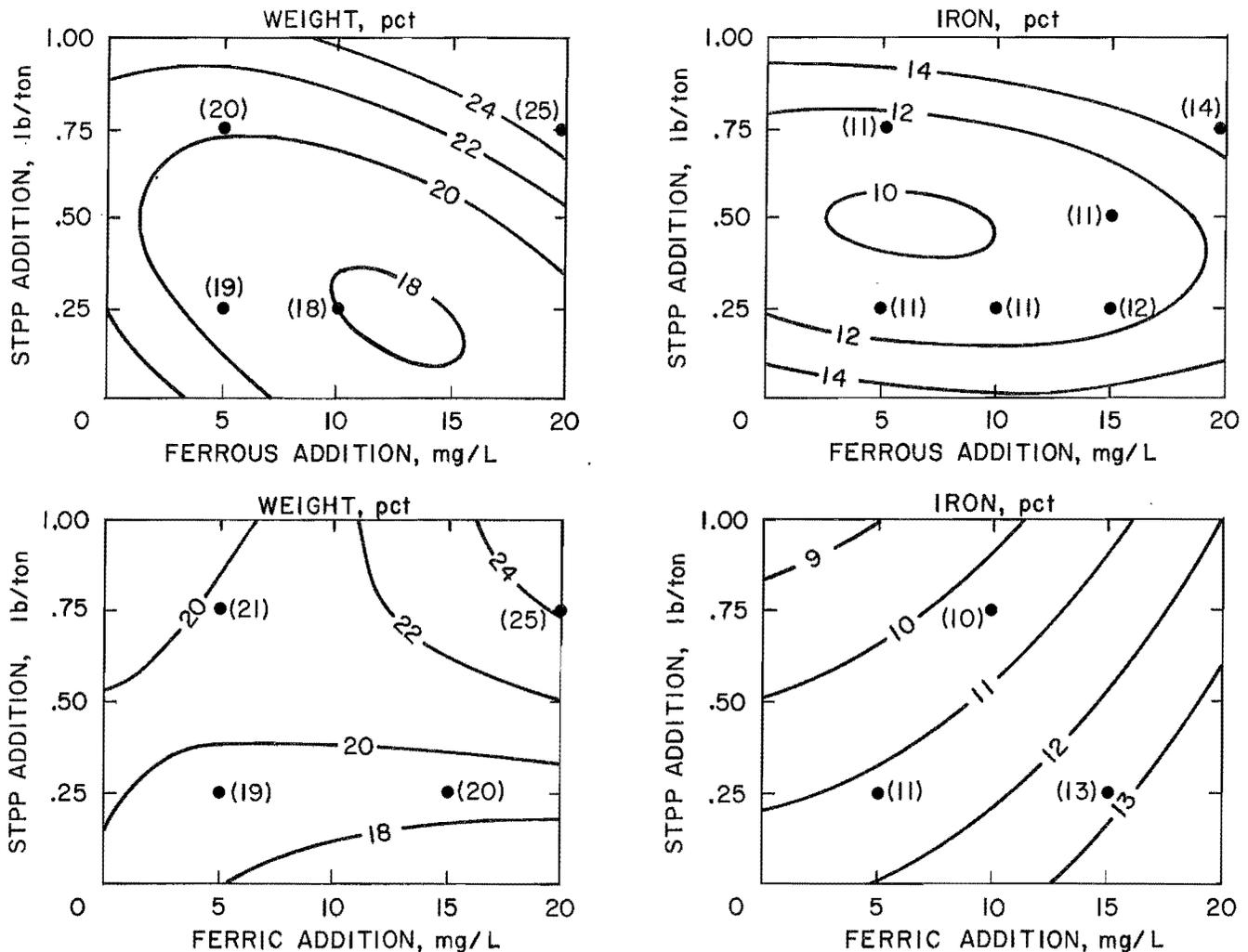


FIGURE 7. - Response-surface diagrams, STPP- Fe^{2+} and STPP- Fe^{3+} system, for percent weight and percent iron in slime A.

the aqueous phase of the pulp showed that the silicate ion level was less than 10 mg/L at low and high STPP addition.

EFFECT OF FERRIC ION AND STPP

An experiment was made with Fe^{3+} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in the range from 0 to 26 mg/L and STPP addition from 0 to 1.0 lb/ton feed. Sodium hydroxide addition was again at 1.0 lb/ton of sample A. Because of the high pH, the ferric ions reacted with dissolved hydroxyl ions to decrease the pH of the pulp from 10.6 to 10.0. According to Van Wazer (15, 20):

When ferric sulfate is added to a solution of sodium tripolyphosphate, the only crystalline phosphate obtained is ferric pyrophosphate. Presumably there is formation of considerable amounts of hydrated ferric oxide which is known to catalyze strongly the degradation of the condensed phosphates.

It is assumed that the degradation of phosphates also applies to the ferric chloride salt.

The effects on the slime weight (fig. 7) are that at low STPP levels increasing the ferric ion addition had little or no effect and most of the STPP was degraded into pyrophosphate and orthophosphates. At high STPP addition, increasing the ferric ion addition increased the slime weight. Increasing the STPP addition also increased the slime weight. The corresponding analyses of the slime show that the iron content decreased with increasing STPP but increased with increasing ferric addition. Analysis of the aqueous phase showed that the silicate ion concentration decreased with increasing STPP and ferric ion additions. A brown coating was observed on the wall of the mixing beaker, on the spatula, and on the mineral particles throughout these tests, and this coating increased in the direction of increased ferric addition.

The ferric salt formed hydrous iron oxide which was adsorbed or inhibited the formation of silicate ions by the caustic dissolution of the siliceous gangue.

CALCIUM ION AND AMINE COLLECTOR

The effects of calcium ion and the amine collector were evaluated in the range from 0 to 28 mg Ca^{2+} /L and 0 to 20 mg amine/L. The sodium hydroxide and STPP were maintained at 1.0 lb and 0.3 lb/ton of sample A, respectively. The pH of the pulp varied slightly from 10.8 to 10.9. Results indicated that the amount of slime rejected was independent of amine addition and strongly dependent on the calcium ion addition. The corresponding iron grade of slime product was between 5.5 and 6.5 over the range evaluated. A corresponding analysis on the filtrate showed that the percent STPP adsorbed or precipitated was increased by increasing the calcium and indicates that a precipitate, probably $\text{NaCa}_2\text{P}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$ (20), was formed.

The amine content in the filtrate was less than the amount of amine added. It remained unchanged with increased calcium addition but increased with increasing amine addition. The results were similar to those of tests conducted with sodium silicate dispersants.

SODIUM SILICATE-TRIPOLYPHOSPHATE DISPERSION SYSTEM

Sodium silicate ranging from 0 to 3.0 lb, STPP ranging from 0 to 1.0 lb, and NaOH at a constant level of 1.0 lb per ton of ore A were used. Figure 8 indicates that the slime weight rejection increased with increasing addition of both sodium silicate and STPP reagents. The minimum iron content in the slime was obtained in the range from 2 to 0.8 lb Na_2SiO_3 /ton and with STPP increasing from 0 to 1 lb/ton. Employing STPP with sodium silicate decreases the iron loss to the slime product.

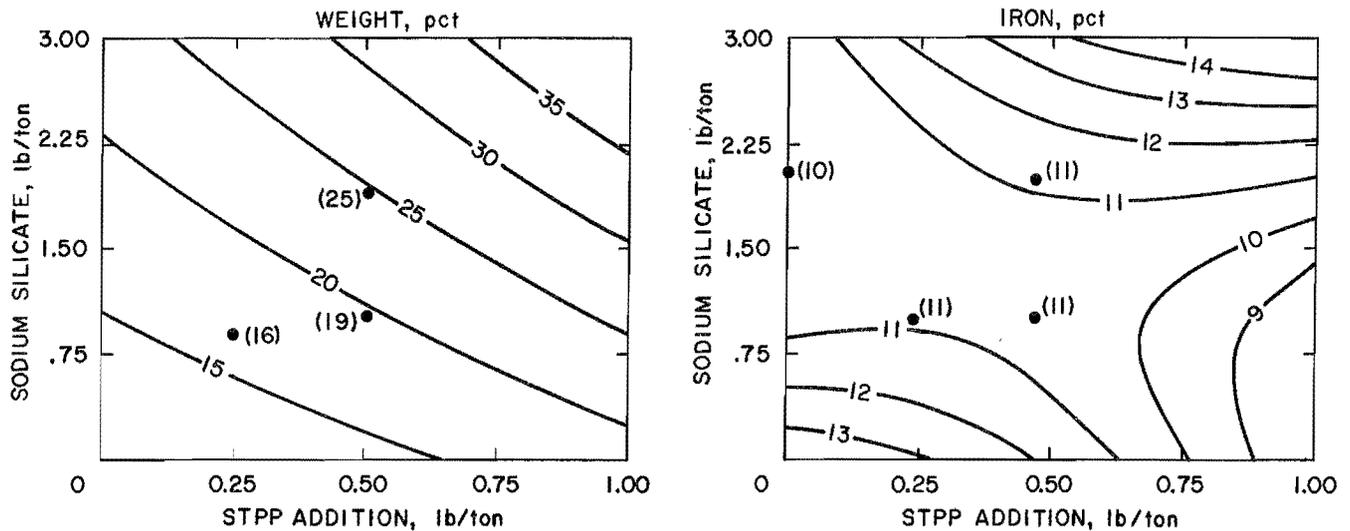


FIGURE 8. - Response-surface diagrams, silicate-STPP system, for percent weight and percent iron in slime A.

SUMMARY

In the hydroxide-silicate dispersion suite, increasing the silicate increased the slime weight appreciably. In control water containing 8 mg Ca^{2+}/L , increasing NaOH addition at all levels of silicate addition decreased the slime weights. Silicate addition up to 2.0 lb/ton decreased the iron lost to slime A; addition of more than 2.0 lb/ton increased the iron loss. Silicate addition increased the iron lost in samples B and C in a manner parallel to changes in the slime weight. NaOH addition had little or no effect. Increasing the silicate with calcium constant caused an appreciable increase in the slime weight, but increasing the calcium ion content with silicate constant decreased the slime weight. The presence of 5 to 12 mg Ca^{2+}/L in the pulp decreased the iron lost to the slimes.

In the hydroxide-tripolyphosphate dispersion suite, the slime weight increased appreciably up to 1.0 lb/ton STPP addition. The addition of NaOH decreased the slime weight of samples A and B but had little or no effect on sample C because of the presence of calcium carbonate in the ore. The addition of 5 to 15 mg Ca^{2+}/L to slurry A decreased the iron lost to the slime product.

The addition of magnesium ions may have reversed the charge of the silica or iron oxide particles or have bound the hydroxy-magnesium complex to these particles. The result is indicated by the increased iron content in the slime product and the decreased silicate ion level in pulp A. At constant STPP addition of less than 0.5 lb/ton, the addition of ferrous ions decreased the slime weight. The amorphous colloidal iron oxide formed acted as a flocculant, coating the mineral particles and/or catalyzing the degradation of the STPP. High STPP addition restored the selective flocculation process to normal.

Adding ferric ion at low STPP levels coagulated the mineral dispersion and decreased the slime weight. Increasing the ferric ion at a high STPP level increased the slime weight. Some of the ferric ions were converted to colloidal hydrous ferric oxide. The nondegraded STPP probably maintained the dispersion characteristics of the pulp. The amorphous iron coating increased when the addition of STPP and ferric ions was increased.

In the hydroxide-silicate-tripolyphosphate dispersion suite both silicate and

STPP contributed to the slime weight rejection. The amount of silicate addition had the most effect on the slime weight. More slime was obtained at minimum STPP adsorption than at maximum adsorption.

The advantage of using STPP was that less iron was lost to the slime product. The disadvantage is that STPP cost more than sodium silicate per unit weight.

CONCLUSIONS

Application of the selective flocculation method to finely ground ores permits removal of slimes at minimum iron loss. Selective flocculation and desliming levels off the differences in flotation characteristics between ores. Analysis of size-distribution data supports the premise of selective flocculation of iron oxides and also indicates that substantial amounts of near-colloidal-sized iron oxides in some ores contribute to incomplete flocculation and a higher iron content in the slime fraction.

The quality of the feed water has an important impact on the quality of the selective flocculation-desliming process. The presence of excess ionic species (>15 mg/L) such as calcium, magnesium, and ferrous, ferric, and precipitated iron salts will cause undesirable metallurgical results. The presence of magnesium ions may cause reversal of charge that leads to increased iron loss. An index

to acceptable selective flocculation-desliming response based on the Ca^{2+} content of the feed water can be established. A level of 1 to 15 mg Ca^{2+} /L should be maintained for acceptable response, but 5 to 10 mg/L is the best operating range. The Ca^{2+} index establishes a common factor that permits the use of different water sources and facilitates the use of reclaimed water. Residual Ca^{2+} content is also useful in translating bench results to pilot plant operation.

All three iron oxide samples tested--the goethite-hematite, hematite, and magnetite-hematite--were amenable to separation by selective flocculation-desliming. The magnetite-hematite mineral sample was least affected by changes in the process, because the magnetite formed magnetic floccules which entrapped the hematite and siliceous gangue.

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APPENDIX.--RESPONSE-SURFACE COEFFICIENTS AND STATISTICAL DATA

Figure		Coefficients						RR, ¹ pct	95-pct confidence level ²
No.	Content	B0	B1	B2	B3	B4	B5		
1..	Wt pct, A.....	7.600	7.768	4.666	-3.111	0.093	-0.583	95.5	2.7
1..	Wt pct, B.....	16.544	-3.518	7.257	.447	.147	.103	97.0	1.7
1..	Wt pct, C.....	6.381	-2.727	9.164	.632	-.852	-1.393	86.6	4.5
2..	Fe pct, A.....	13.031	1.216	-3.847	.322	.981	-.500	85.1	1.4
2..	Fe pct, B.....	2.545	.547	.997	-.028	1.322	-.582	98.3	2.1
2..	Fe pct, C.....	4.637	-3.925	.066	1.221	.289	-.322	96.4	.7
3..	pH profile, A..	8.160	2.765	.174	-.625	.006	-.129	97.7	.3
3..	Sol. silica, A.	2.805	12.665	2.173	-1.070	1.986	4.718	97.9	7.1
4..	Wt pct, A.....	19.053	-.682	1.732	-.008	-.188	.344	93.7	2.7
4..	Fe pct, A.....	11.107	.265	-2.149	.003	.696	-.095	75.5	1.7
4..	Wt pct, B.....	32.193	-1.670	-1.322	.004	1.550	.308	98.4	2.5
4..	Fe pct, B.....	11.987	-.694	-3.948	.034	2.842	-.292	76.0	1.6
4..	Wt pct, C.....	-4.911	1.082	10.510	-.038	-1.209	-.102	97.5	2.4
4..	Fe pct, C.....	3.684	.309	-1.994	-.003	.524	-.073	84.0	1.9
5..	Wt pct, A.....	24.168	-16.600	19.158	2.193	-11.281	8.768	90.7	3.8
5..	Fe pct, A.....	9.254	-2.849	17.653	2.223	-9.407	-7.219	71.4	2.2
5..	pH profile, A..	8.445	2.418	.478	-.502	-.251	-.151	97.3	.13
5..	Sol. silica, A.	-38.063	71.184	-2.515	-20.172	-10.869	9.297	94.0	3.5
6..	Wt pct, A + Ca.	14.696	.200	14.778	-.007	-8.657	.090	84.1	2.1
6..	Fe pct, A + Ca.	10.534	.414	-8.249	.009	14.377	-.928	67.0	2.6
6..	Wt pct, A + Mg.	-3.290	.686	91.497	-.066	-90.985	1.022	83.0	2.9
6..	Fe pct, A + Mg.	-2.430	1.185	52.224	-.054	-53.973	-.224	66.4	2.3
7..	Wt pct, A + Fe ²	24.506	-.806	-14.093	.026	12.675	.674	90.8	1.8
7..	Fe pct, A + Fe ³	15.713	-.300	-21.339	.014	21.192	.268	90.8	1.6
7..	Wt pct, A + Fe ³	19.473	-.302	4.175	.004	-5.946	.627	90.8	1.6
7..	Fe pct, A + Fe ³	12.040	-.059	-1.425	.009	-1.807	.029	96.2	1.0
8..	Wt pct, A.....	11.278	3.422	3.389	3.754	.159	3.874	97.0	1.5
8..	Fe pct, A.....	13.844	-2.083	-4.118	-3.872	.975	3.689	96.3	.4

¹Sum of the squares due to regression divided by sum of the squares about the mean.

²Based on 7 degrees of freedom.