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A SCREENING STUDY ON PHOSPHATE DEPRESSANTS FOR BENEFICIATING FLORIDA PHOSPHATE MINERALS

prepared by

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Phosphate Research

March 2002

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A SCREENING STUDY ON PHOSPHATE DEPRESSANTS FOR BENEFICIATING FLORIDA PHOSPHATE MINERALS

FINAL REPORT

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with

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DISCLAIMER

PERSPECTIVE

DEVELOPMENT OF ALTERNATIVE TO THE CRAGO PROCESS

Although the Crago "double float" process is a very mature technique for phosphate beneficiation, potential benefits of a single-collector flotation process have encouraged some investigators to search for a substitute for the Crago process. The advantages of a single-collector system over the double float process include reduced capital and energy costs, a simplified flowsheet, and the minimized discharge of chemicals into the environment. Several research programs have generated promising results, including the Anionic Rougher-Cleaner Process developed by Zellars-Williams, the Double Depression Process proposed by the U.S. Bureau of Mines, and the Reagent Starvation Process invented by the University of Florida. Unfortunately, these processes achieved single-collector flotation by sacrificing either recovery or concentrate grade. Replacement of the Crago process with a single-collector process could only be realized by using either a very selective collector, or a highly efficient depressant. Although anionic flotation of phosphate with silica depression seems to be the logical approach for developing a single-collector process, inverse flotation of silica with phosphate depression also has potential. Most of the previous studies on phosphate depressants were focused on separating carbonate from phosphate. The ideal depression conditions for carbonates separation may not be those suitable for silica removal.

REMOVAL OF DOLOMITE FROM PHOSPHATE

Of all the dolomite separation processes, reverse flotation of dolomite while simultaneously depressing phosphate offers the most promises. The difficulty in separating phosphate from carbonates is attributed to their similarity in surface properties. Therefore, surface modification is essential for separating carbonates from phosphates efficiently. Besides the additions of pH modifiers, collector extenders, and frothers, the addition of a depressant is the most frequently used method of surface modification. Based on our preliminary literature review, about a dozen reagents have the potential of depressing phosphate. Most phosphate depressants are ore specific and pH dependent. Extensive experimentation is essential for determining the best depressant for a particular ore, and mineralogical composition may also play a critical role.

RESEARCH NEEDS

The information base on phosphate depressants needs to be expanded in the following areas: (a) phosphate depression mechanisms, (b) relationships between mineralogy and depression efficiency, (c) optimal parameters for each of the depressants, (d) ranking of depressants for Florida ores, (c) the potential of depressant mixtures. Recognizing these research needs, the FIPR Board of Directors approved funding for this in-house research program.

Patrick Zhang
Research Director, Mining & Beneficiation

ABSTRACT

Numerous phosphate depressants were evaluated for both the phosphate/silica and phosphate/dolomite systems. Starch was found to be most suitable form floating fine silica from phosphate, while sodium tripolyphosphate (STPP) proved to be more efficient for separating coarse silica from coarse phosphate. It was also concluded that STPP was the most effective depressant for separating dolomite from phosphate. Based on those findings, an all-cationic flotation process was developed for Florida siliceous phosphates. A reverse Crago process was also developed, which involves floating fine silica with an amine and a polymer, followed by fatty acid flotation. More than a dozen of polymers were tested as slime “blinder” in floating silica from phosphate.

ACKNOWLEDGMENTS

The support and technical input of the FIPR Beneficiation Technical Advisory Committee are high appreciated. The following companies have been very cooperative in sample collection: Cargill Fertilizer, CF Industries, IMC Phosphates and PCS Phosphate. IMC Phosphates and PCS Phosphate are especially recognized for hosting and supporting in-plant testing of the two new processes developed under this project, with Chaucer Hwang and Joe Shoniker deserving extra credits. The FIPR analytical lab staff, Aaron Medley, Richard Puchstein and Jon Harris worked hard on sample collection, preparation and analysis. Ed Finch and Francisco Sotillo of PerUsa , and Boris Slutskiy of Colorado Minerals Research Institute were instrumental in conducting the pilot testing program.

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EXECUTIVE SUMMARY

At their July 1994 meeting, the FIPR Board of Directors approved funding for the three-year project "A Screening Study on Phosphate Depressants for Beneficiating Florida Phosphate Minerals." The primary goal of the project was to identify the best phosphate depressants for the Florida ores with the dual purposes of developing more efficient processing flowsheets for the currently mined siliceous deposits as well as for removing dolomite from the future reserves.

This project was one of the most fruitful projects FIPR ever funded in flotation process development, with two new flotation processes developed, the All-Cationic and the Reverse Crago.

During the first year, different depressants were compared using a typical siliceous phosphate ore. It was found that starch is ideal for floating fine (-35 mesh) silica from phosphate, while sodium tripolyphosphate may be the best for coarser (+35 mesh) feeds. Based on the results, an all-cationic flotation process was developed and tested on two feeds. Laboratory flotation results indicated the new process is technically feasible for siliceous phosphates, and could be economically superior over the currently used Crago double-float process. The All-Cationic flotation process involves using a relatively inexpensive amine condensate, with or without a suitable phosphate depressant, to float fine quartz from "unsized" feed, followed by (1) sizing the cell underflow product at 14 and 35 mesh and (2) subjecting the two size fractions (14x35 and 35x150) to second-stage cationic flotation using higher-quality cationic reagent systems including phosphate depressants to reject the remaining quartz sand and produce final concentrates analyzing at least 30-31% P_2O_5. Table 1. Shows the performance of the All-Cationic process on five different flotation feeds.

Table 1. Performance of the All-Cationic Flotation Process on Five Different Feeds With Tap Water.

Feed ID	+35 M Wt.%	-150 M Wt.%	Feed %P_2O_5	Conc. %P_2O_5	Conc. % Insol	% BPL Recov.	$/Ton Conc.
A-F	14.8	1.5	9.62	31.03	4.77	88.96	2.391
A-C	26.4	0.5	9.44	31.09	3.35	91.91	2.836
B	13.9	3.5	5.43	31.50	5.76	81.37	3.439
C	8.7	7.4	8.43	32.61	5.14	91.30	2.541
Spiral	100	0	19.82	30.61 31.58	10.88 7.42	96.50 94.50	0.782 1.515

Potential advantages of this process include: (1) coarse phosphate loss is minimal since the phosphate is never required to float, (2) no vertical conditioners are required for rougher feed reagentizing--only the second-stage coarse feed fraction requires high % solids conditioning using preferably a rotary drum unit, (3) no acid scrub and wash circuit is required to de-oil the rougher concentrate, (4) large quantities of fuel oil are not required in the initial prefloat stage, (5) smaller feed sizing sections are needed since only the second-stage flotation feed (about 30-55% of the unsized feed) requires sizing before flotation, (6) spirals or belt separators are not needed to process the coarse (14/35 mesh) feed size, and (7) plant return water circuitry could possibly be simplified since all flotation circuits use only cationic reagents.

The new flowsheet designated as "Reverse Crago" involves four basic steps for a relatively fine, unsized flotation feed: (1) prefloating fine sand with an inexpensive amine, (2) dewatering the prefloat concentrate, (3) conditioning the prefloat concentrate with a fatty acid/surfactant/fuel oil blend, and (4) floating the phosphate. This process shows great economic potential. Table 2 summarizes the performance of the Reverse Crago (amine-fatty acid flotation) process on six different feeds on batch scale. In every case, total reagent consumption is below $2 per ton of concentrate.

Table 2. Performance of the Reverse Crago (Amine-Fatty Acid Flotation) Process on Six Different Feeds with Tap Water.

Feed ID	+35 M Wt. %	-150 M Wt. %	Feed %P_2O_5	Conc. %P_2O_5	Conc. % Insol	% BPL Recov.	$/Ton Conc.
A-F	14.8	1.5	9.62	31.10	6.23	93.1	1.41
A-C	26.4	0.5	9.44	31.87	4.17	92.1	1.50
				32.08	3.69	94.7	1.79
B	13.9	3.5	5.43	31.40	9.30	90.6	2.04
				32.13	7.30	94.9	1.96
C-H	20.9	2.6	8.60	33.42	5.69	94.1	1.10
C-L	18.4	2.0	6.77	30.23	10.82	90.6	1.65
				31.06	7.85	92.9	1.77
Coarse	100	0	13.82	31.17	10.56	98.1	0.98

Even more encouraging is that the process performed well with plant water and plant feeds. As is shown in Table 3, even with a water containing 150 ppm TSS, the overall reagent cost was only about $2 per ton of concentrate.

One of the superior advantages and a common benefit of both of the new processes is the potential reduction in the total consumption of both organic and inorganic chemicals in upgrading phosphate minerals, as shown in Table 4.

Table 3. Performance of the Reverse Crago Process on a Low-Grade (3.5% P_2O_5) Plant Feed with Plant Water.

TSS in Water ppm	Pre-Float Amine Use, Lb/TOF	Conc. %P_2O_5	Conc. % Insol	% BPL Recovery	Total Cost, $/TOC
3	0.36	31.38	6.10	95.40	1.37
150	0.65	31.07	5.73	94.1	2.01

Table 4. Comparison of Reagent Consumption (Pounds per Ton of Concentrate) among the Crago, the All-Cationic, and Reverse Crago Processes.

Process ID	Fatty Acid + Oil	Amine	Soda Ash	H_2SO_4	Other Reagents	Total
Present Crago	16.2	1.20	5.50	6.40	---	29.30
All-Cationic	3.44 (no fatty acid)	4.89	0	0	2.17	10.50
Reverse Crago	4.37	3.93	2.87	0	---	11.17

A test program was also conducted to identify the most effective phosphate depressants for both silica/phosphate and dolomite/phosphate systems. Five depressants were compared in silica/phosphate system with cationic collectors. Starch was found to be most desirable for floating fine (-35 mesh) silica from phosphate, while sodium tripolyphosphate may be the best for coarser (+35 mesh) feeds. Sodium tripolyphosphate also appeared to be the most effective depressant for floating dolomite from phosphate under slightly acidic conditions. The effects of depressants on metallurgical performance were examined using both fine and coarse flotation feeds.

INTRODUCTION

THE RESERVE SHORTAGE AND RECOVERY PROBLEMS

It is estimated that the Florida phosphate reserves that can be economically processed with the available technology may only last for about 20-30 years at the current mining rate. As the phosphate mining moves further south, the phosphate matrix will be leaner in grade and higher in dolomitic impurities. While development of a viable dolomite separation process is critical to extending Florida's phosphate reserve, improvement in P_2O_5 recovery from the currently mined siliceous phosphates is equally important.

Phosphate recoveries from the flotation feeds in most plants in Florida do not exceed 85%, with <80% being more common. Assuming that Florida's total production of flotation concentrate is about 20 million tons per year at 70% BPL from feeds averaging 15% BPL, a one percentage point improvement in BPL recovery represents about 250,000 tons of additional rock; an improvement of 4% translates to over a million tons of rock. Improvement in BPL recovery also means a significant reduction in acreage of the disturbed lands for the same amount of product. Based on the information from the Phosphate Council, approximately 185 acres of land have to be disturbed to produce one million tons of phosphate rock.

ANALYSIS OF THE CRAGO DOUBLE FLOAT PROCESS

It may be of help to briefly describe how phosphate is processed in Florida. After desliming, the phosphate ore is subjected to sizing, Figure 1 (Gieseke 1985). Typical sizing involves using a hydrosizer to size the deslimed feed into coarse (16x35 mesh) and fine (35x150 mesh) fractions. In some more sophisticated operations as shown in Figure 2, three fractions are produced (16x24, 24x35,and 35x150 mesh).

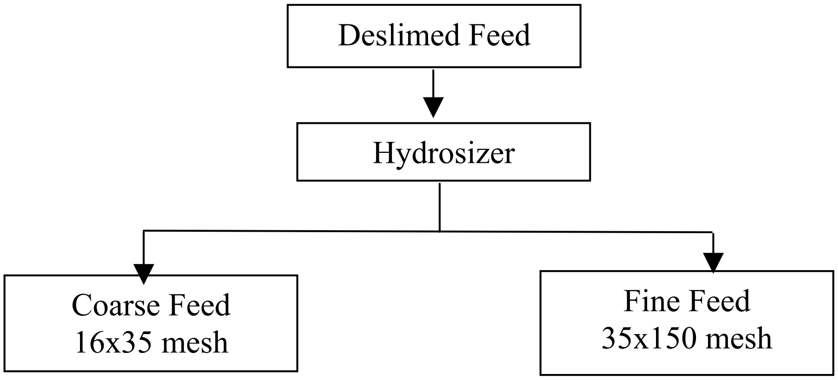


Figure 1. Simple Sizing of Flotation Feed.

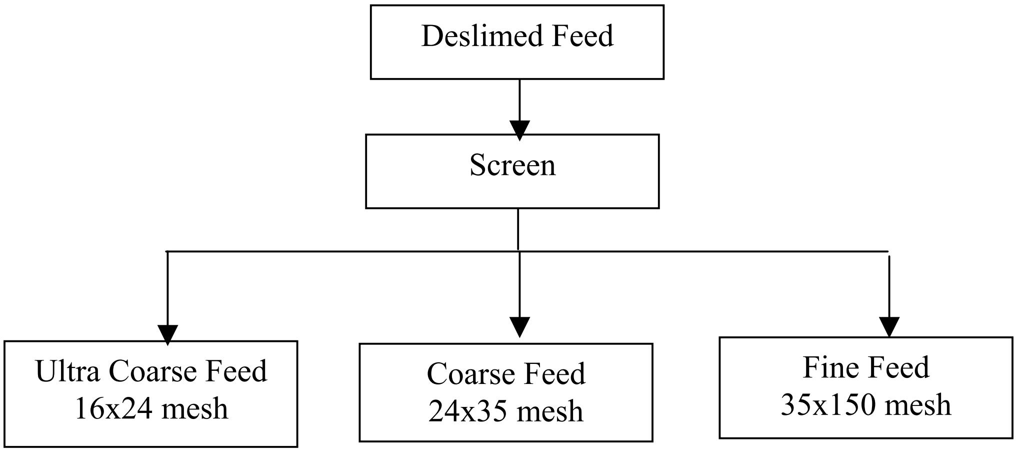


Figure 2. Sophisticated Sizing of Flotation Feed.

The sized feed is first subjected to rougher flotation (Figure 3). In this process the sized feed is dewatered and conditioned at about 70% or higher solids with fatty acid/fuel oil at pH about 9 for three minutes, and then the phosphate is floated. It must be emphasized that a significant amount (30-40%) of silica is also floated in this step.

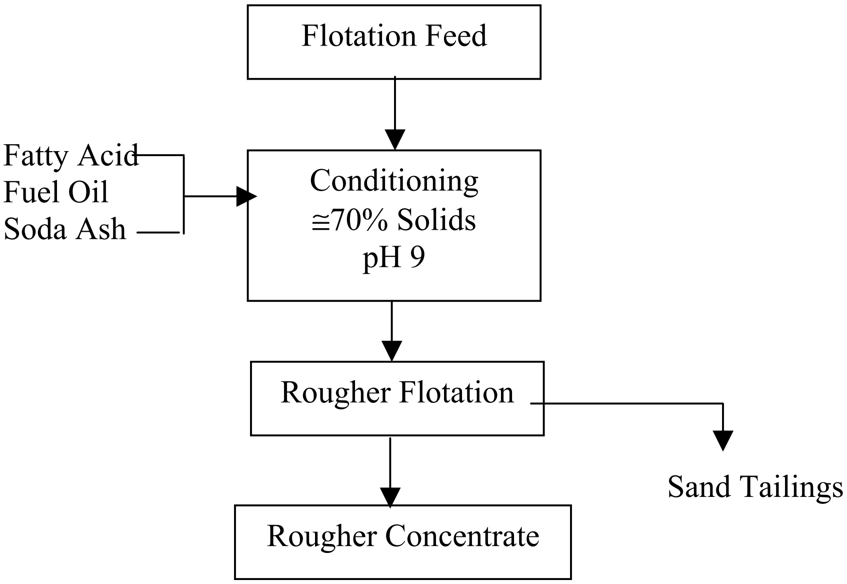


Figure 3. Rougher Flotation.

The rougher concentrate goes through dewatering cyclone, acid scrubber, and wash box to remove the reagents from phosphate surfaces (Figure 4). After rinsing, the feed is transported into flotation cells where amine (sometimes with diesel) is added, and the silica is floated at neutral pH.

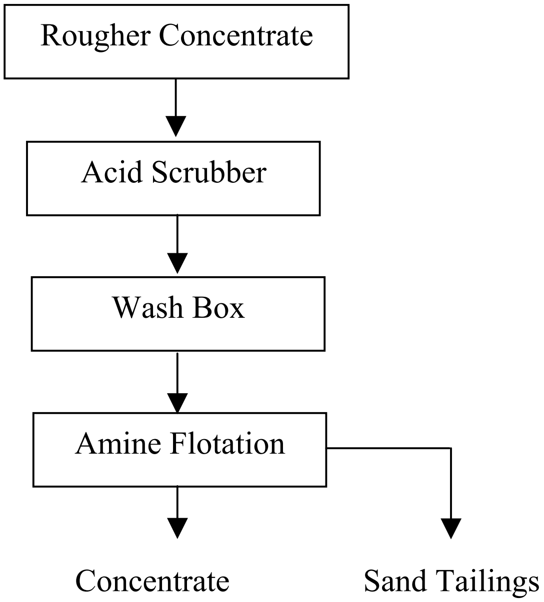


Figure 4. Cleaner Flotation.

In the conventional Double Float (Crago) process for phosphate minerals, 30-40% by weight of the sands present in the feed are floated twice, first by fatty acid and then by amine. The Crago process is, therefore, inefficient in terms of collector efficiency. Fatty acid dosage for floating "pure" phosphate was found to be about 0.18 kg per ton. So, the theoretical dosage for floating a feed of 6.86% P_2O_5 (15% BPL) is only 0.027 kg/TOF. Actual plant fatty acid consumption for such a feed is about 0.54 kg/TOF. Therefore, plant collector efficiency is merely 5% (0.027/0.54). The rest of the reagents are wasted primarily because of silica.

However, there were a number of reasons for the phosphate industry to endorse the process enthusiastically: (1) fatty acid was much cheaper than amine so that anionic flotation followed by amine flotation made more economic sense than otherwise, (2) desliming was not sophisticated, leaving significant amount of clay in the flotation feed so that amine usage would have been prohibitive had silica been floated first, and (3) the ore was high in grade, so the adsorption of fatty acid on silica was tolerable compared with that on phosphate in the rougher flotation stage. The situation is quite different today: the amine price is approximately twice that of fatty acid compared to nearly 10 times in the 1950s; the desliming technology has been upgraded to reduce the fine slimes in the flotation feed; and the phosphorus content in the currently-mined phosphate ores is about half that in the past. These trends do not favor the standard Crago process.

Another factor to consider is surface chemistry. Fatty acids adsorb readily on both phosphate and silica. On the other hand, amine adsorption on phosphate is insignificant compared with that on silica. This is mainly attributed to the high zeta potential of silica on the minus side. At pH above 6, there exists a big difference between zeta potential of silica and that of apatite. Flotation tests showed that cationic collectors do not readily float phosphate. With dodecylammonium chloride, nearly 100% of silica could be floated from pH 4 to 12; while the maximum apatite recovery within the same pH range was less than 3% (15, 16).

The above discussions suggest that the conventional processing flowsheet should be reevaluated.

In recognition of those changes discussed above, FIPR undertook this major research effort in searching for more efficient techniques for processing siliceous phosphates.

REMOVAL OF DOLOMITE FROM FUTURE DEPOSITS

One way to extend Florida phosphate mine life would be to develop an efficient and economical technology for separating dolomite from apatite. Generally, acidulation of phosphate rock requires a feed of less than 1% MgO content, which, except for the IMC heavy media technique, has not been achieved at a commercial scale with ores high in MgO. Dolomite is also a worldwide problem.

Systematic research in beneficiation of carbonate phosphate ore started in the early fifties. Since then, research efforts in this area have been extensive. As a result, many processes have been proposed, tested, or even commercialized. These processes include direct flotation of phosphate while depressing carbonate, inverse flotation of carbonate with a phosphate depressant, acid leaching, calcination, and some physical methods.

Of all these processes, reverse flotation of carbonates while simultaneously depressing phosphate has been studied most extensively. There are good reasons for this trend: (1) flotation is, in many cases, the least expensive mineral processing operation, (2) flotation of the minor gangue also has many advantages over floating the major phosphate minerals (reducing capital cost and saving reagents, for example), and (3) plant modifications would be minimal if flotation is used for processing the high dolomite phosphate ores.

As is well understood, the difficulty in separating phosphate from carbonates is due to their similarity in electro-chemical properties. Therefore, surface modification is essential for separating carbonates from phosphates efficiently. Besides the additions of pH modifiers, collector extenders, and frothers, the addition of depressant is the most frequently used method of surface modification.

The following reagents have showed the potential of depressing phosphate (Rule and Daellenbach 1985; Ratobylskaya and others 1975; Hsieh and Lehr 1985; Rao and others 1989; Gruber and others 1995; Smani and others 1975; Houot 1982; Lehr and Hsieh 1981):

Hydrofluosilicic acid
Orthophosphoric acid
Phosphoric acid

Diphosphonic acid
Sulfuric acid
Aluminum sulfate and tartaric acid
Phosphates
Dipotassium hydrogen phosphate
Sodium tripolyphosphate
Alizarin Red S (ARS)
Ethoxylated alkyl phenol
Starch

One of the major characteristics of the phosphate depressants is their mineral specificity. A recent study conducted at the International Fertilizer Development Center compared several phosphate depressants and found that the phosphoric acid depression process gave the best results (Lawendy and McClellan 1993). Hydrofluosilicic acid, starch and dipotassium hydrogen phosphate, have been extensively tested on a carbonaceous ore from India, and results indicated that dipotassium hydrogen phosphate was superior to the others in depressing phosphate in the test sample. Cornstarch was found effective on several high-dolomite Brazilian phosphate ores (Leal Filho and others 1993). According to Dr. Ronald Wiegel (1996), starch is the best phosphate depressant for Florida ores. It is, therefore, very evident that there is no universal phosphate depressant. Experiments are essential for finding the best depressant for a specific ore, and mineralogical composition may play a critical role.

Another important feature of most phosphate depressants is their pH dependence. Many of them could be used either as a carbonate depressant or an apatite depressant by selecting the appropriate pH range of the flotation pulp.

Some recent studies indicate that the separation of dolomite from phosphate may be accomplished by carefully controlling flotation parameters, such as conditioning time, stages and pH, particle size, pulp density and modifier type.

The effect of pH and collector type on the flotation selectivity of a Moroccan sedimentary ore was studied in detail by Smani and others (1975). The study found that whichever collector is used, calcite floats first and the phosphate minerals are depressed under the following conditions:

$pH \approx 6$ with sodium oleate
$pH > 4$ with sodium dodecylsulfonate
$pH < 4$ with dodecylamine

RESEARCH NEEDS

To enhance its competitive position in the international market and extend its longevity, the Florida phosphate industry urgently needs a sound process for economically recovering the phosphate associated with dolomite gangue. Flotation of carbonate with a selective phosphate depressant has the potential to solve this problem.

To conserve water/energy resources and reduce its environmental impact, the Florida phosphate industry should undertake an updated evaluation on the half-century-old Crago double flotation process. Single-collector flotation offers the opportunity to improve the industry efficiency.

The information base on phosphate depressants needs to be expanded in the following areas:

(1) Phosphate depression mechanisms
(2) Relationships between mineralogy and depression efficiency
(3) Optimal parameters for each of the depressants
(4) Ranking of all the depressants for Florida ores
(5) Potential of depressant mixtures

PART I. SCREENING PHOSPHATE DEPRESSANTS FOR SILICEOUS PHOSPHATES

SCREENING PHOSPHATE DEPRESSANTS FOR SILICEOUS PHOSPHATES

SUMMARY

The use of phosphate depressants in the cationic flotation if silica from francolite in the Florida phosphate industry is rarely practiced. The occasional use of gelatinized starch derivatives and pH adjustments to assure a slightly alkaline flotation feed slurry pH have been used in some processing plants to improve selectivity. This report presents a preliminary laboratory comparison of several potential phosphate depressants for use with the flotation of coarse silica from spiral feed provided by IMC/Agrico.

Five potential phosphate flotation depressants were subjected to evaluation during cationic flotation of coarse silica using the quaternary/oil collector "Q" process. IMC/Agrico's Kingsford plant spiral feed was used for all tests. The potential depressants included sodium tripolyphosphate, fluosilicic acid, diphosphonic acid, starch, and sodium silicate. Sodium tripolyphosphate was found to be the most effective depressant, confirming previous results using "unsized" feed as described in Progress Report No. 1. Using STPP, concentrates were produced analyzing 30-31+% P_2O_5/7-10+ % insol at 94-96+% recovery of P_2O_5. Depressant level required was depended upon collector level used and ranged from 0.25-1.00 lb. per ton of feed for best results. Diphosphonic acid and fluosilicic acid were less effective, whereas starch and sodium silicate were considered ineffective as selective phosphate depressants.

LABORATORY TESTWORK

Description of Spiral Feed Sample

A 100 lb. sample of Kingsford plant spiral feed was obtained from IMC/Agrico on 6/3/95. Chemical analysis of the as-received sample and the calculated feed analysis obtained from 33 laboratory flotation tests were as follows:

Sample	% P_2O_5	% Insol	% P_2O_5 (0% Insol)
Analytical Head	19.82	40.28	33.19
Calculated Head	20.14	39.49	33.28

An abbreviated dry screen analysis of the spiral feed sample showed the following particle size distribution:

Tyler Mesh	% Wt.	Cum. % Wt.
+14	6.5	6.5
14/20	24.9	31.4
20/35	56.1	87.5
-35	12.5	100.0
Total	100.0	-

Hot acid digestion (1:1 HCl) of a 50 g feed sample yielded 38.2% weight of insol residue. Dry screening of the residue revealed that 6.8% of the total was larger than 20 mesh, and 60.5% of the total was 20/35 mesh.

Reagents

Laboratory flotation tests were performed to compare the effectiveness of five selected depressants using the following two levels of collector reagents:

Arquad 2HT-75	Philflo Oil	Tergitol NP-10
0.4	1.2	0.05
0.5	1.5	0.05

The following depressants were tested at addition levels of 0.25, 0.50, and 1.00 lbs. per ton of feed:

Depressant	Source
Sodium tripolyphosphate (STPP)	Monsanto
Fluosilicic acid	Fisher Scientific
Diphosphonic acid (Dequest 2010)	Monsanto
Starch (CCD-2112)	Westvaco
Sodium silicate (N-Brand)	Phila. Quartz

Additional flotation tests were performed, using the same two collector levels listed above, with pH adjustments in both the acid and alkaline ranges. Sulfuric acid and soda ash were used for pH regulation.

Flotation Tests

Standard vertical mixer conditioning for 15 seconds at 72% solids was used for all tests. Depressant (or pH regulator) was added to the conditioner slurry first followed by the collector and oil. Frother was added in the flotation cell. The 500g laboratory Denver cell was used for all flotation tests performed for this project.

RESULTS AND DISCUSSION

For easier data interpretation, the results were plotted as concentrate % P_2O_5, % insol and % recovery P_2O_5 vs. depressant level used. The results are presented in Figures 5-9 in accordance with the following legend:

Figure	Phosphate Depressant	Cond. pH	Flot. pH
5	Sodium tripolyphosphate	6.7-6.9+	7.0-7.2
6	Fluosilicic acid	3.0-4.0+	5.3-6.9
7	Diphosphonic acid	4.1-5.7	5.8-6.9
8	Starch	7.0-7.4	7.0-7.4
9	Sodium silicate	7.3-7.8	N.A.

The pH ranges measured when no depressant was used were 6.7-6.8 during conditioning and 7.0-7.2+ during flotation. No pH regulators were intentionally used during the depressant comparison testwork; the pH ranges that resulted were caused by the specific depressant added.

For a phosphate depressant to be considered effective, its use in flotation should result in an increase in P_2O_5 recovery without a significant parallel increase in concentrate % insol. Also, the performance of a "true" depressant is often depended upon the type and level of collector used. Referring to Figures 5-9, only STPP, diphosphonic acid, and to a lesser degree fluosilicic acid appeared to exhibit useful depressant activity when used with the quaternary/oil collector combination.

Figures 5a and 5b illustrate that using 0.25 lb. STPP per ton of feed with the lower collector level produced a 30.61% P_2O_5/10.88% insol concentrate at 96.5% P_2O_5 recovery compared to a 31.07% P_2O_5/10.04 insol concentrate at 88.8% P_2O_5 recovery when no depressant was used. Using the higher collector level, a better grade concentrate analyzing 31.58% P_2O_5/7.42% insol was produced at 94.5% P_2O_5 recovery; however, the STPP required to maintain high P_2O_5 recovery increased to about 1.00 lb. per ton of feed. Using only 0.25-0.50 lbs. STPP per ton of feed yielded concentrates analyzing 31.65-32.19% P2O5/6.06-6.62% insol at 84.9-85.3% P_2O_5 recovery. When no depressant was used, the concentrate analyzed 31.01% P_2O_5/9.49% insol at only 77.0% P_2O_5 recovery.

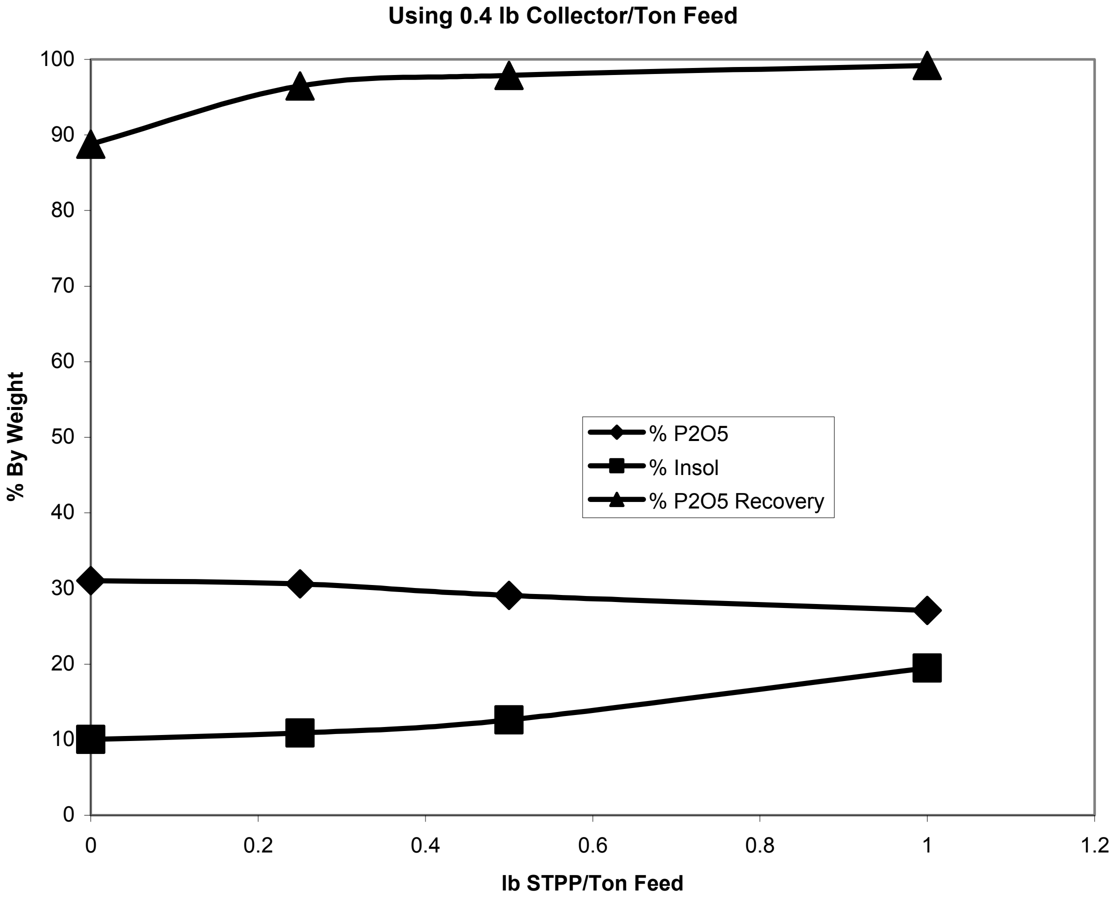


Figure 5a. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

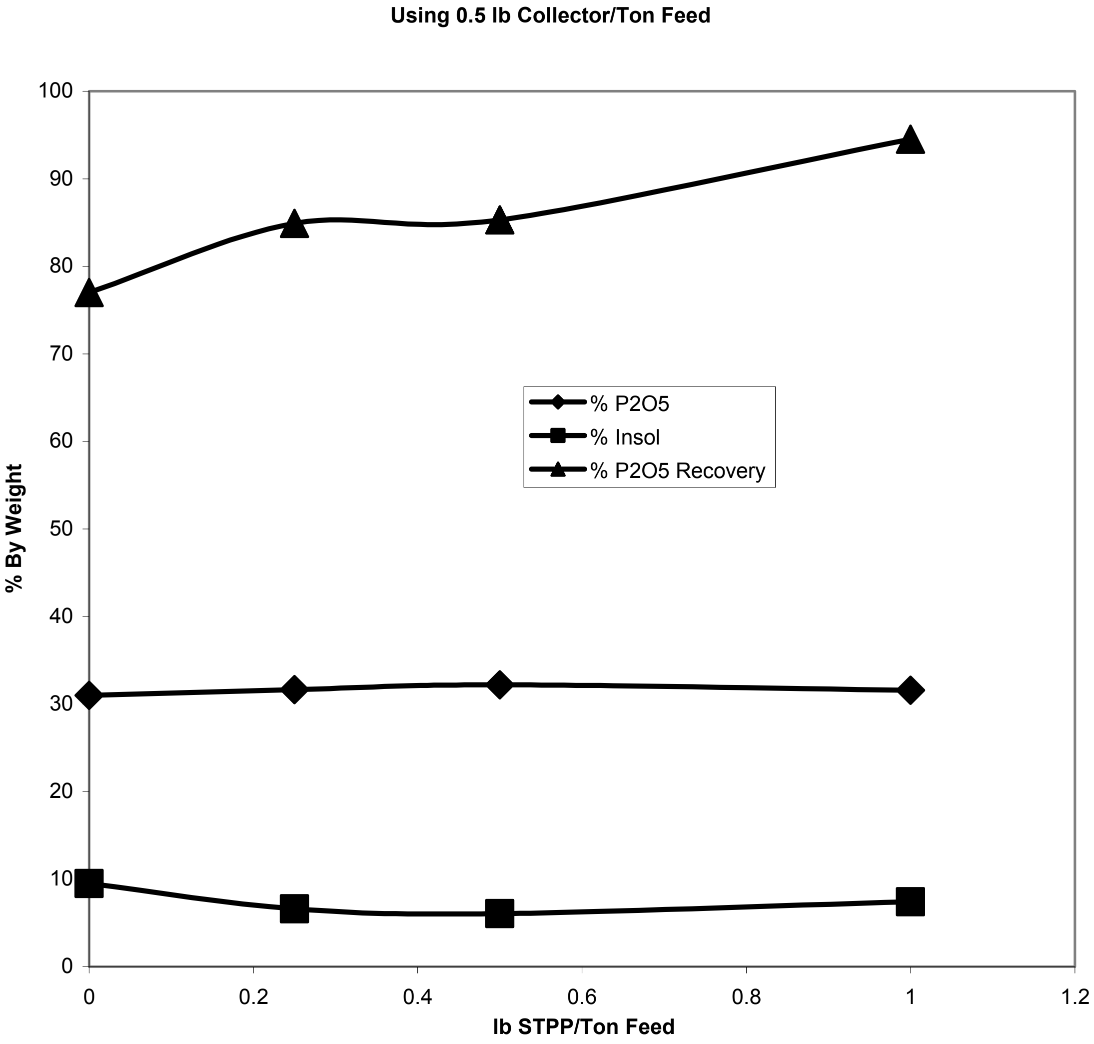


Figure 5b. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Figures 6a and 6b show that fluosilicic acid use in the 0.25-1.00 lb. per ton of feed range was effective in depressing phosphate and resulted in P_2O_5 recoveries exceeding 92% for all tests performed. However, no concentrates analyzing 30% P_2O_5 or higher were produced. The use of more than 0.5 lb. of collector is indicated as necessary to produce a 30+% P_2O_5 concentrate. Using the 0.5 lb. collector level with 0.25 lb. of fluosilicic acid per ton of feed produced a phosphate concentrate reported to analyze 29.13% P_2O_5/9.29% insol at 92.4% P_2O_5 recovery. When no depressant was used, the concentrate analyzed 31.01% P_2O_5/9.49% insol at 77.0% P_2O_5 recovery. Possible analytical error is indicated.

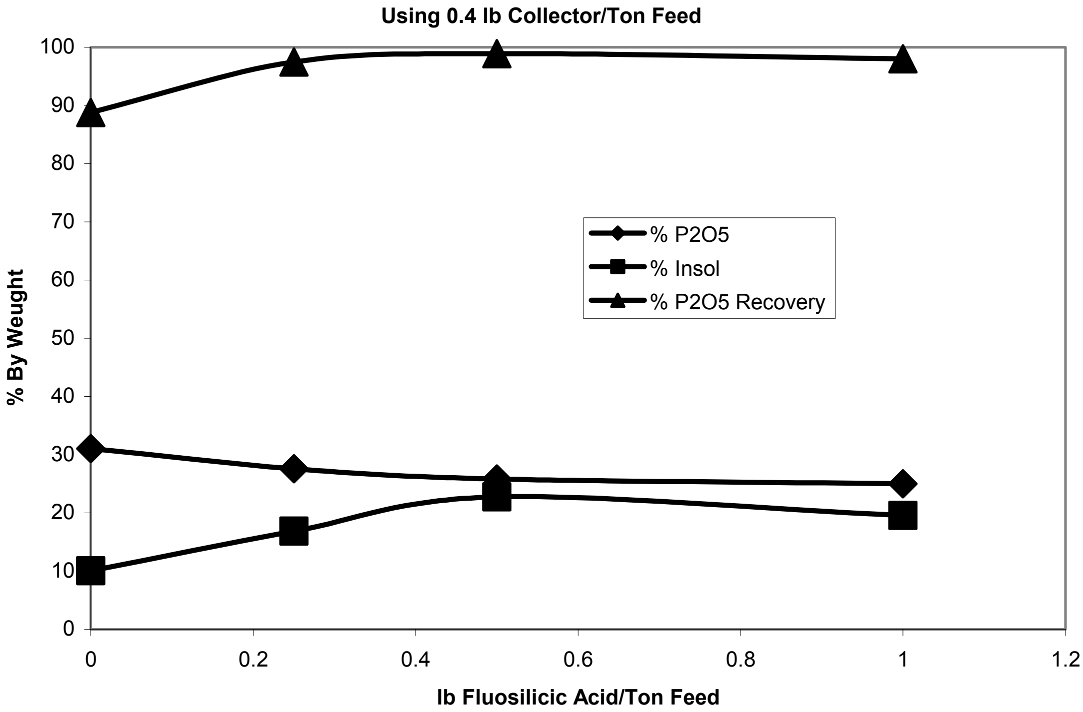


Figure 6a. Flotation Concentrate Grade/Recovery Using Various FSA Levels.

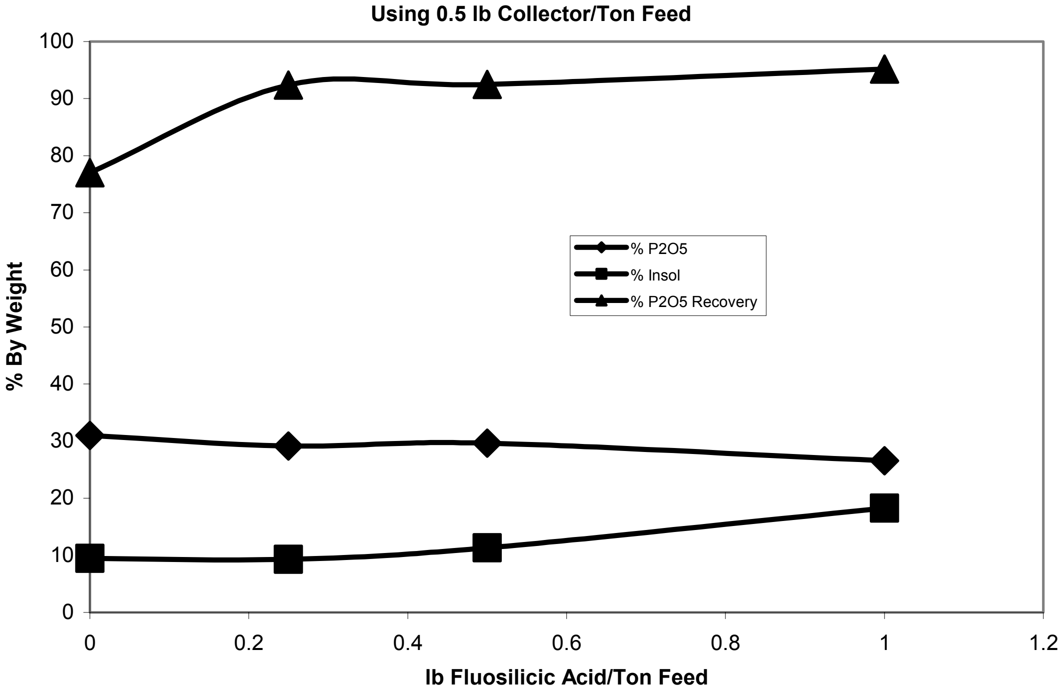


Figure 6b. Flotation Concentrate Grade/Recovery Using Various FSA Levels.

Figures 7a and 7b indicate that diphosphonic acid was an effective phosphate depressant when used at the 0.50 lb. per ton of feed level with the higher collector level. A phosphate concentrate was produced analyzing 31.15% P_2O_5/6.06% insol at 91.8% P_2O_5 recovery. Using less depressant resulted in a significant decrease in P_2O_5 recovery, and using more depressant produced lower grade concentrate. Diphosphonic acid appears to be very sensitive to the level used and is considered to be inferior to STPP as a selective phosphate depressant when used with the quaternary/oil collector combination used to float coarse silica.

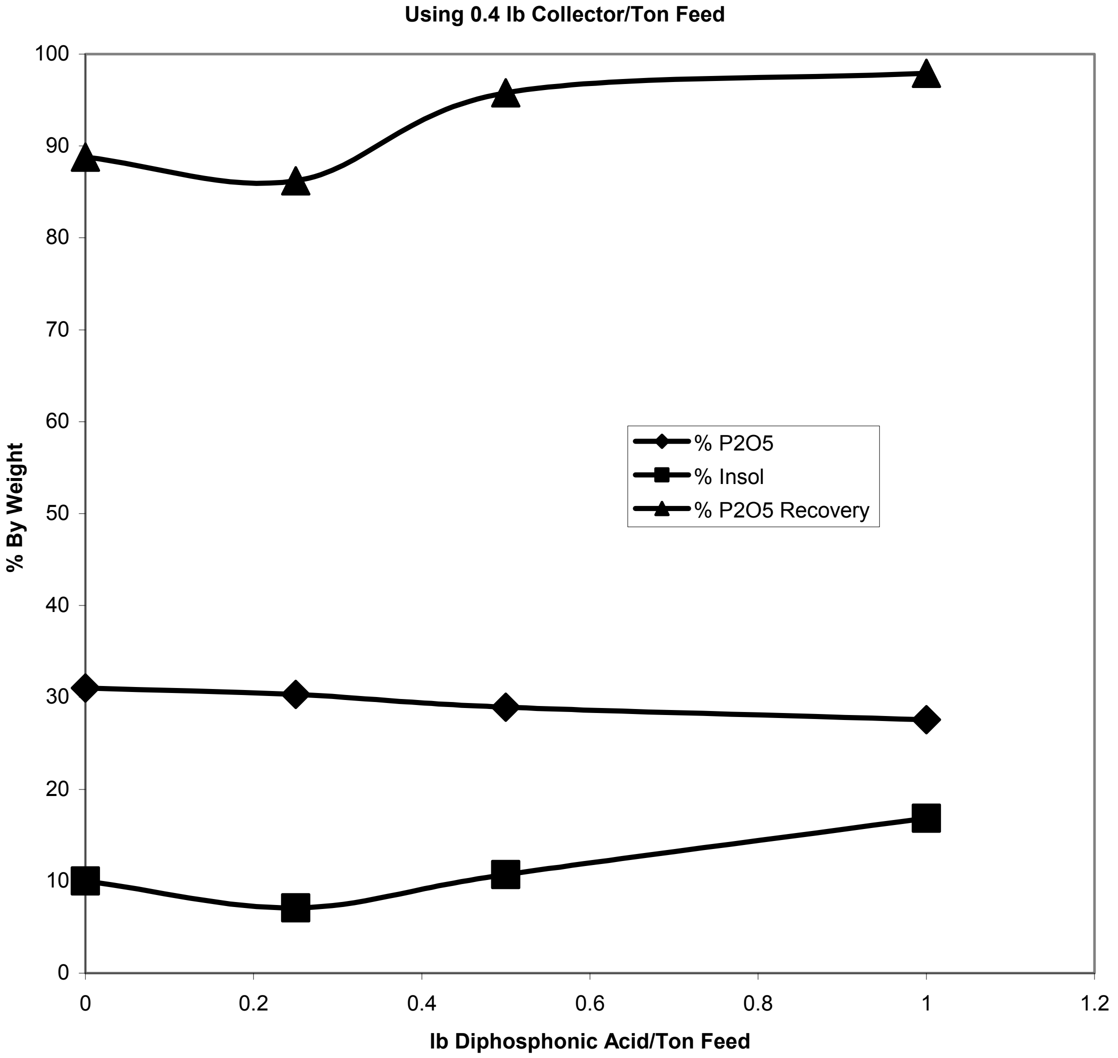


Figure 7a. Flotation Concentrate Grade/Recovery Using Various DPA Levels.

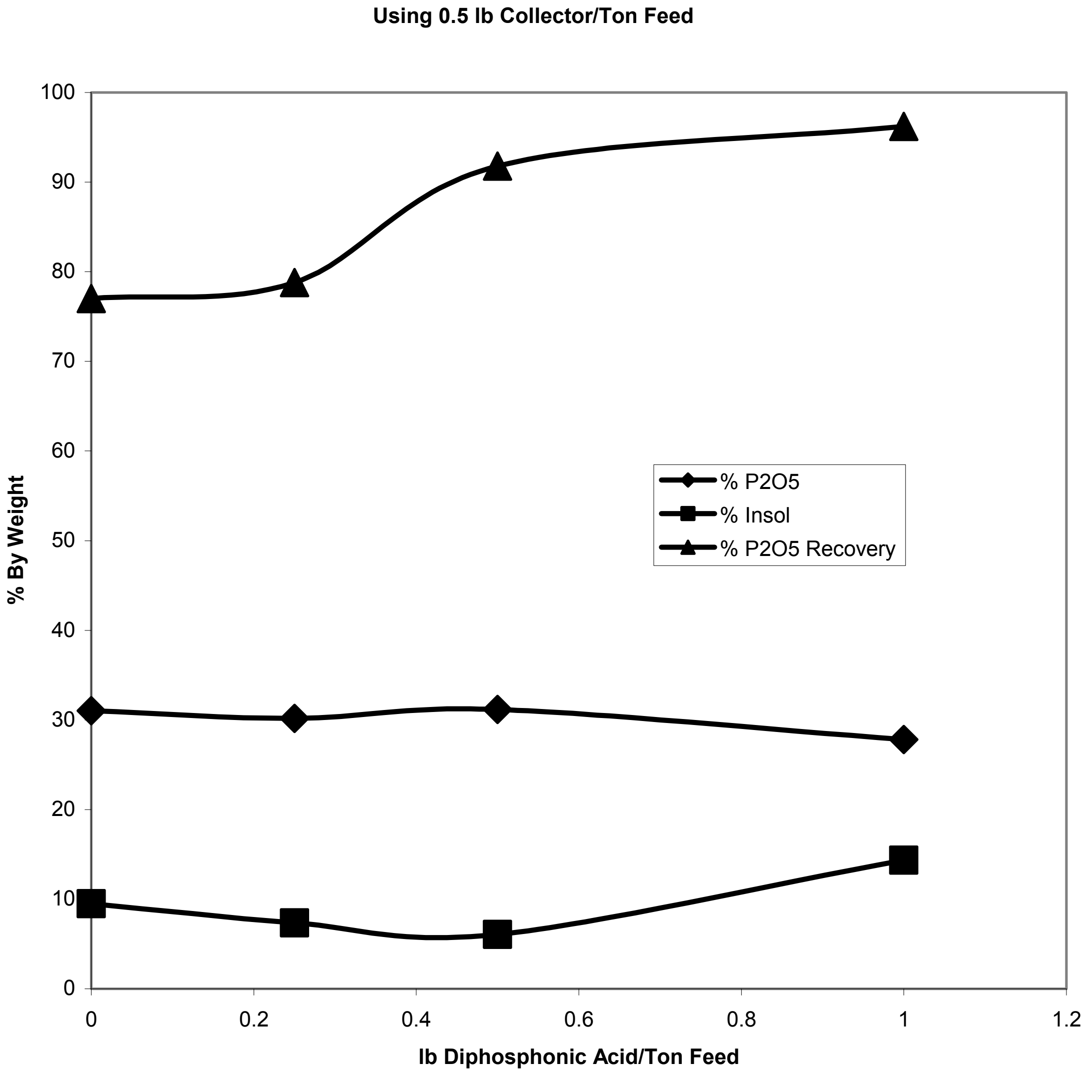


Figure 7b. Flotation Concentrate Grade/Recovery Using Various DPA Levels.

Figures 8 and 9 illustrate that neither Westvaco starch nor N-Brand sodium silicate performed as selective phosphate depressants with this flotation process. At all usage levels tested, lower-grade phosphate concentrates were produced compared to the standard no-depressant tests. Sodium silicate was expected to be detrimental to coarse silica flotation because of possible chemical reaction with the quaternary collector. The use of higher starch plus quaternary/oil collector levels could possibly yield a 30+% P_2O_5 concentrate at 90+% P_2O_5 recovery. A more detailed study of starch effectiveness at higher collector addition levels is beyond the current scope of the planned testwork.

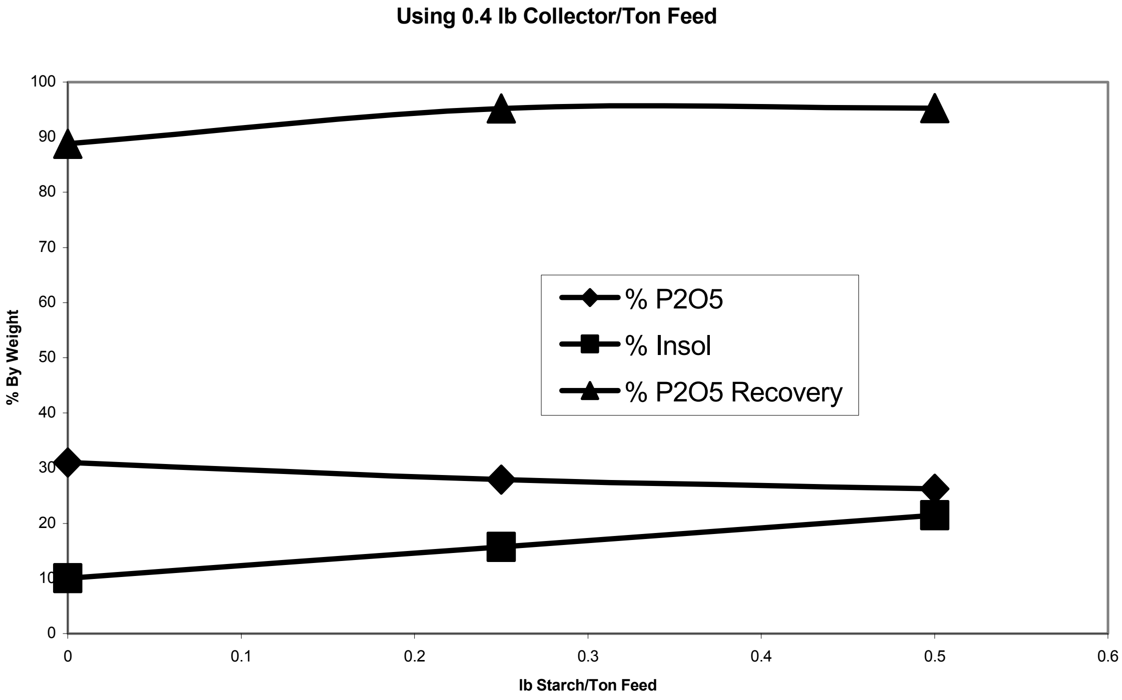


Figure 8a. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

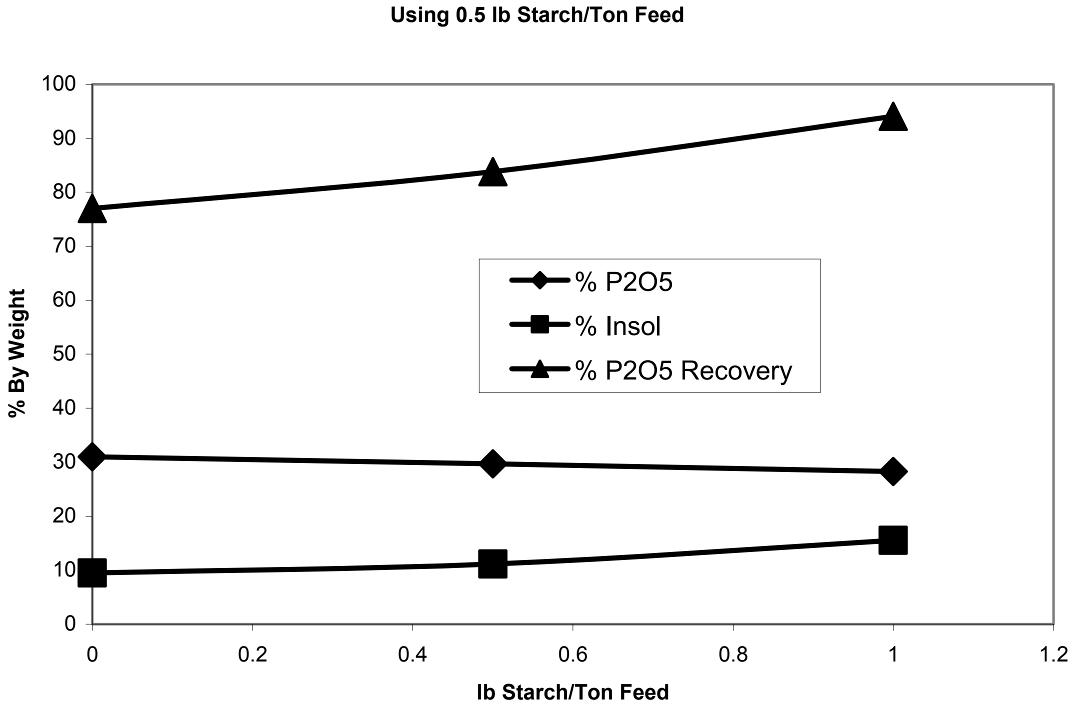


Figure 8b. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

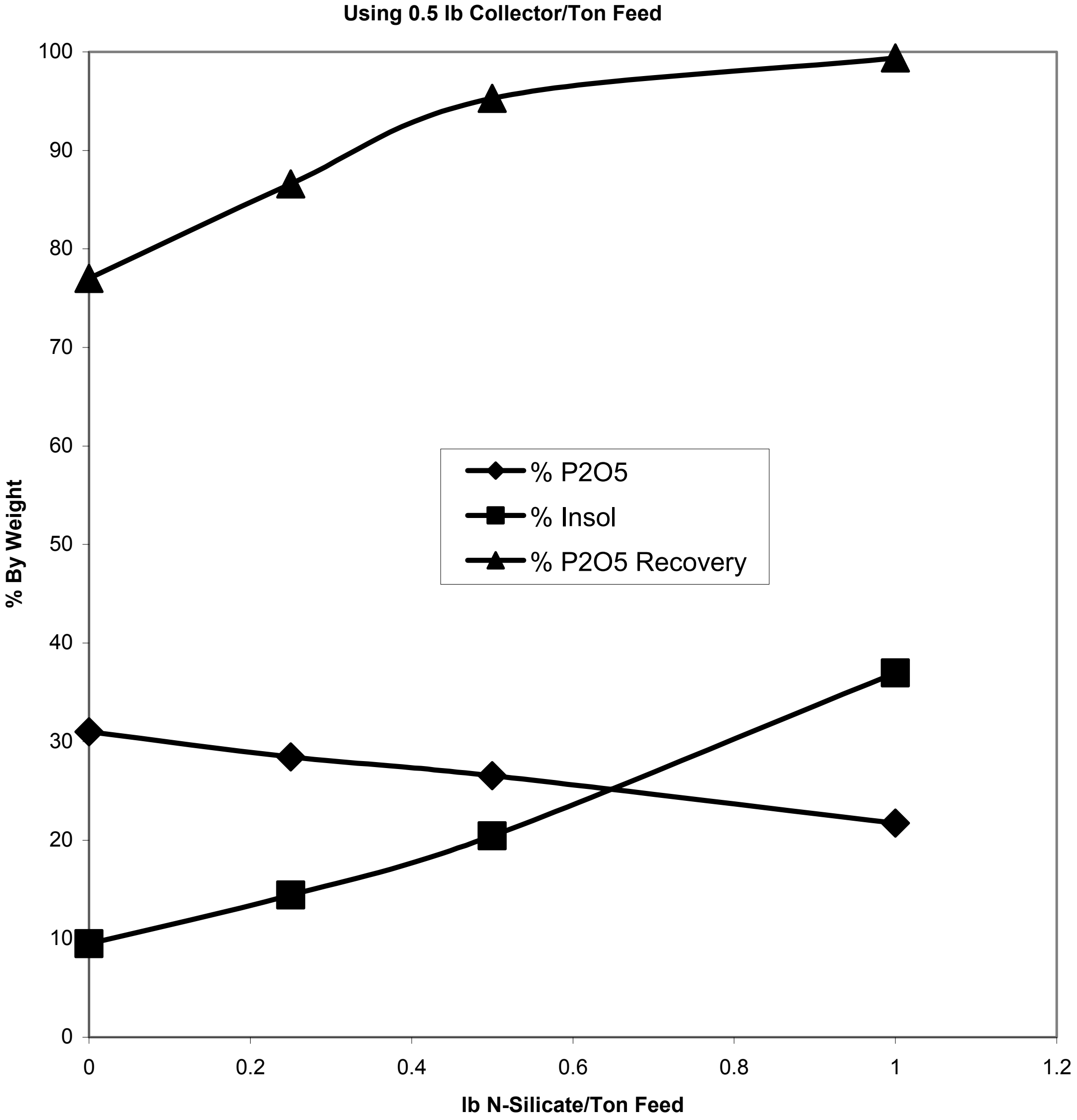


Figure 9. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

The effect of conditioning pH on flotation response was briefly investigated with no depressant addition. The results are shown in Figure 10. The most obvious effect of altering the "natural" 6.7+ conditioning pH to the higher level (9.2+) was the lower resultant P_2O_5 recovery and slightly lower concentrate grade. Decreasing the pH from 6.7+ to 5.1 also resulted in some lowering of P_2O_5 recovery and concentrate % insol only when the higher collector level was used. The pH changes that accompanied the use of the various depressants tested probably contributed to the overall flotation performance and further complicated the collector level-depressant level interactions.

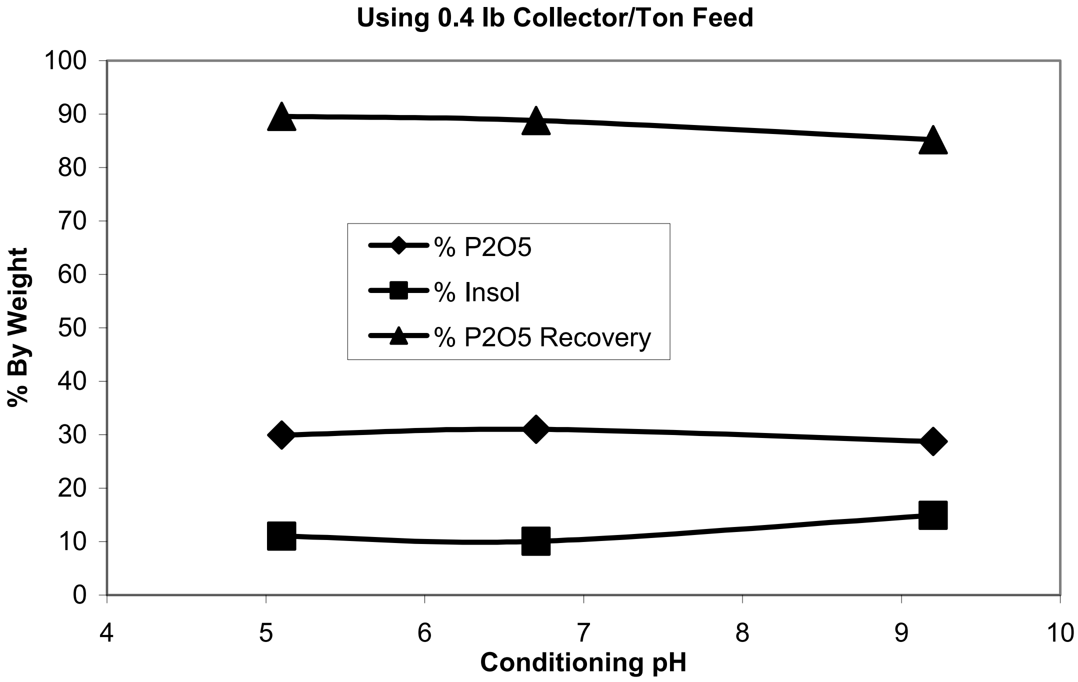


Figure 10a. Flotation Concentrate Grade/Recovery at Various pH Levels.

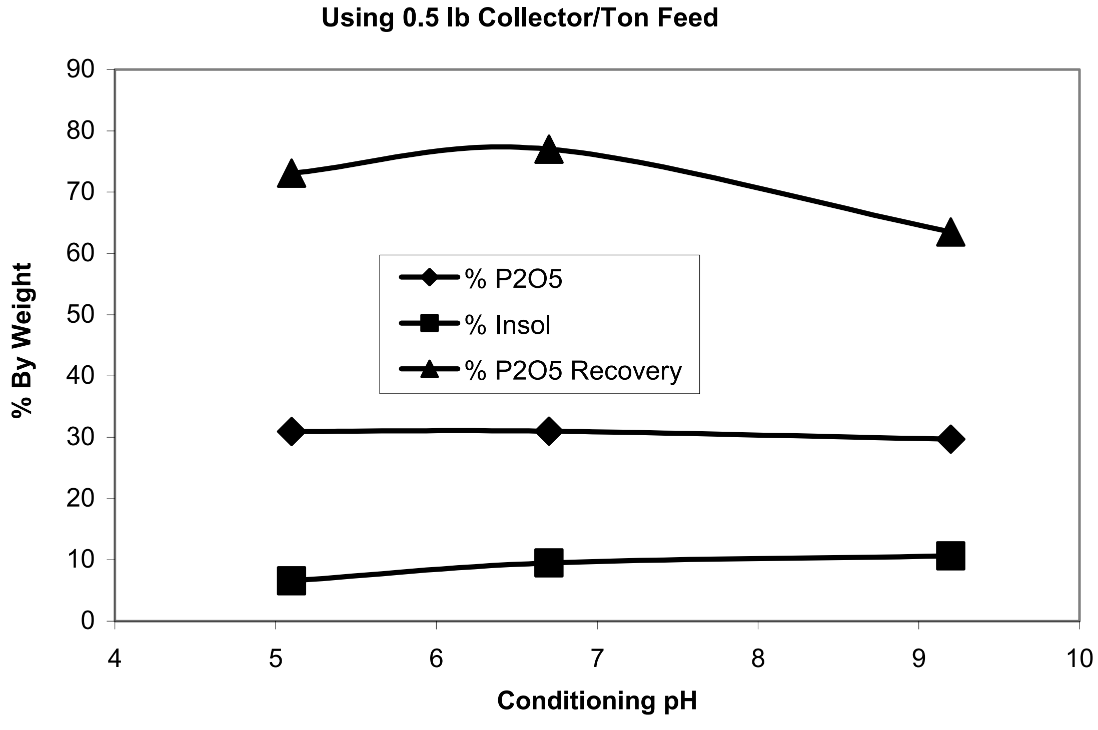


Figure 10b. Flotation Concentrate Grade/Recovery at Various pH Levels.

Figure 11 presents a concentrate % P_2O_5 vs. % P_2O_5 recovery diagram for all flotation tests performed with and without depressant additions. The superiority of STPP compared to other depressants, as defined by the boundary curve, is very apparent.

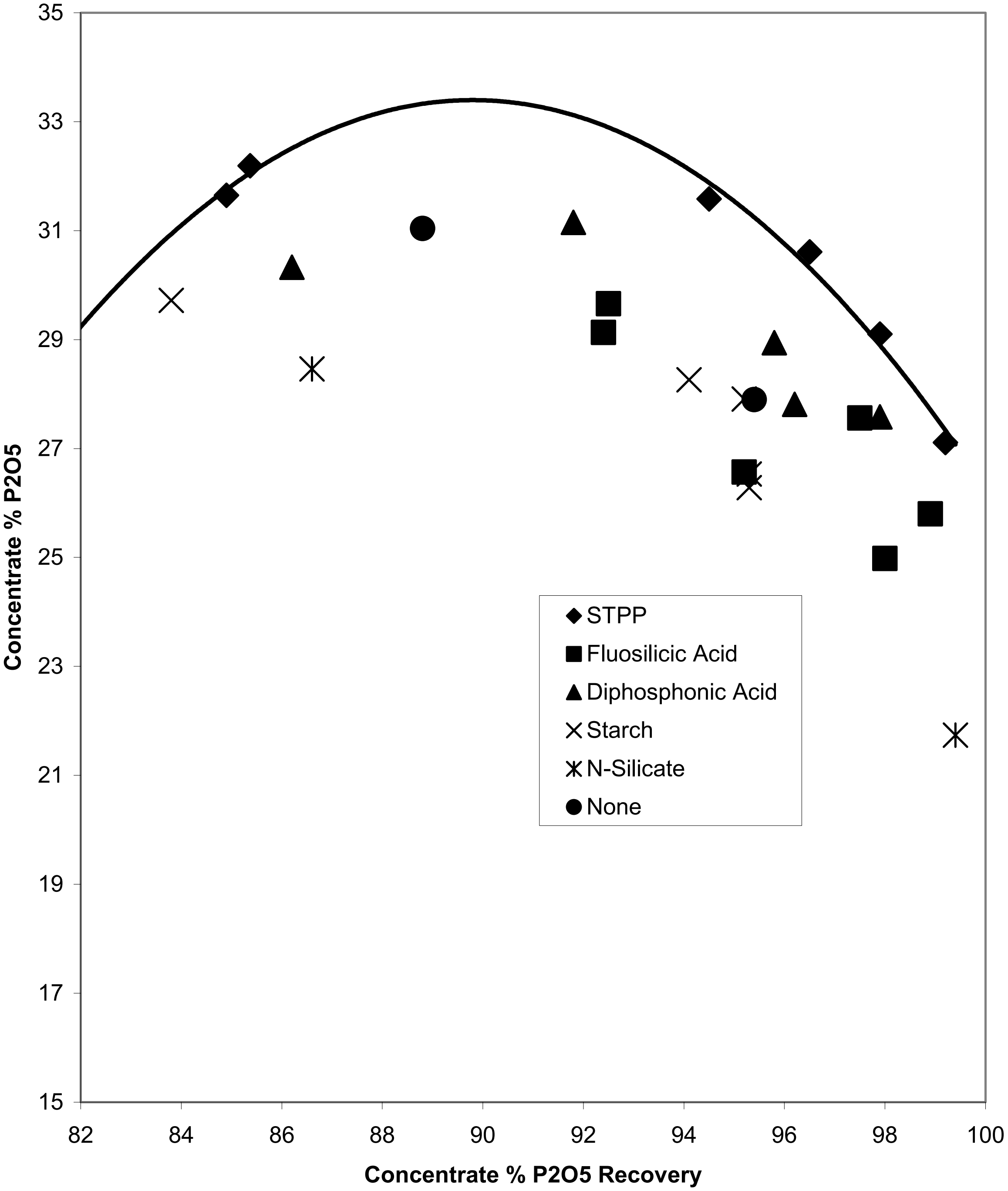


Figure 11. Flotation Concentrate Grade vs. Recovery for All Depressant Tests.

SCREENING PHOSPHATE DEPRESSANTS FOR FLOATING FINE SILICA FROM PHOSPHATE

SUMMARY

The preceding section summarized laboratory cationic flotation test results obtained using a quaternary/oil collector, with and without potential phosphate depressants, to float coarse quartz from IMC/Agrico's Kingsford plant spiral feed. This report presents the results obtained recently using an amine condensate/diesel fuel collector, with and without potential phosphate depressants, to float fine quartz from IMC/Agrico's Kingsford plant amine feed.

Five potential phosphate flotation depressants were evaluated during laboratory amine flotation of fine quartz from phosphate, using a commercial amine condensate/ diesel fuel collector combination to process the above-cited plant amine feed. The potential phosphate depressants included gelatinized starch, sodium tripolyphosphate (STPP), diphosphonic acid (Dequest 2010), fluosilicic acid and orthophosphoric acid. From an overall cost/performance standpoint, starch was considered to be the best phosphate depressant. STPP was considered to be almost equally as effective, but more costly, compared with starch as a selective phosphate depressant. Using starch or STPP, concentrates were produced analyzing 32-33+ % P_2O_5/3-4% insol at 95-96% P_2O_5 recovery using as little as 0.25 lb. of depressant per ton of feed. Similar results were obtained using diphosphonic acid at the 0.25-0.50 lb. per ton of feed level provided that the amine collector level was more carefully controlled. Using starch or STPP at a higher level (0.50-1.00 lb. per ton of feed) had almost no detrimental effect on flotation concentrate grade provided that adequate amine collector quantity was used.

When no depressant was used about 12% P_2O_5 recovery loss occurred when the amine collector level was increased from 0.4 to 0.5 lb. per ton of feed. The proper use of starch, STPP or diphosphonic acid prevented this loss. Fluosilicic acid and orthophosphoric acid failed to effectively control P_2O_5 recovery when the amine level was increased from 0.4 to 0.5 lb. per ton of feed. These two acids were considered to be ineffective as phosphate depressants within the range of test conditions employed.

LABORATORY TESTWORK

Description of Amine Feed Sample

A 40 lb. sample of Kingsford plant amine feed was obtained from IMC/Agrico on 6/3/95. Chemical analysis of the as-received sample and the calculated feed analysis obtained from 34 laboratory flotation tests were as follows:

Sample	% P_2O_5	% Insol	% P_2O_5 at 0% Insol
Analytical Head	22.45	33.81	33.92
Calculated Head	22.47	33.71	33.90

Standard dry screen analysis of the amine feed sample showed the following particle size distribution:

Tyler Mesh	% Wt.	Cum. % Wt.
+35	4.4	4.4
35/48	9.7	14.1
48/65	16.8	30.9
65/100	39.9	70.8
100/150	22.5	93.3
150/200	5.4	98.7
-200	1.3	-100.0

Reagents

Laboratory flotation tests were performed to compare the effectiveness of five selected phosphate depressants using the following two levels of collector reagents:

Custamine 738	Diesel Fuel
0.40	0.48
0.50	0.60

The following depressants were tested at addition levels of 0.25, 0.50 and 1.00 lbs. per ton of flotation feed:

Depressant	Source
Starch (CCD-2112)	Westvaco
Diphosphonic acid (Dequest 2010)	Monsanto
Sodium tripolyphosphate	Monsanto
Fluosilicic acid	Fisher Scientific
Orthophosphoric acid	Fisher Scientific

Additional flotation tests were performed, using the same two collector levels previously cited, with pH adjustments in the alkaline and in the acidic ranges. Soda ash and sulfuric acid were used for pH regulation.

Flotation Tests

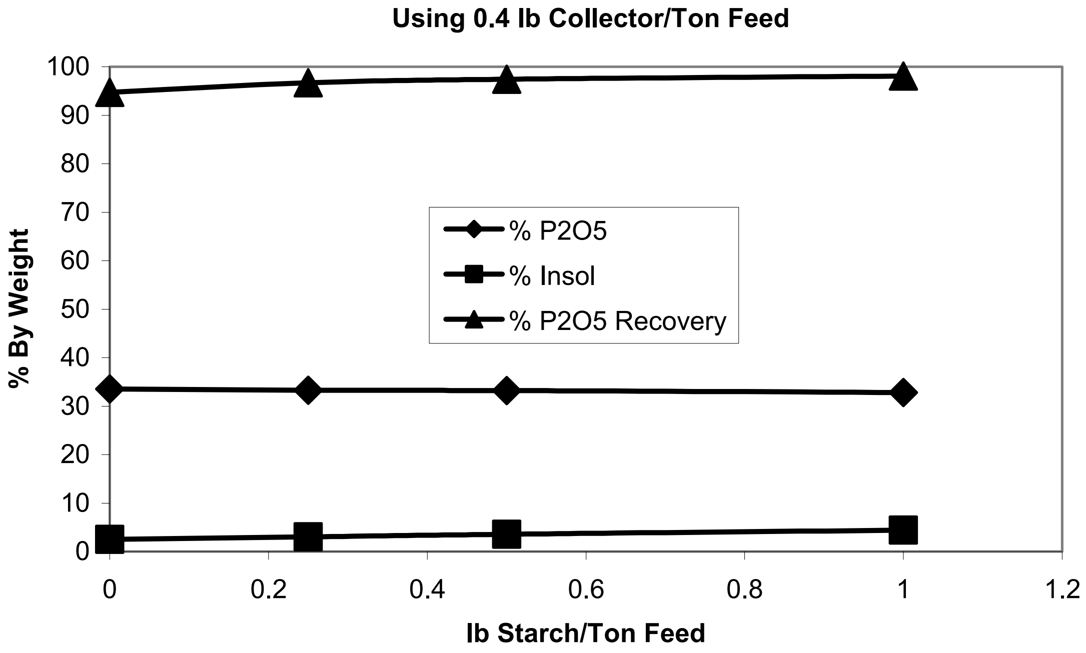
All reagents were added directly to the flotation feed slurry in the 500 g laboratory Denver cell. Depressant or pH regulator was added first with collector being added about 10 seconds later.

RESULTS AND DISCUSSION

Flotation results were plotted as concentrate % P_2O_5, % insol and % P_2O_5 recovery vs. depressant level used. The graphical results are shown in Figures 12-16 in accordance with the following legend:

		Flotation pH	
Figure	Phosphate Depressant	Initial	Final
12	Starch	7.3-7.4	7.7-7.7+
13	Sodium tripolyphosphate	7.2-7.3	7.7-7.7+
14	Diphosphonic acid	6.3-6.9	7.3-7.7+
15	Fluosilicic acid	4.0-6.5	5.8-7.4
16	Orthophosphoric acid	6.3-6.9	7.1-7.7

When no depressants were used, the flotation pH range was 7.3-7.7. When depressants were used, the reported initial pH ranges were caused by the specific depressant added unless otherwise reported.



Using 0.4 lb Collector/Ton Feed

Figure 12a. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

Referring to Figures 12-16, only starch, STPP and diphosphonic acid exhibited flotation selectivity enhancing properties characteristic of an effective phosphate depressant.

Figure 12 illustrates that using 0.25 lb. of starch per ton of feed with the lower collector level produced a 33.26% P_2O_5/3.04% insol concentrate at 96.7% P_2O_5 recovery compared to a 33.50% P_2O_5/2.48% insol concentrate at 94.7% P_2O_5 recovery when no depressant was used. Using the higher collector level, the concentrate analyzed 32.82% P_2O_5/3.04% insol at 94.4% P_2O_5 recovery compared to 33.25% P_2O_5/2.14% insol at 82.7% P_2O_5 recovery when no starch was used. The use of starch with the higher amine level greatly reduced the 12% P_2O_5 recovery loss (experienced when amine level increased from 0.4 to 0.5 lb. per ton of feed with no depressant addition) that occurred when no depressant was used, and had very little detrimental effect upon the final concentrate % insol. The use of higher starch levels had only a small positive or negative effect on concentrate grade and % P_2O_5 recovery depending upon the amine level employed.

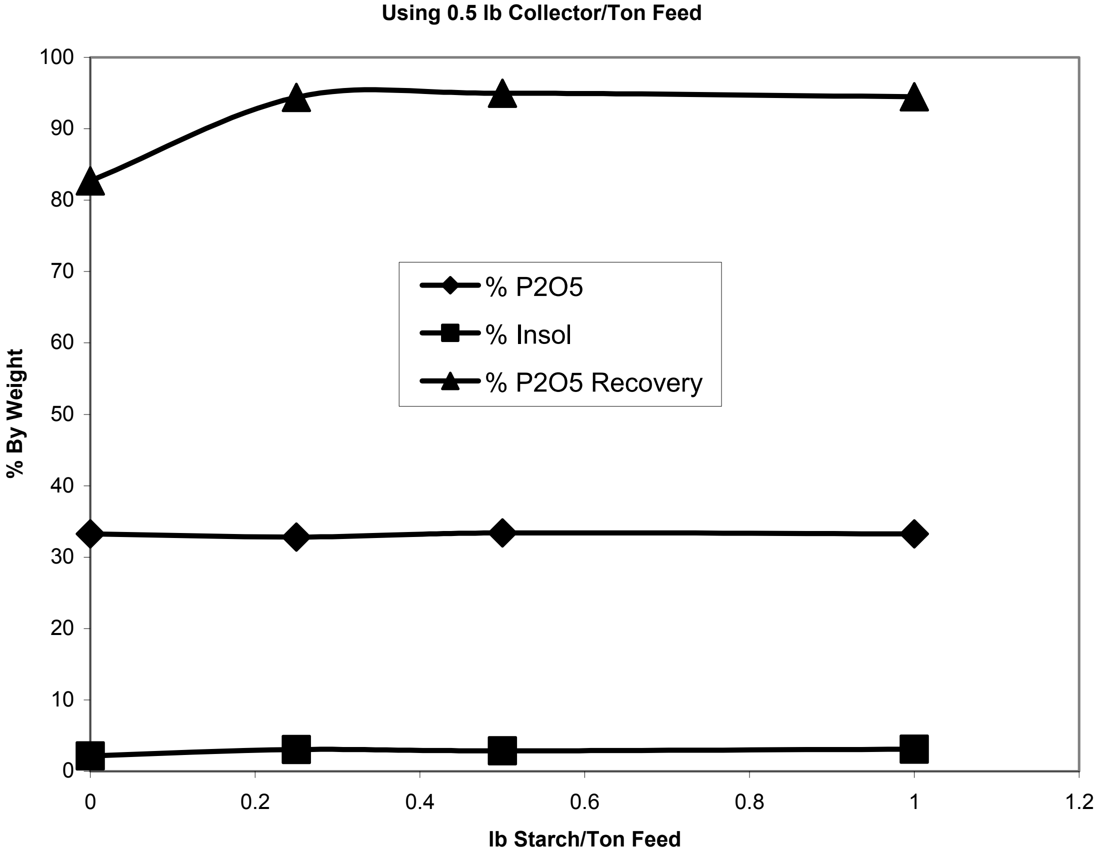


Figure 12b. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

Figure 13 presents flotation performance curves using STPP depressant that are very similar to those previously obtained using starch as the phosphate depressant. P_2O_5 recoveries ranged from about 95-96% for nearly all levels of STPP and amine collector tested. Using 0.25 lb. of STPP per ton of feed, concentrates analyzed 32.85% P_2O_5/ 2.90% insol at 95.1% P_2O_5 recovery using the lower amine level and 32.86% P_2O_5/ 3.20% insol at 96.1% P_2O_5 recovery using the higher amine level. The small difference in results obtained using the different collector levels is believed to be insignificant and probably was caused by experimental and/or analytical error. Using higher STPP addition levels had practically no positive or negative effect on subsequent flotation performance when either the higher or lower amine level was used.

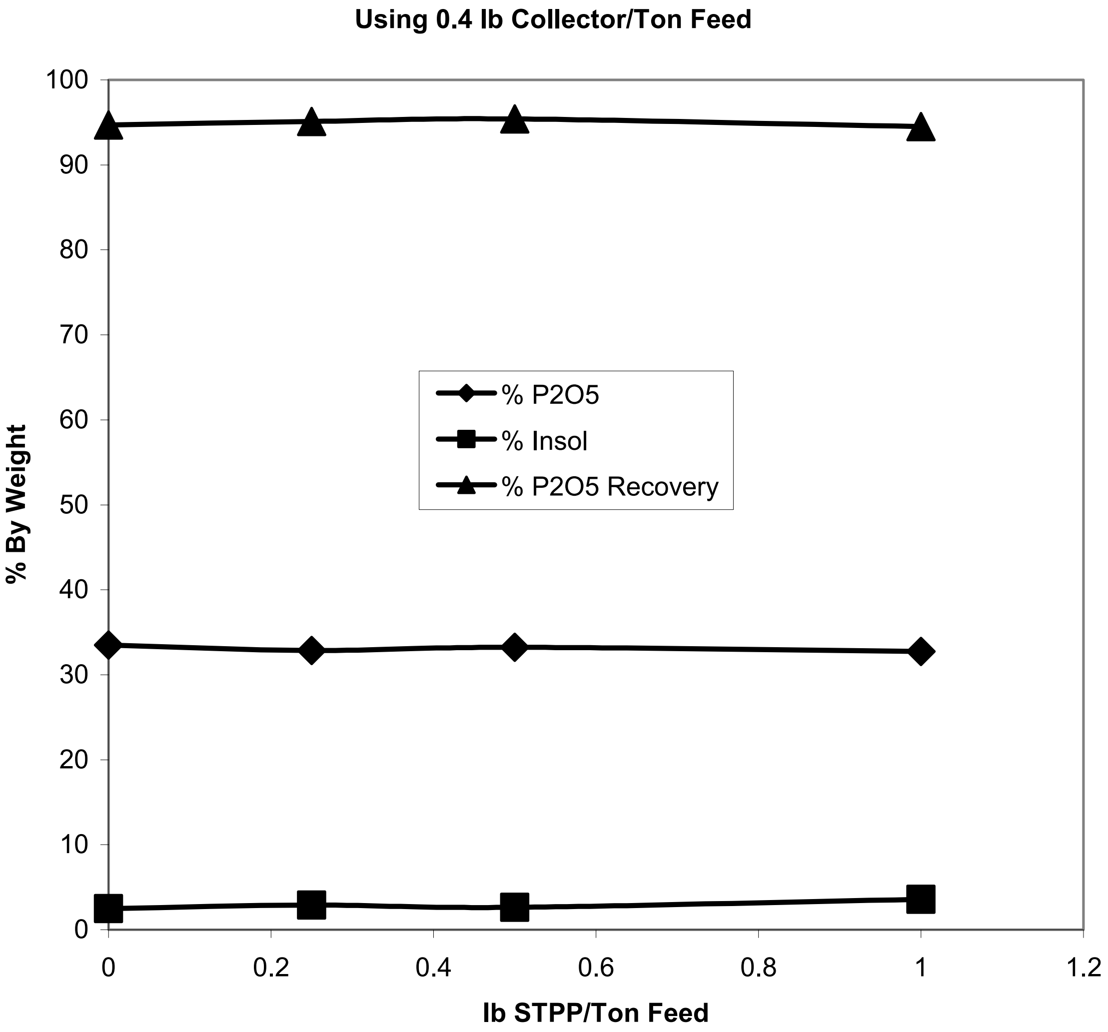


Figure 13a. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

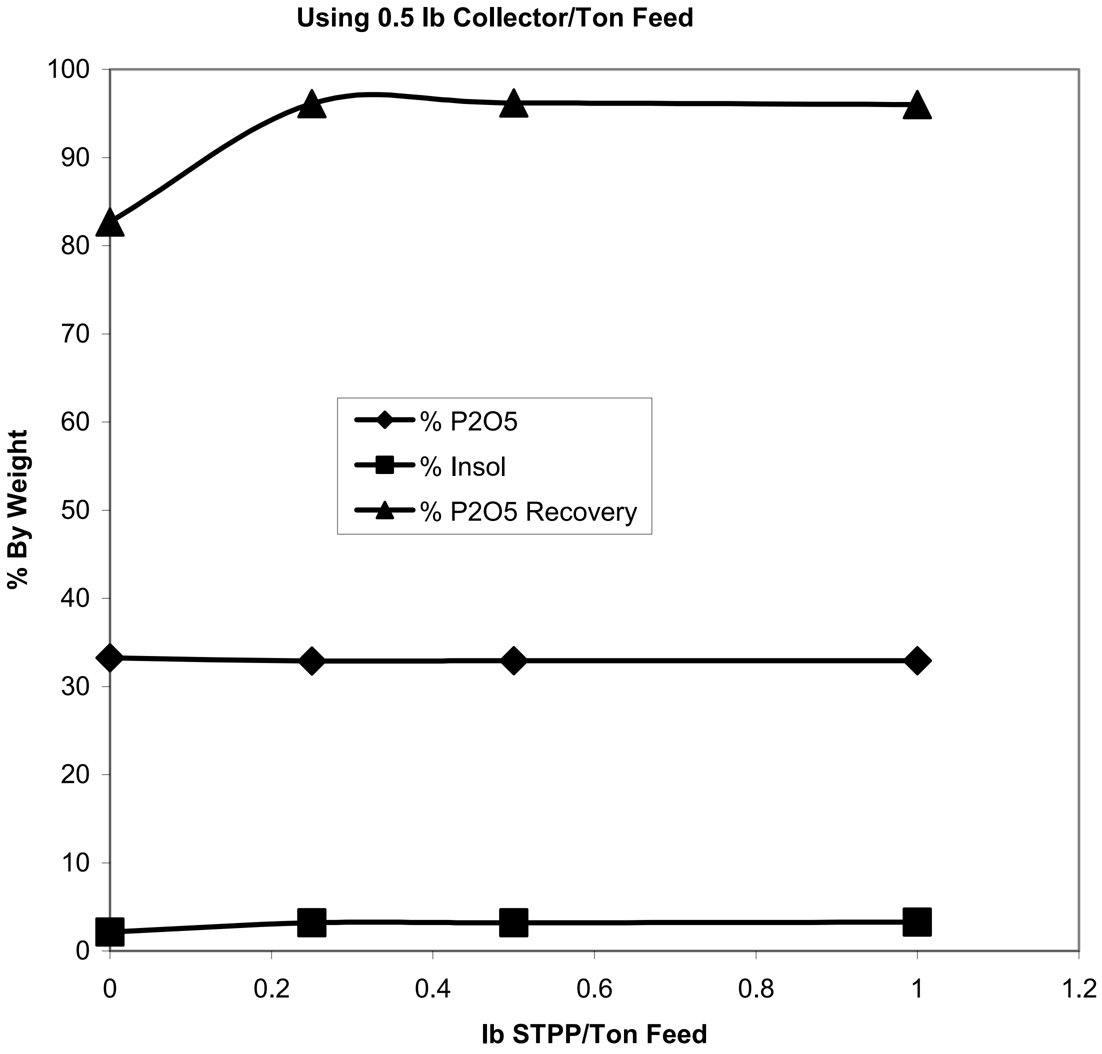


Figure 13b. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Figure 14 shows that diphosphonic acid used at the 0.25 lb. per ton of feed level was an effective phosphate depressant and resulted in P_2O_5 recoveries exceeding 95%. Concentrates analyzed 32.85% P_2O_5/3.47% insol at 97.0% P_2O_5 recovery using the lower amine level and 33.48% P_2O_5/2.68% insol at 95.3% P_2O_5 recovery using the higher amine level. Similar to when starch was used, the use of diphosphonic acid greatly reduced the 12% P_2O_5 recovery loss (experienced when amine level was increased from 0.4 to 0.5 lb per ton of feed) that occurred when no depressant was used and did not adversely effect final concentrate grade. However, when the diphosphonic acid level was increased above 0.25 lb. per ton of feed, concentrate grade decreased using either collector level.

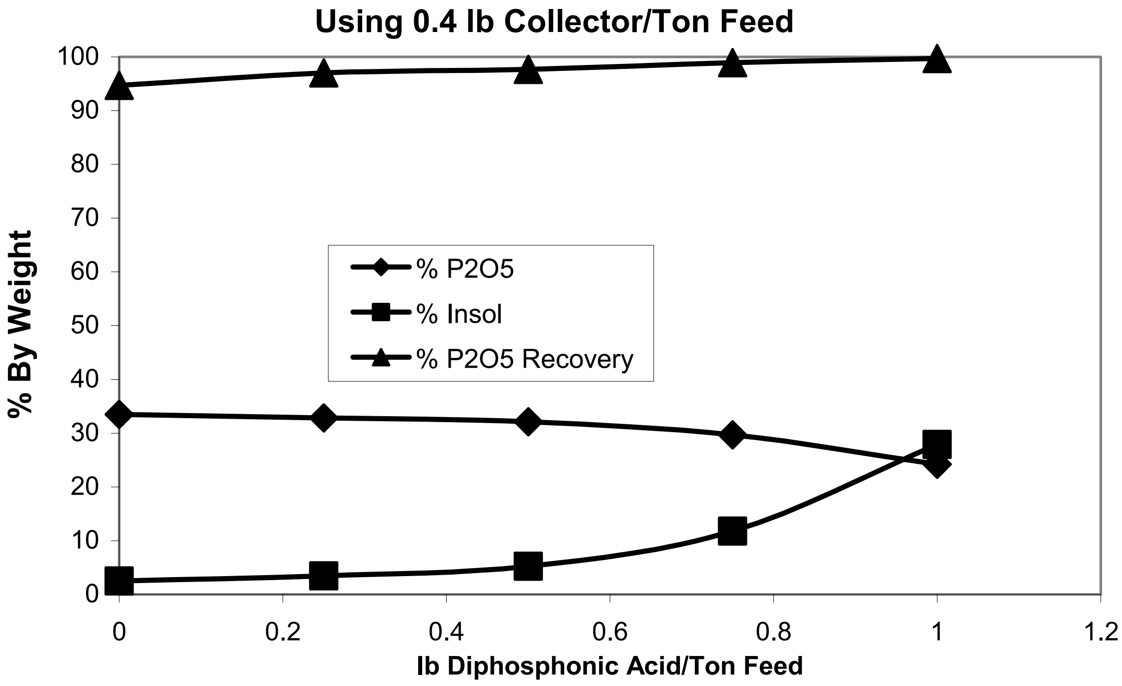


Figure 14a. Flotation Concentrate Grade/Recovery Using Various DPA Levels.

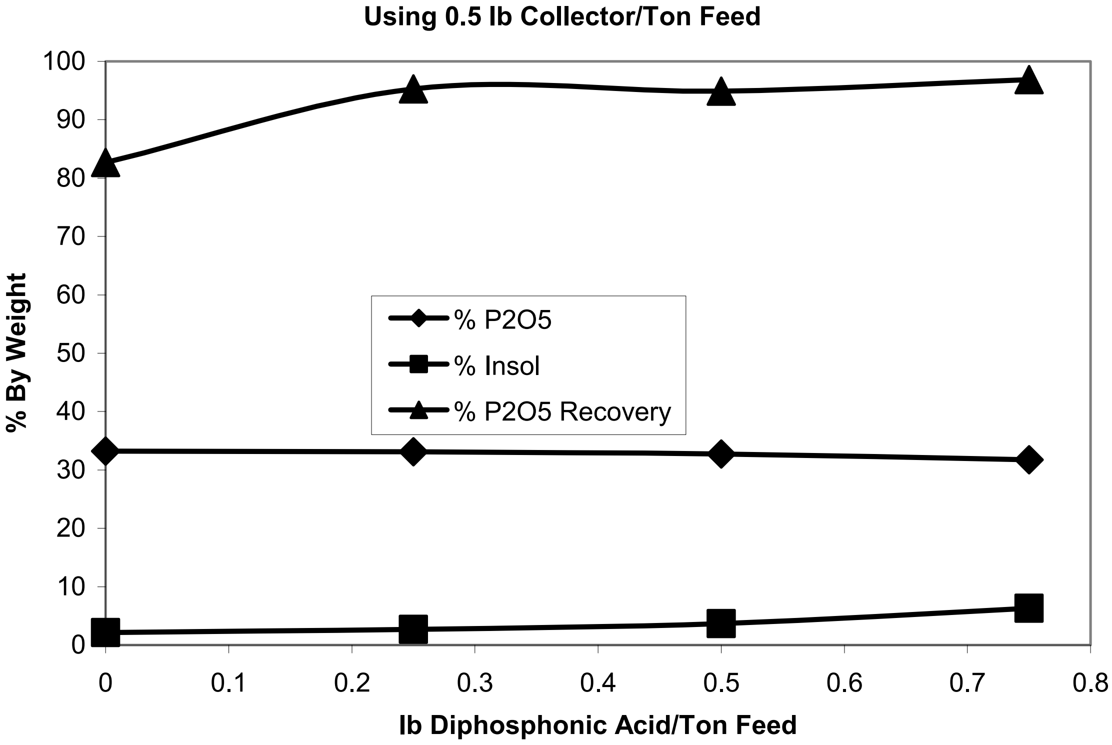


Figure 14b. Flotation Concentrate Grade/Recovery Using Various DPA Levels.

Figures 15 and 16 indicate that fluosilicic acid and orthophosphoric acid failed to perform as selective phosphate depressants using the lower collector level. Concentrate % P_2O_5 recovery decreased with very little change in % P_2O_5 when either of these acids were used compared to no depressant addition results. Using fluosilicic acid at the highest addition level, a 4.1% P_2O_5 recovery loss resulted. Using orthophosphoric acid at the highest addition level, a 7.9% P_2O_5 recovery loss occurred. Further reducing the collector level to only 0.3 lb. per ton of feed (tests KA34 and KA35) when 0.5 lb. per ton of fluosilicic acid or orthophosphoric acid was used resulted in poor concentrates analyzing 10% insol or higher.

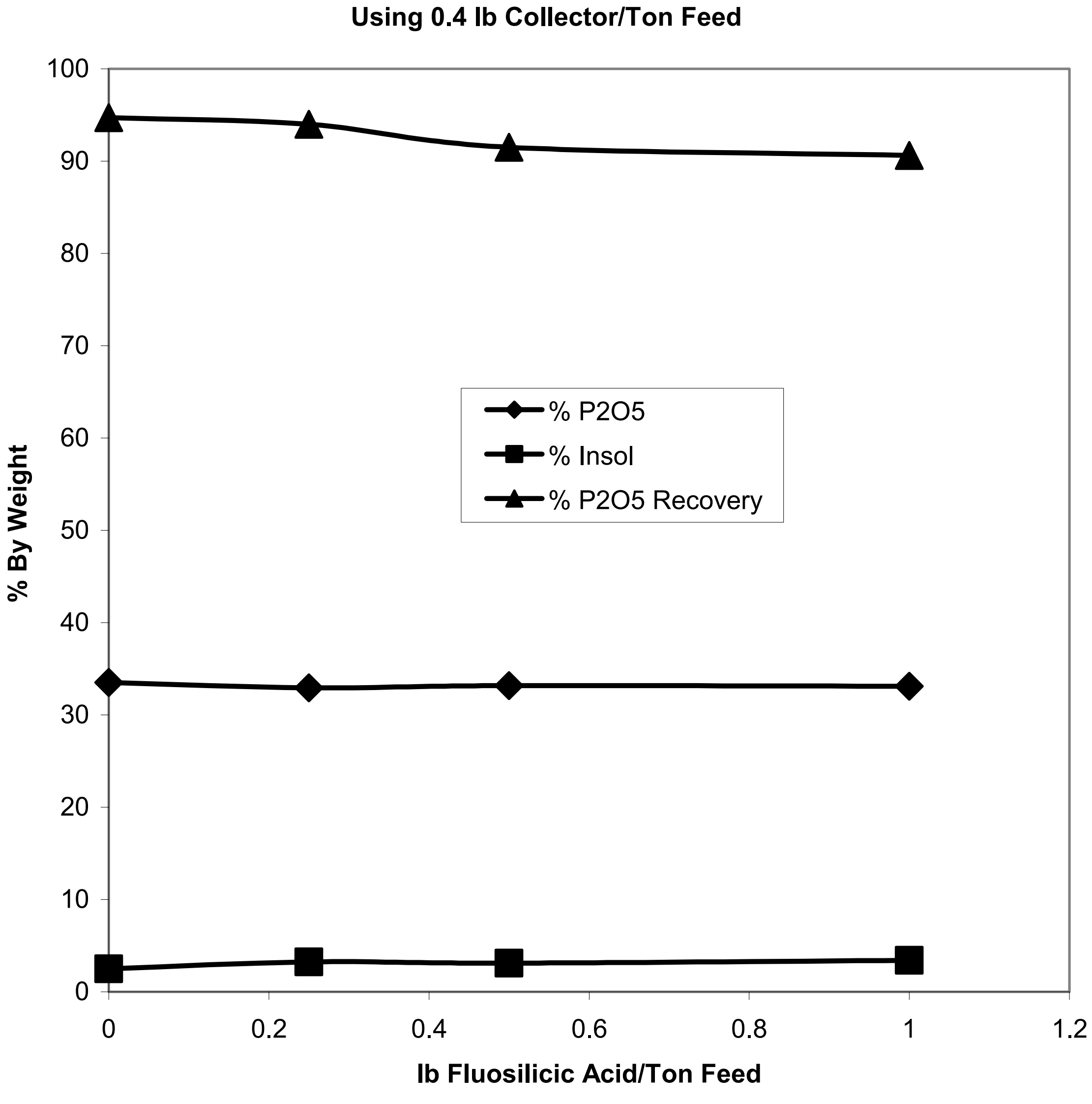


Figure 15. Flotation Concentrate Grade/Recovery Using Various FSA Levels.

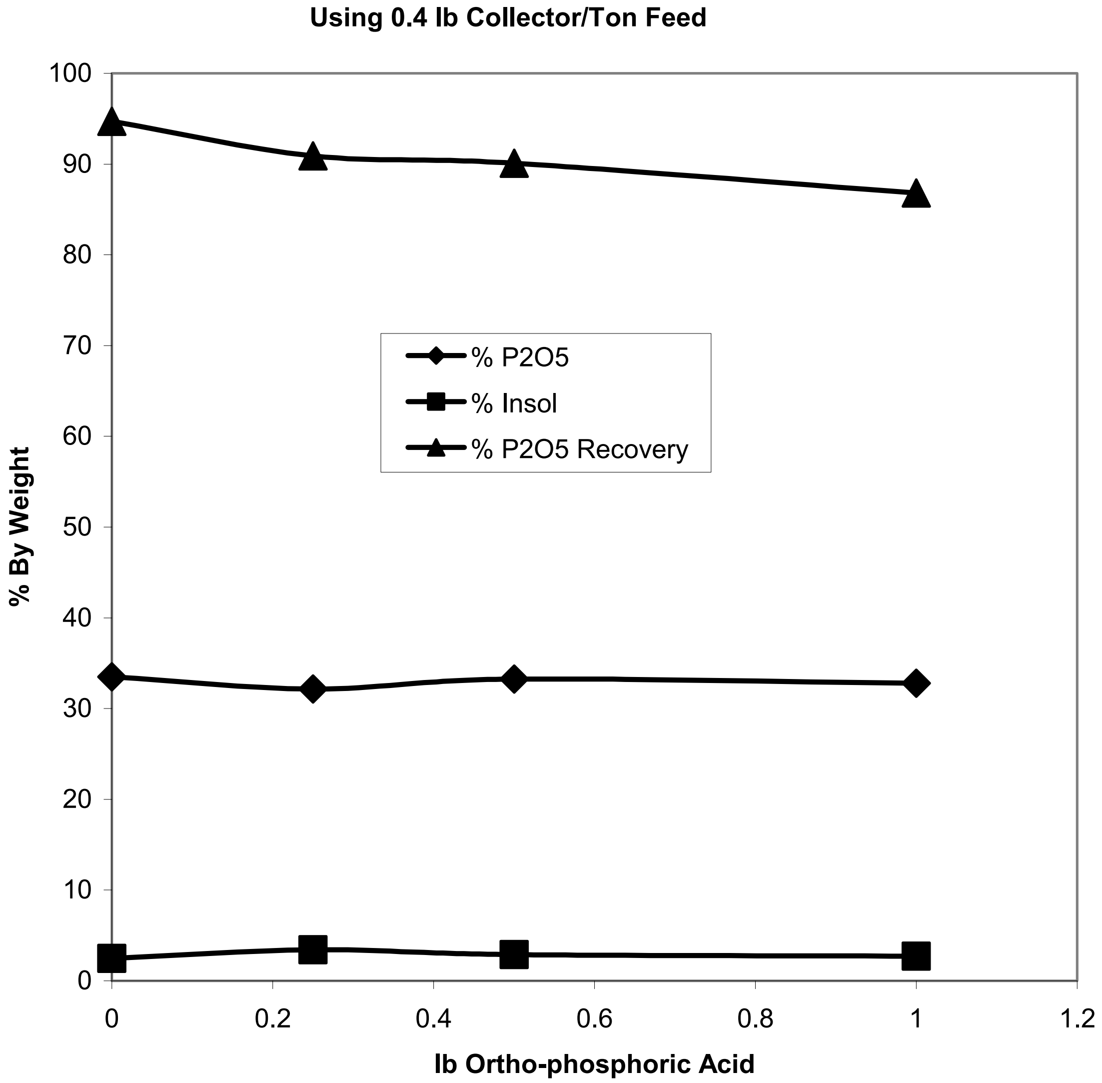


Figure 16. Flotation Concentrate Grade/Recovery Using Various OPA Levels.

The effect of conditioning pH on flotation response was briefly investigated with no depressant addition. Figure 17 presents the flotation response for the pH range 5.9-8.5. Changing the "natural" initial flotation pH (7.3) to the higher level (8.5) increased % P_2O_5 recovery using either the lower or the higher collector level. However, concentrate % P_2O_5 decreased as the pH was increased unless the higher collector level was used—a possible indication of partial amine precipitation at higher alkalinity. Decreasing the pH from 7.3 to 5.9 resulted in a lowering of % P_2O_5 recovery, particularly using the higher collector level, while the concentrate % P_2O_5/% insol was not adversely affected.

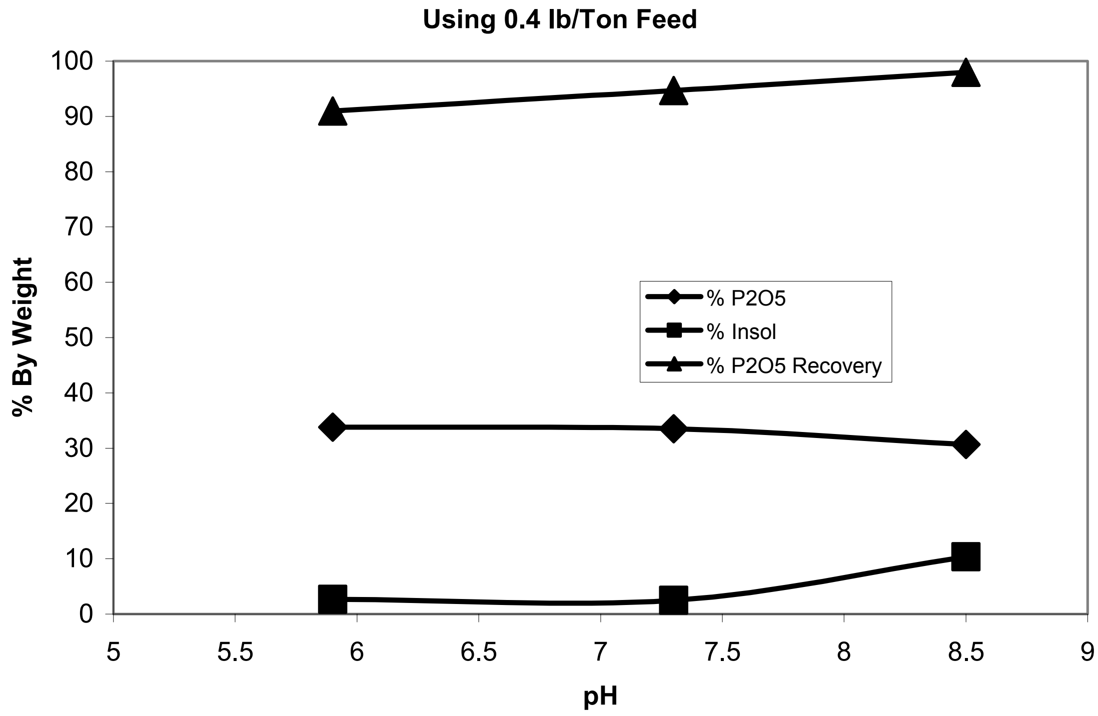


Figure 17a. Flotation Concentrate Grade/Recovery Using Various pH Levels.

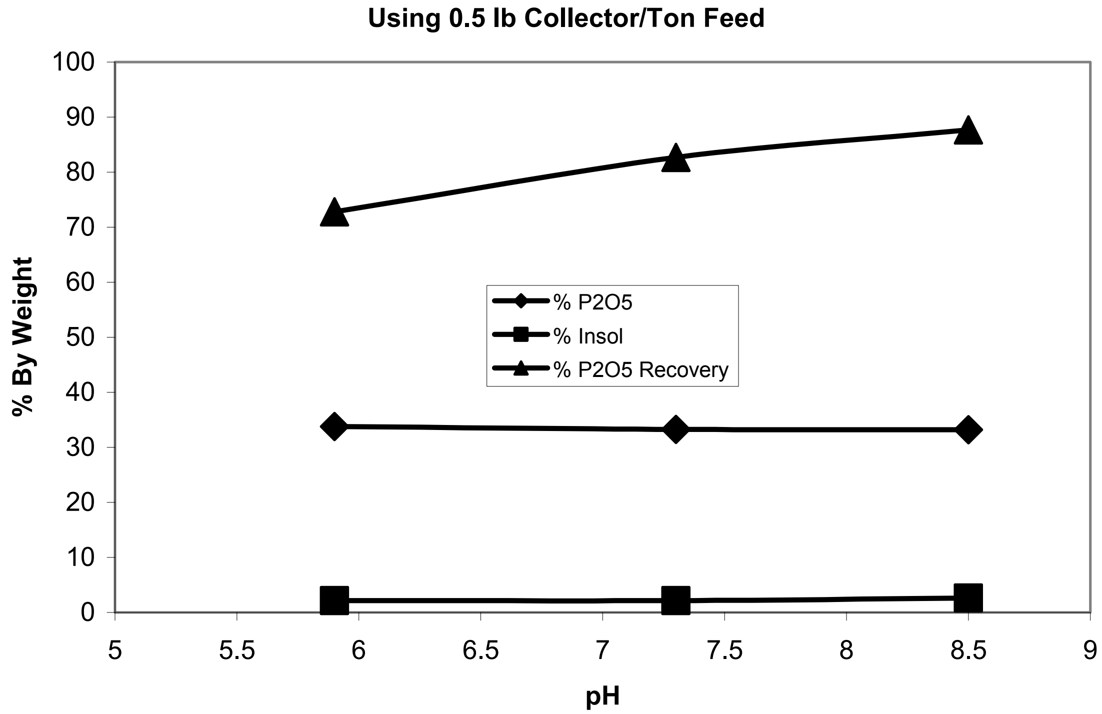


Figure 17b. Flotation Concentrate Grade/Recovery Using Various pH Levels.

Figure 18 presents a concentrate % P_2O_5 vs. % P_2O_5 recovery diagram for all flotation tests performed with and without depressant addition. The slight superiority of starch, as indicated by the boundary curve, over STPP and diphosphonic acid is apparent.

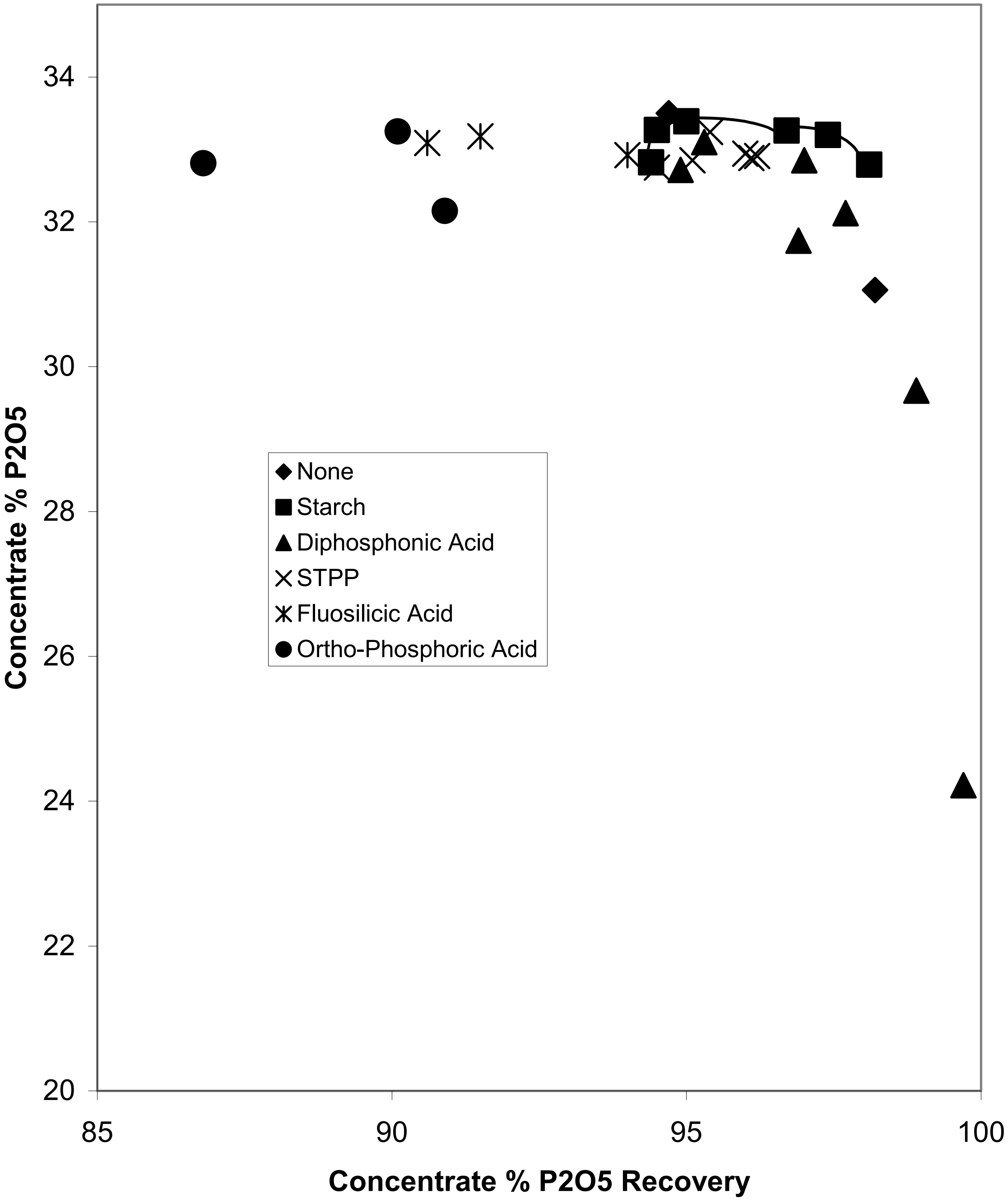


Figure 18. Flotation Concentrate Grade/Recovery for All Tests.

DEVELOPMENT OF THE ALL-CATIONIC FLOTATION PROCESS

SUMMARY

The development of an all-cationic flotation process for upgrading Florida phosphate has been an interesting concept since the 1950s. The process has been rejected by industry in past years for two primary reasons:

- The reagent cost was excessive compared to the conventional Crago double-float process.
- Clay slimes in the Bone Valley type flotation feed interfered with the initial cationic flotation stage at times and resulted in high amine reagent consumption.

Also, phosphate producers were not interested in making drastic changes in flotation plants actively producing concentrates at a profit with many years of remaining plant life expectancy.

From the late 1950s throughout the 1960s amine reagents cost about \$0.30-\$0.35/lb., and soap/tall oil cost about \$0.025-\$0.050/lb. The ratio of amine cost to tall oil cost per pound was about 8-10:1. Currently, amines can be purchased for about \$0.24/lb. and tall oil costs at least \$0.10-\$0.12/lb. The ratio of amine cost to tall oil cost per pound is currently only about 2-3:1. Fuel oil price increases since the 1960's have also added significantly to conventional rougher flotation reagent costs. The concept behind the testwork performed in this project consists of using a relatively inexpensive amine condensate, with or without a suitable phosphate depressant, to float fine quartz from 14/150 mesh "unsized" feed, followed by (1) sizing the cell underflow product at 35 mesh and (2) subjecting the two size fractions (coarse and fine feeds) to second-stage cationic flotation using higher-quality cationic reagent systems including phosphate depressants to reject the remaining quartz sand and produce final concentrates analyzing at least 30-31% P_2O_5.

Potential advantages of this process include:

(1) Coarse phosphate in the flotation feed that results from screen leaks, improper sizing, etc. is not lost during rougher flotation since the phosphate is never required to float.
(2) No vertical conditioners are required for rougher feed reagentizing. Only the second-stage coarse feed fraction requires high % solids conditioning using preferably a rotary drum unit.
(3) No acid scrub and wash circuit is required to de-oil the rougher concentrate. The result is a power, maintenance and acid cost elimination from the flotation process.

(4) Large quantities of fuel oil are not required in the initial prefloat stage that requires an amine condensate, some diesel fuel and probably starch depressant for optimum flotation.
(5) Smaller feed sizing sections are needed since only the second-stage flotation feed (about 30-55% of the unsized feed) requires sizing before flotation.
(6) Spirals or belt separators are not needed to process the coarse (14/35 mesh) feed size.
(7) Plant return water circuitry could possibly be simplified since all flotation circuits use only cationic reagents with diesel fuel and depressants.
(8) Suitable cationic collectors could most probably be produced from vegetable oil fatty acid blends with tall oil thereby reducing the demand for tall oil in times of supply shortage.
(9) New plant capital investment conceivably could be lower using the All-Cationic process.

Potential disadvantages of the All-Cationic process flowsheet include:

(1) Phosphate producers could be at the mercy of cationic reagent producers.
(2) The processing reagent costs could increase drastically if feed desliming and water clarification are not properly performed at all times.

EXPERIMENTAL

Flotation Feeds

Most of the flotation feeds tested are unsized, and were collected from operating plants. Generally, the feeds were rinsed to remove slimes before they were subjected to flotation. Tables 5 and 6 show size distribution and the basic chemical properties of the four feeds. These feeds vary significantly both in physical and chemical characteristics.

Table 5. Size (Mesh) Distribution (Wt. %) of the Flotation Feeds.

Sample ID	+20	20/28	28/35	35/150	-150
Plant A Fine	1.3	3.3	10.2	83.7	1.5
Plant A Coarse	4.7	6.1	15.6	73.1	0.5
Plant B	3.0	3.1	7.8	82.6	3.5
Plant C	1.9	2.0	4.8	83.9	7.4
Spiral Feed	31.4	20/35m 56.1	---	-35m 12.5	---

Table 6. Chemical Analysis of the Flotation Feeds.

Sample ID	% P_2O_5	% Insol
Plant A Fine	9.26	70.60
Plant A Coarse	9.44	70.45
Plant B	5.43	83.49
Plant C	8.43	74.80
Spiral feed	19.82	40.28

Flotation Reagents

Flotation reagents used in both prefloat and the second-stage fine flotation included an amine condensate, a starch and diesel fuel. The reagent scheme in the second-stage coarse flotation included a quaternary amine, a frother, Tergitol NP-10, sodium tripolyphosphate (STPP) and Philflo oil. Bartow tap water was utilized in all the tests. Current prices of these reagents are listed in Table 7.

Table 7. Reagent Prices.

Reagent Name	Cost ($/lb)
Westvaco CCD-2112 starch	0.20
Azamine 36A	0.24
Diesel fuel	0.15
Sodium tripolyphosphate	0.49
Arquad 2HT-75	0.86
Philflo oil	0.15
Tergitol NP-10	0.59

Flotation

All the flotation tests were conducted in a standard one-liter Denver cell with a charge of about 500 g dry feed.

Initial Amine Prefloat Testwork

The primary objective of the amine prefloat tests performed was to reject 70% weight or more of quartz tailings to yield an upgraded cell underflow product (prefloat concentrate) analyzing less that 50% insol at a P_2O_5 recovery exceeding 94%. A typical amine condensate collector (Azamine 36A) was used at a 1:1 ratio with diesel fuel as the quartz collector with and without causticized starch as the phosphate depressant.

Flotation of 35/150 Mesh Fine Prefloat Concentrate

The prefloat concentrate was sized at 14 and 35 mesh to obtain a mini-pebble (+14 mesh), a fine (14x35) and a coarse (35x150) second-stage flotation feeds. The +14 mesh material would be blended with the final flotation concentrate. The fine prefloat concentrate was floated at various levels of starch and Azamine 36A (1:1 ratio with diesel fuel). Concentrates analyzing >30% P_2O_5 and insol of 3-8 were considered satisfactory.

Flotation of 14/35 Mesh Coarse Prefloat Concentrate

Second-stage "Q" flotation tests were performed on the coarse prefloat concentrate using two STPP depressant levels with various levels of Arquad 2HT-75 (1:3 with Philflo oil) and 0.05 lbs. of Tergitol NP-10 frother per ton of coarse feed. Conditioning for 15 seconds at 72% solids was used for all tests.

RESULTS AND DISCUSSION

Initial Amine Prefloat Testwork

Table 8 summarizes the prefloat conditions and metallurgical performance on different feeds in producing the prefloat concentrates. In each case, the major objective was met, but amine consumption was higher for coarser feeds or the feeds with more slimes.

Table 8. Cationic Bulk Silica Prefloat Material Balance for Different Feeds.

Feed and Reagent Dosage	Product	% Wt.	% P_2O_5	% Insol	% P_2O_5 Distribution
Plant A Feed #1	Amine Tail	56.5	0.83	93.02	4.9
1 lb/TOF amine	Amine Conc.	43.5	20.87	35.86	95.1
lb/TOC starch					
Plant A Feed #2	Amine Tail	56.9	0.92	96.88	5.3
1.4 lb/TOF amine	Amine Conc.	43.1	22.67	30.32	94.7
0.2 lb/TOC starch					
Plant B Feed	Amine Tail	75.4	0.35	98.54	4.6
0.7 lb/TOF amine	Amine Conc.	24.6	21.78	35.75	95.4
0.4 lb/TOC starch					
Plant C Feed with 1.2	Amine Tail	67.8	0.84	96.80	6.5
lb/TOF amine and no starch	Amine Conc.	32.2	25.55	26.15	93.5

Flotation of Fine Prefloat Concentrate

Figure 19 demonstrates the effect of amine dosage on concentrate grade and BPL recovery in the second-stage flotation of the fine prefloat concentrate from plant A feed. Recovery of above 95% could be achieved with a satisfactory concentrate. Since the coarse feed from plant A contains more slime, the effect of scrubbing was tested. As indicated in Table 9, scrubbing reduced amine use dramatically with improved concentrate grade.

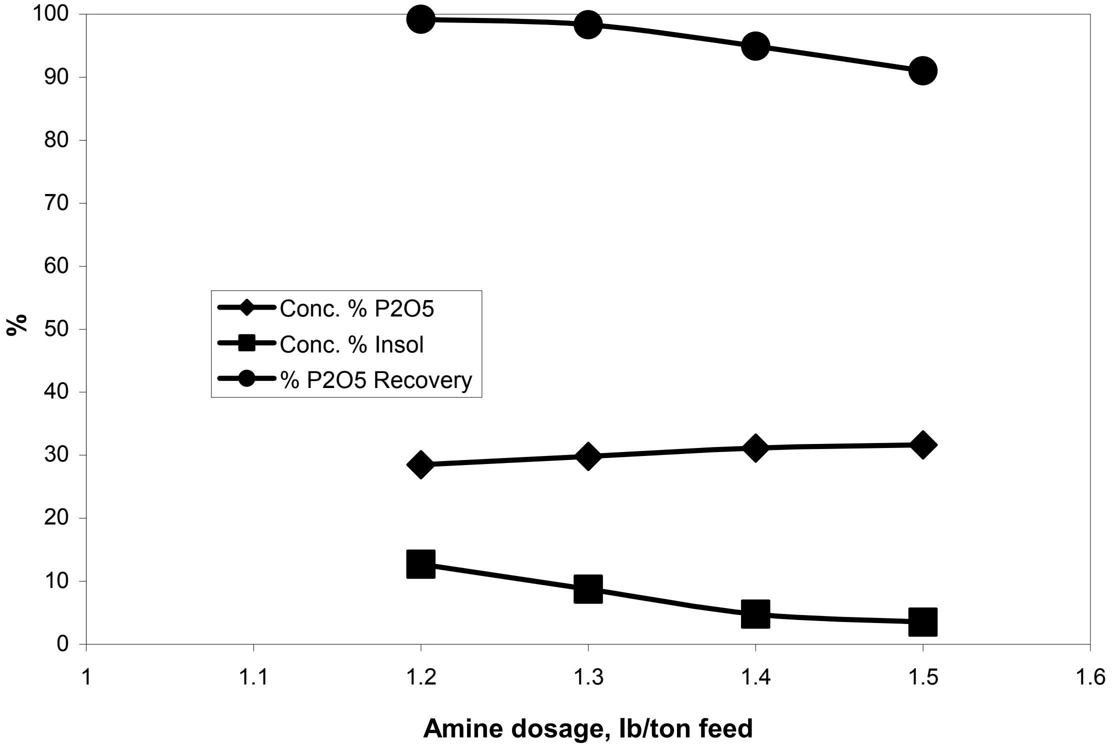


Figure 19. Effect of Amine Dosage on the Final Concentrate Grade and Recovery.

Table 9. Effect of Amine Dosage on Concentrate Grade and BPL Recovery for the 35/150 Mesh Fraction of the Prefloat Concentrate from Plant A Coarse Feed at 0.4 Lb of Starch per Ton of Feed.

Amine Dosage lb/TOF	Concentrate % P_2O_5	Concentrate % Insol	% BPL Recovery
<u>With Scrubbing</u>			
0.8	31.50	2.23	97.6
1.0	31.73	1.97	96.4
1.2	31.63	2.58	91.1
<u>No Scrubbing</u>			
1.4	29.03	11.60	99.4
1.6	30.75	5.49	97.0

As is shown in Tables 10 and 11, scrubbing had the similar effect on the fine fractions of prefloat concentrates from feeds taken from plants B and C.

Table 10. Effect of Amine Dosage on Concentrate Grade and BPL Recovery for the 35/150 Mesh Fraction of the Prefloat Concentrate from Plant B Feed.

Amine Dosage lb/TOF	Concentrate % P_2O_5	Concentrate % Insol	% BPL Recovery
Without Starch			
0.8	27.7	18.49	92.6
1.2	32.47	3.89	88.1
1.4	31.58	6.49	81.0
With 0.4 lb/TOC Starch			
1.4	31.78	4.5	91.9
1.6	32.22	3.79	72.2

Table 11. Effect of Amine Dosage on Concentrate Grade and BPL Recovery for the 35/150 Mesh Fraction of the Prefloat Concentrate from Plant C Feed.

Amine Dosage lb/TOF	Concentrate % P_2O_5	Concentrate % Insol	% BPL Recovery
Without Starch			
0.6	31.33	9.83	97.3
0.8	32.90	4.65	91.6
With 0.4 lb/TOC Starch			
0.8	31.72	7.18	97.8
1.0	32.64	5.00	96.8

Flotation of Coarse (14x35 Mesh) Prefloat Concentrate

Figure 20 shows the effect of quaternary amine on the coarse fraction for plant A feed. Since quaternary amine is expensive, one should probably focus on recovery, not the grade, in this step.

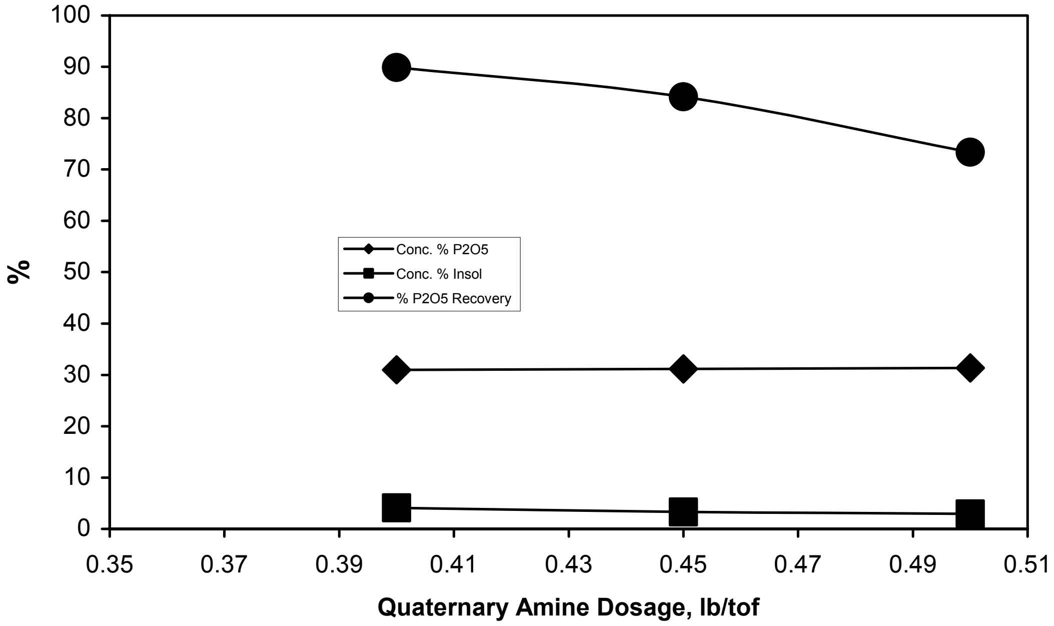


Figure 20. Effect of Quaternary Amine on Coarse Flotation.

Figure 21 indicates the effect of quaternary amine dosage on the coarse prefloat concentrate from Plant B feed. Again, improving concentrate grade was costly.

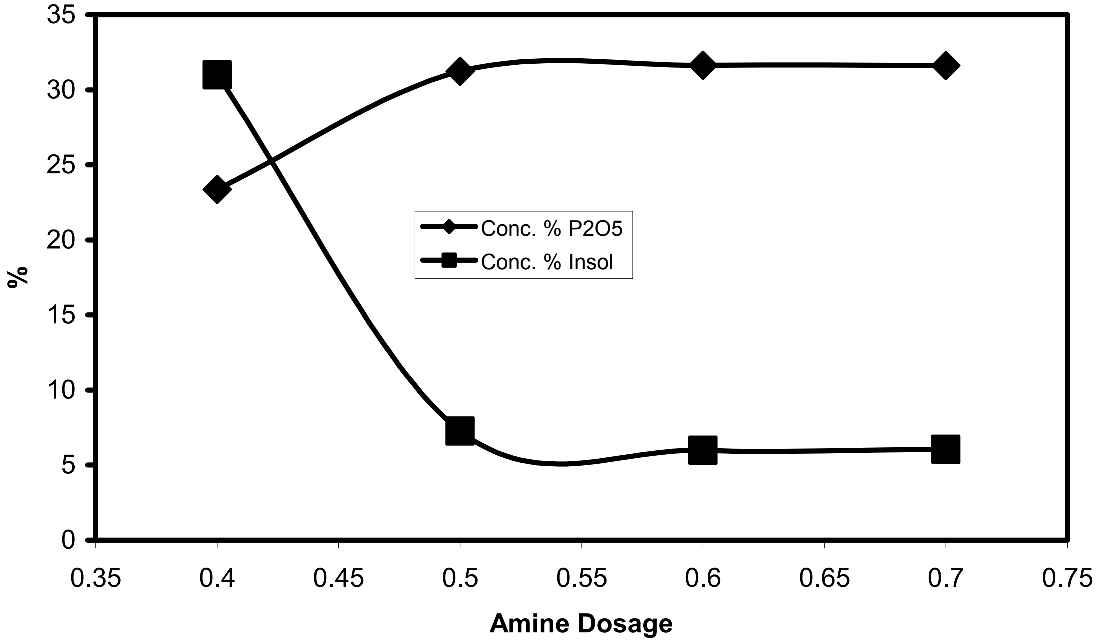


Figure 21. Effect of Quaternary Amine Dosage on Flotation of the Coarse Fraction of Prefloat Concentrate from Plant A Feed.

Effect of scrubbing on concentrate grade and recovery from the 14/35 mesh fraction of the prefloat concentrate of Plant A coarse feed is shown in Table 12. Table 13 indicates again that the cost is substantial to reduce concentrate insol by a few percentage points.

Table 12. Effect of Quaternary Amine Dosage on Concentrate Grade and BPL Recovery for the 14/35 Mesh Fraction of the Prefloat Concentrate from Plant A Coarse Feed at 1 Lb. of STPP per Ton of Feed.

Amine Dosage lb/TOF	Concentrate % P_2O_5	Concentrate % Insol	% BPL Recovery
With scrubbing			
0.6	31.13	2.96	89.9
0.8	30.95	3.09	82.3
No scrubbing			
1.0	26.2	19.04	98.2
1.4	27.9	13.73	96.2

Table 13. Effect of Quaternary Amine Dosage on Concentrate Grade and BPL Recovery for the 14/35 Mesh Fraction of the Prefloat Concentrate from Plant C Coarse Feed at 1 Lb of STPP per Ton of Feed.

Amine Dosage lb/TOF	Concentrate % P_2O_5	Concentrate % Insol	% BPL Recovery
0.6	30.95	10.68	93.5
0.8	32.64	5.38	92.8

It should be mentioned that the All-Cationic process performed particularly well on a spiral feed, generating concentrates analyzing 30.6-32.3% P_2O_5 and 7.4-10.9% insol.

Cost of the Process

Based on the prices listed in Table 3, the overall reagent costs and typical metallurgical performance for different feeds are summarized in Table 14. These costs seem to be higher than most of the current industrial operations. However, they don't take into account the savings in sizing, acid scrubbing, conditioning, etc.

Table 14. Overall Comparison for Different Feeds.

Feed	Total Conc. % P_2O_5	Total Conc. % Insol	Total BPL Recovery	Cost ($/TOC)
Plant A #1Scenario I	31.03	4.77	88.96	2.391
Plant A #1 Scenario II	31.47	3.73	85.91	2.538
Plant A #2 Scenario I	31.09	3.35	91.91	2.836
Plant A #2 Scenario II	30.63	5.37	91.57	2.981
Plant B Scenario I	31.93	5.44	78.97	3.494
Plant B Scenario II	31.50	5.76	81.37	3.439
Plant C Scenario I	32.61	5.14	91.30	2.541
Plant C Scenario II	31.58	7.80	92.21	2.780
Spiral Scenario I	30.61	10.88	96.5	0.782
Spiral Scenario II	32.31	7.42	94.5	1.515

Conclusions

The All-Cationic flotation process is technically feasible for all the feeds tested. The reagent cost is somewhat higher than most of the current operations. However, savings in conditioning, acid wash and sizing should warrant a detailed economic analysis on the process. The process will certainly be more promising as the fatty acid price increases. The process is definitely more environmentally friendly than the present operation. This process requires minimal changes in an existing processing plant.

Slime content in the flotation feed makes a difference in amine consumption in the first stage flotation of fine silica for this process. All the tests were conducted using Bartow tap water. It is expected that the amine consumption may be higher using plant water.

Starch may be the optimal phosphate depressant for floating fine silica, while STPP is the best choice for coarser feed.

Sizing after prefloat is essential for reducing the overall reagent consumption and maximizing phosphate recovery. The sizing scheme tested so far may not be the optimal approach

PART II. SCREENING OF PHOSPHATE DEPRESSANTS FOR DOLOMITE/PHOSPHATE SEPARATION

SCREENING OF PHOSPHATE DEPRESSANTS FOR DOLOMITE/PHOSPHATE SEPARATION

SUMMARY

Numerous phosphate mineral depressants have been reported in the literature for use during anionic flotation of dolomite from carbonate fluorapatite in slightly acid circuits. The laboratory tests described in this report are intended to compare the effectiveness of several of the reported depressants to process rodmilled, deslimed high-MgO Florida phosphate pebble from the southern mining area's Four Corners reserves currently mined and processed by IMC/Agrico. In order to minimize the detrimental effects of hard water on flotation efficiency using fatty acids or their soaps, sulfonated oleic acid soap (plus oil) was used as the dolomite collector for all tests. The use of this collector is described in U.S. patents 4,364,824 (12/21/82) and 4,372,843 (2/8/83) assigned to International Minerals and Chemical Corporation.

Ten potential phosphate depressants were evaluated during laboratory anionic flotation of dolomite from phosphate in a slightly acid circuit using a sulfonated oleic acid soap plus oil as the dolomite collector. Eight of the depressants have been used by various investigators with foreign and domestic carbonate-phosphate ores, and the results were reported in numerous technical publications. The flotation feed used for this study was prepared by wet rodmilling and desliming Florida pebble (25.8% P_2O_5, 2.6% MgO) to yield a -48+325 mesh product (26.5% P_2O_5, 1.6% MgO) for testing. The -325 mesh grinding slimes (27.0% wt.) contained 23.6% of the total P_2O_5 and 54.5% of the total MgO present in the original pebble sample.

Four of the depressants were found to be reasonably effective during the current flotation study, namely: sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP), tetrasodium pyrophosphate (TSPP) and diphosphonic acid (DPA).

Without depressants, the sulfonate collector required to produce cell underflow phosphate products containing <0.80% MgO and MgO/ P_2O_5 ratio <.033 was 2.5 lbs./ton of flotation feed at a flotation pH range = 5.5-6.0. Using this collector level with 2-3 lbs./ton of feed of STPP, SHMP or TSPP yielded phosphate products analyzing 0.73-0.92% MgO and MgO/P_2O_5 ratios = .027-.034 at 90.0-96.8% P_2O_5 recovery. Similar grade phosphate products were obtained using DPA as the phosphate depressant at 84.1-87.5% P_2O_5 recovery. When no depressant was used, a similar grade phosphate product was obtained at only 65.9% P_2O_5 recovery.

Using orthophosphoric acid (OPA), disodium hydrogen phosphate (DSHP), starch, aluminum tartrate complex, or Alizarin Red S (ARS) as the potential phosphate depressant at the same collector level and pH range also yielded similar phosphate product grades, however P_2O_5 recovery was only 56.4-70.5%. Fluosilicic acid, when used at the 1 lb./ton of feed level at pH=5.5-6.0, yielded results very similar to those obtained using no depressant. Using this acid at the 1.5 lb./ton of feed level resulted in an

operating pH range of 4.1-4.6. At this lower pH range, best test phosphate products were obtained analyzing 0.91-1.04% MgO and MgO/P_2O_5 ratio = .033-.038 at 85.4-94.2% P_2O_5 recovery. These results are considered to be inferior to those obtained using STPP, SHMP or TSPP as the depressant at pH=5.5-6.0.

Flotation tests were performed in which dolomite was floated using Sulfonate OA-5R with STPP, SHMP and TSPP as the phosphate depressant followed by cationic flotation of the dewatered/washed cell underflow to reject silica and produce final phosphate concentrates suitable for chemical plant feed. These concentrates analyzed 30.5-31.3% P_2O_5, 1.4-2.6% insol, 0.80-0.91% MgO and MgO/P_2O_5 ratio = .026-.030 at 86.9-92.1% P_2O_5 recovery overall. The use of the phosphate depressants in the dolomite flotation stage did not appear to have any detrimental effect upon the cationic flotation stage.

Finally, three other sulfonated tall oil collectors were compared with Sulfonate OA-5R using STPP as the phosphate depressant at pH 5.5-6.0. These less pure (probably less expensive) collectors all exhibited good flotation selectivity but lower collecting strength compared to the standard Sulfonate OA-5R.

LABORATORY TESTWORK

Description of High-MgO Pebble Sample

A 97 lb. sample of Four Corners high-MgO pebble was obtained from the Noralyn metallurgical laboratory pile in July 1995. Chemical analysis of a cone and quarter sample of the pebble yielded the following composition: 25.77% P_2O_5, 9.55% insol, 2.56% MgO, with a MgO to P_2O_5 ratio of 0.099.

The bulk pebble sample was batch rodmilled (wet) in stages to -48 mesh and deslimed by pulping and decanting over a 325 mesh screen. The grinding/sizing material balance and chemical analyses of products were as follows:

Product	% Wt.	% P_2O_5	% Insol	%MgO
48/325 Feed	73.0	26.52	11.80	1.60
-325 slime	27.0	22.17	5.42	5.20

A total (dry basis) of 70.7 lbs. of flotation feed and 26.1 lbs. of rodmill slimes were produced.

Table 15 shows a standard wet/dry size-assay analysis of the -48+325 mesh flotation feed.

Table 15. Analyses of the High-Dolomite Sample Used for Depressant Screening.

Tyler Mesh	% Wt.	% P_2O_5	% Insol	% MgO	% Dist. MgO
65	23.7	27.1	12.34	1.30	19.4
65/100	27.9	27.03	12.62	1.60	28.1
100/150	17.4	26.74	13.00	1.70	18.1
150/200	12.0	27.23	11.22	1.60	11.9
200/325	12.6	27.92	9.99	1.60	12.5
-325	6.4	26.81	6.92	2.50	10.0

Other samples were also tested with the most promising phosphate depressants using the previous sample. Table 16 summarizes the analyses of these feeds.

Table 16. Chemical Analyses of Dolomitic Samples.

Feed	% P_2O_5	% MgO	% Insol
A	26.18	1.54	12.98
B	25.77	2.56	9.55
C	24.63	3.54	9.03
D	22.98	4.60	7.68

Flotation

Laboratory dolomite flotation tests were performed using Sulfonate OA-5R collector at levels ranging from 1.0-2.5 lbs. per ton of feed. Philflo oil, at a 1:2 ratio with the sulfonate collector, was used as a froth modifier/auxiliary collector. Sulfuric acid was used to maintain a flotation pH of 5.5-6.0 during the initial test series and about 4.9-5.3 during the second test series.

All reagents were added to the mixing flotation feed slurry (approximately 25% solids) in the 500 g laboratory Denver cell. The pH regulator was added first to obtain an initial pH of about 5.5 (or 4.9). Collector/oil was then added, and the slurry was conditioned for 1 minute before starting flotation. Flotation time was 3 minutes for all tests. Sulfuric acid (10%) was added throughout conditioning and flotation to maintain the target pulp pH ranges cited.

RESULTS AND DISCUSSION

Dolomite Flotation at Different pH and Collector Levels

Results from the initial flotation tests performed are presented in Figures 22a-22c. The initial pH test results were also plotted as concentrate % MgO, % P_2O_5 recovery and % MgO recovery vs. Sulfonate OA-5R levels used. Figure 22a shows that about 2.25-

2.50 lbs. of Sulfonate OA-5R collector per ton of feed were required to produce a phosphate concentrate containing less than 0.9% MgO. Test 2 produced a phosphate concentrate analyzing 26.3% P_2O_5, 0.78% MgO and MgO/P_2O_5 ratio = 0.030 at 65.9% P_2O_5 recovery when 2.5 lbs. of collector per ton of feed was used. Figure 22 shows that using the same collector level at the lower flotation pH range, flotation yielded a phosphate concentrate analyzing 27.3% P_2O_5, 1.00% MgO and MgO/P_2O_5 ratio = 0.037 at 82.9% P_2O_5 recovery. Using the lower pH conditions and the same collector level, P_2O_5 recovery was substantially improved at the expense of a higher concentrate % MgO. Essentially the same concentrate grade and P_2O_5 recovery was obtained with only 1.5 lbs. of collector using the higher pH range during conditioning/flotation. Consequently, the initial flotation tests comparing potential phosphate depressants were performed using 2.5 lbs.of Sulfonate OA-5R and a flotation pH = 5.5-6.0 to have the best chance of producing phosphate concentrates having MgO/P_2O_5 ratios of 0.030 or less. All concentrates and tailings were flocculated with polyacrylamide before dewatering and drying to minimize losses of -325 mesh particles. This procedure was used for all subsequent tests.

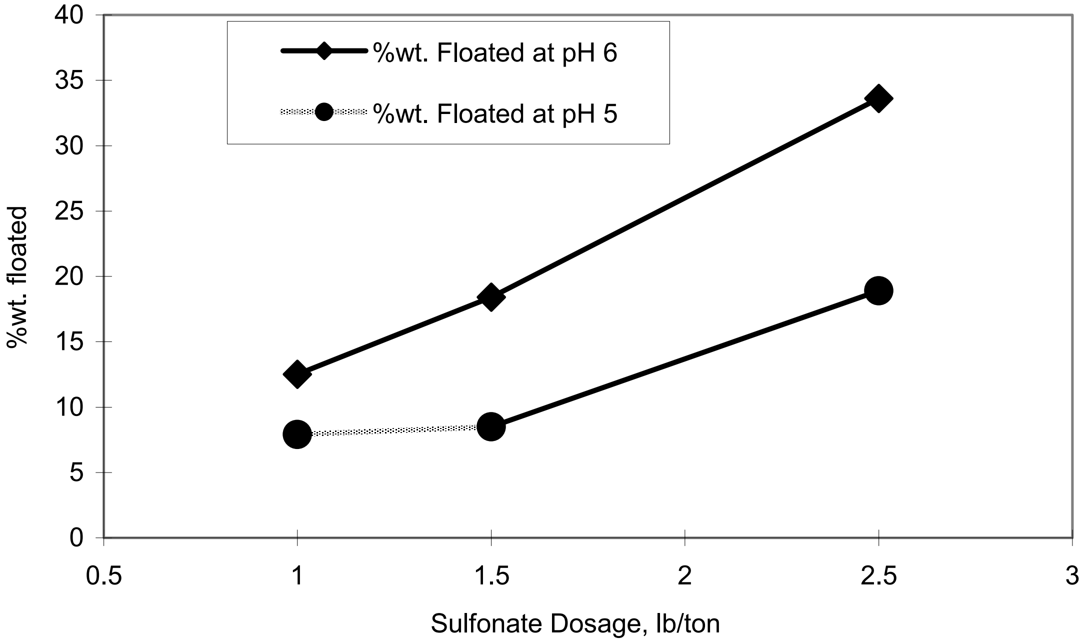


Figure 22a. Effect of Collector Dosage on the Amount Floated.

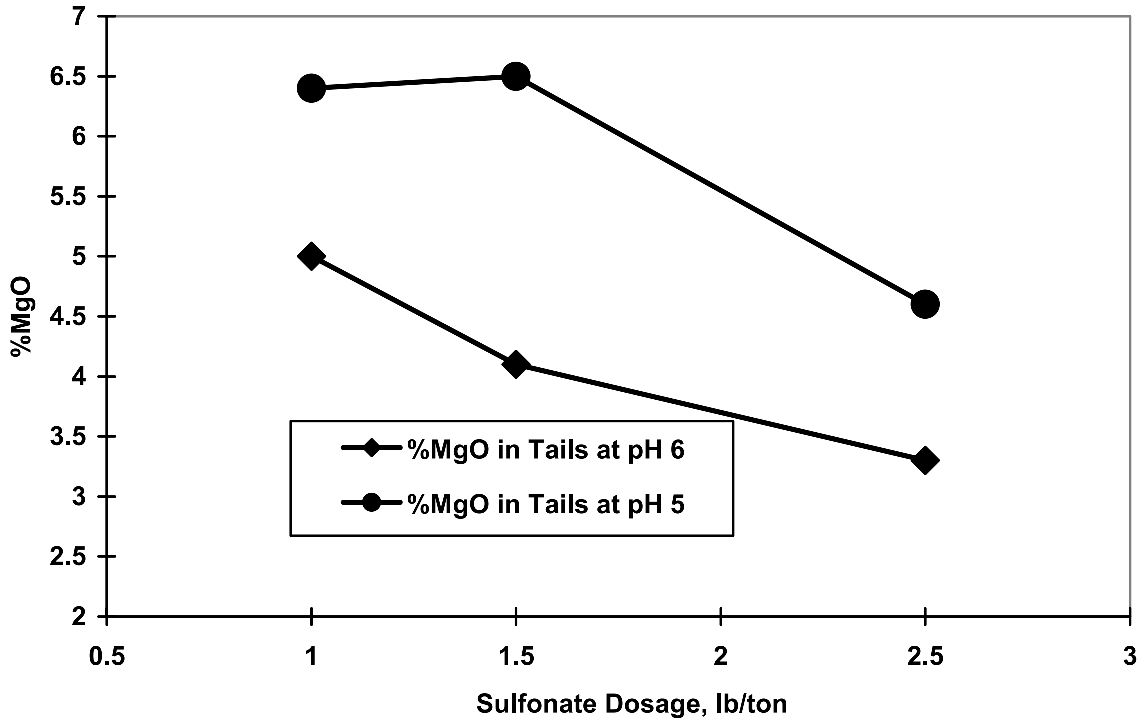


Figure 22b. Effect of Collector Dosage on MgO in Tails.

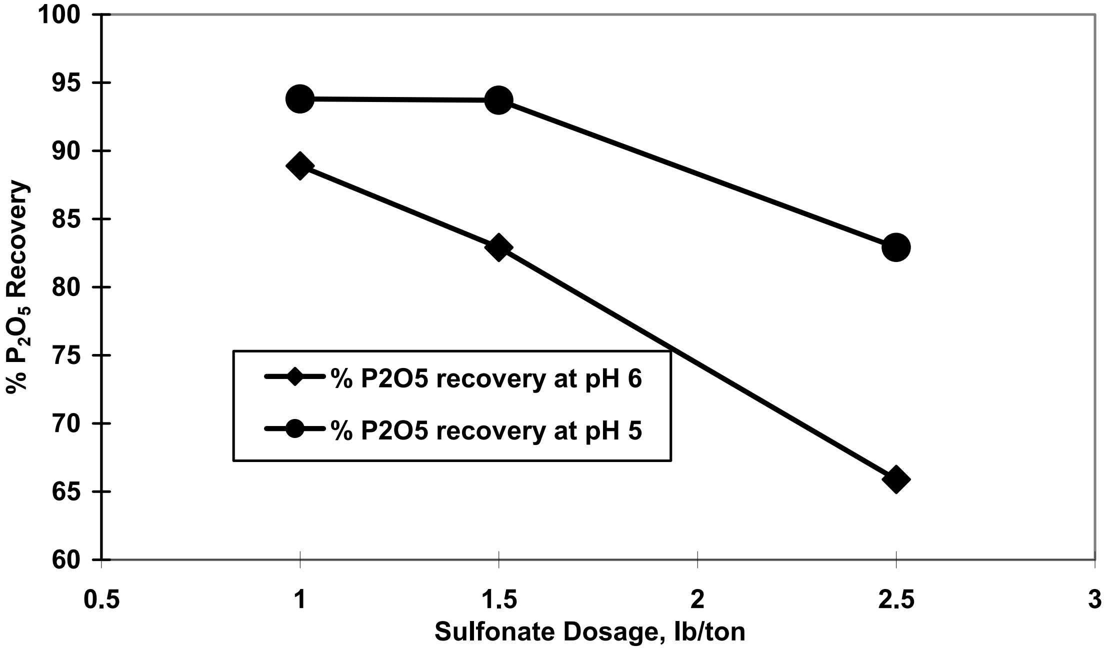


Figure 22c. Effect of Collector Dosage on Flotation Recovery.

Dolomite Flotation Comparing Various Phosphate Depressants

A series of laboratory flotation tests was performed comparing the effectiveness of 10 potential phosphate depressants. Depressant addition levels ranged from 1-3 lbs. per ton of feed. The depressants evaluated were as follows: Sodium tripolyphosphate (STPP), diphosphonic acid (DPA), sodium hexametaphosphate (SHMP), tetrasodium pyrophosphate (TSPP), orthophosphoric acid (OPA), aluminum tartrate complex, disodium hydrogen phosphate (DSHP), Starch CCD-2112, fluosilicic acid, 23% (FSA), and Alizarin Red S (ARS).

The tartrate complex consisted of 2 parts by weight of aluminum sulfate plus 1 part by weight of sodium potassium tartrate.

Sulfuric acid for pH regulation and the selected depressant were added first to the flotation cell containing feed slurry (approximately 25% solids) and conditioning allowed to proceed for 1 minute. Sulfonate OA-5R solution (5%) and Philflo oil were added, and conditioning continued for 1 minute before introducing air to start flotation. A 3-minute flotation time with small sulfuric acid additions for pH control was used again for all flotation tests.

Most of the flotation results are plotted as concentrate % MgO, % P_2O_5 recovery and % MgO recovery vs. depressant level used. The graphical results are shown in Figures 23-34 in accordance with the following legend:

Figure	Phosphate Depressant	Initial Flotation pH	Final Flotation pH
23	STPP	5.5	6.0
24	DPA	5.5	6.0
25	SHMP	5.5	6.0
26	TSPP	5.5	6.0
27	OPA	5.5	6.0
28	Al Tartrate Complex	5.5	6.0
29	OPA	5.5	6.0
30/31	Starch	5.5	6.0
32	ARS	5.5	6.0
33a	FSA	5.5	6.0
33b	FSA	4.1	4.6
34	FSA/Sulfuric Acid	Var.	Var.

Figures 31, 32, 33a and 33b present flotation results plotted as concentrate % MgO, % P_2O_5 recovery and % MgO recovery vs. Sulfonate OA-5R collector level used at a fixed depressant level. Figure 34 presents concentrate % MgO vs. % P_2O_5 recovery curves using FSA and sulfuric acid at various pH ranges and collector levels.

Performance curves for the most effective phosphate depressants (STPP, DPA, SHMP and TSPP) are presented in Figures 23-26, respectively. Using 2 lbs. and 3 lbs. of depressant per ton of feed, the following summarized flotation results are compared:

			Phosphate Concentrate		
Figure	Test	Depressant	% MgO	MgO/P_2O_5	% Recov. P_2O_5
23	1,4	STPP	0.73,0.80	.027,.029	90.0,92.9
24	7,6	DPA	0.80,0.91	.029,.033	84.1,87.5
25	28,10	SHMP	0.83,0.92	.029,.034	94.5,95.8
26	31,30	TSPP	0.79,0.90	.029,.033	94.5,96.8

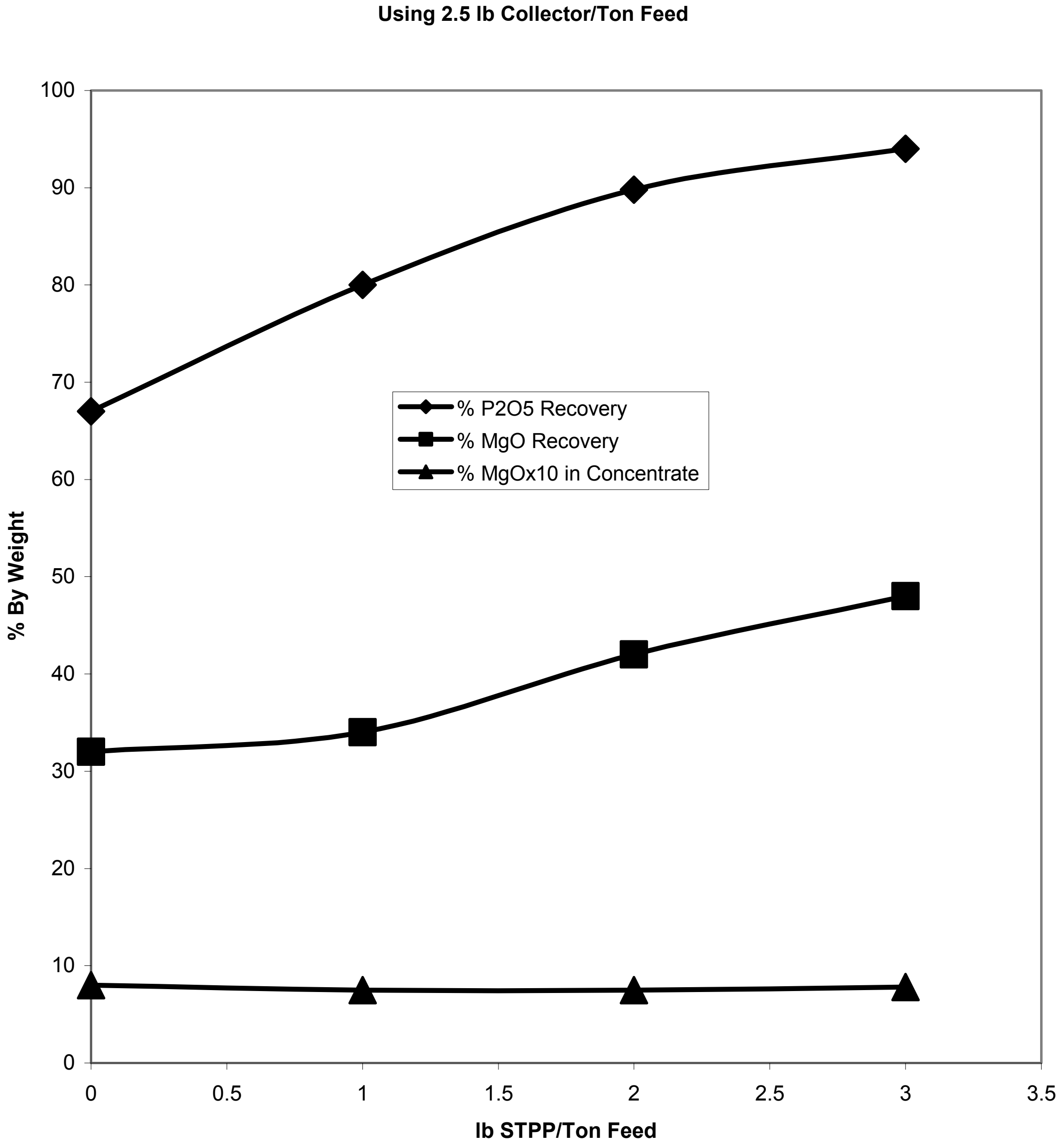


Figure 23. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

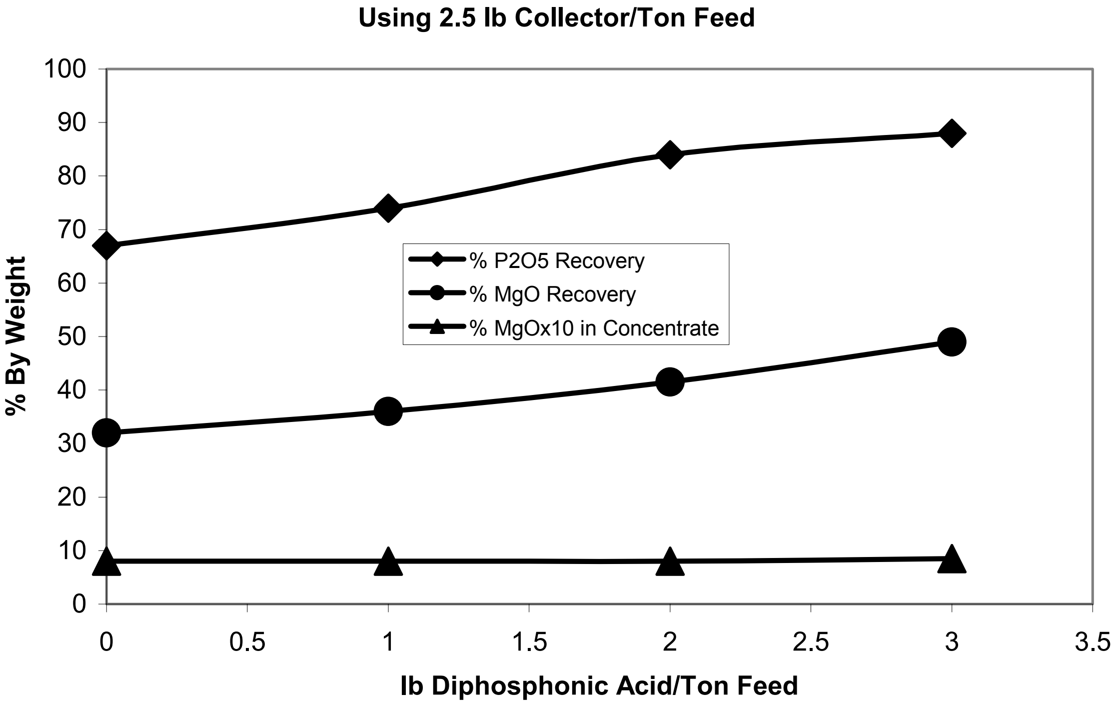


Figure 24. Flotation Concentrate Grade/Recovery Using Various DPA Levels.

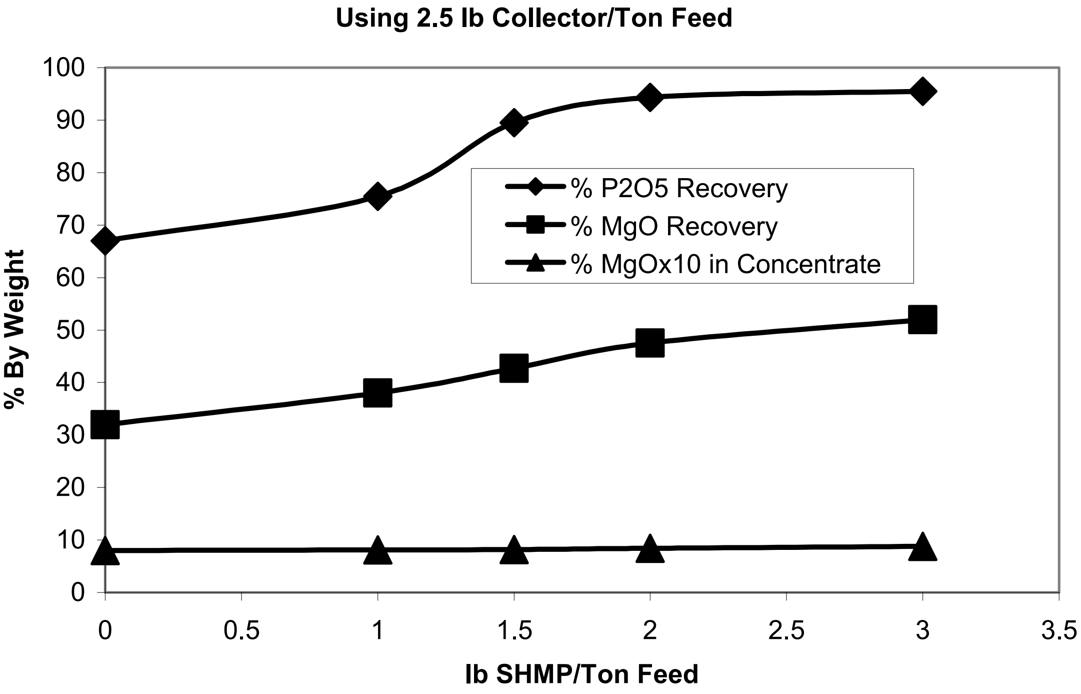


Figure 25. Flotation Concentrate Grade/Recovery Using Various SHMP Levels.

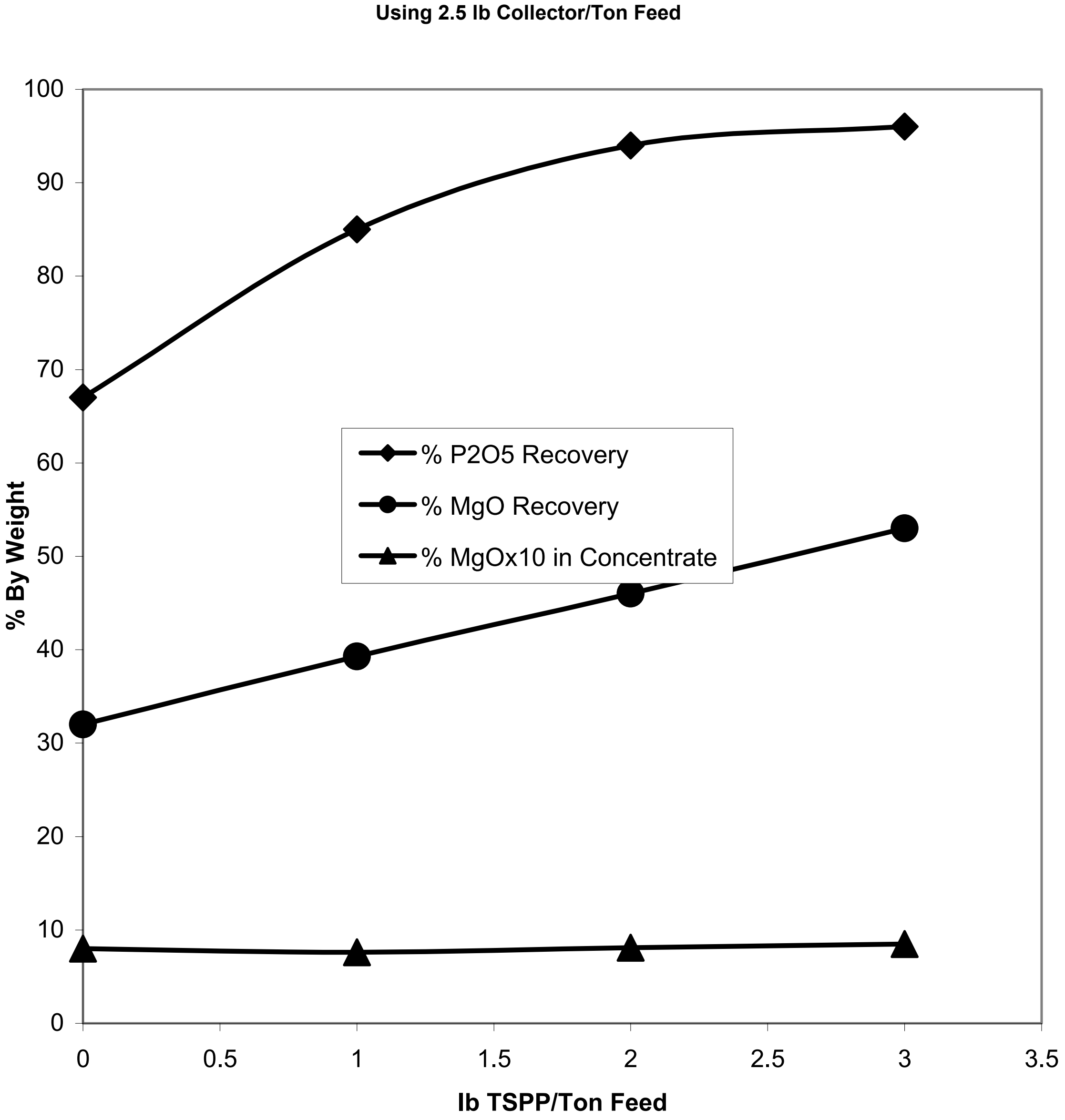


Figure 26. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

All of the above test P_2O_5 recoveries were considerably superior to the Test 2 (Table 1) results (conc. = 0.78% MgO, MgO/P_2O_5 = .030% and 65.9% recovery P_2O_5) wherein no depressant was used. DPA was considered to be the least powerful and most expensive of the four effective depressants for the test conditions employed. There appeared to be very little difference between STPP, SHMP and TSPP with respect to their performance as good phosphate depressants. STPP is currently preferred by this investigator because its cost per pound is less than for SHMP and TSPP.

Performance curves for the practically non-effective phosphate depressants (OPA, aluminum tartrate, DSHP and starch) are presented in Figures 27-30, respectively. Using

2 lbs. and 3 lbs. of depressant per ton of feed, the following flotation results illustrate the failure of these reagents to depress phosphate effectively and yield high P_2O_5 recoveries:

			Phosphate Concentrate		
Figure	Test	Depressant	% MgO	MgO/ P_2O_5	%Recov. P_2O_5
27	25,8	OPA	0.79,0.85	.030,.031	69.3,70.3
28	22,15	Al Tartrate	0.79,0.78	.029,.029	70.5,70.1
29	27,26	DSHP	0.77,0.86	.029,.032	68.6,69.7
30	37,18	Starch	0.84,0.77	.032,.030	63.9,56.4

The use of starch actually yielded lower P_2O_5 recovery than Test 2, wherein no depressant was used and a 65.9% P_2O_5 recovery was obtained.

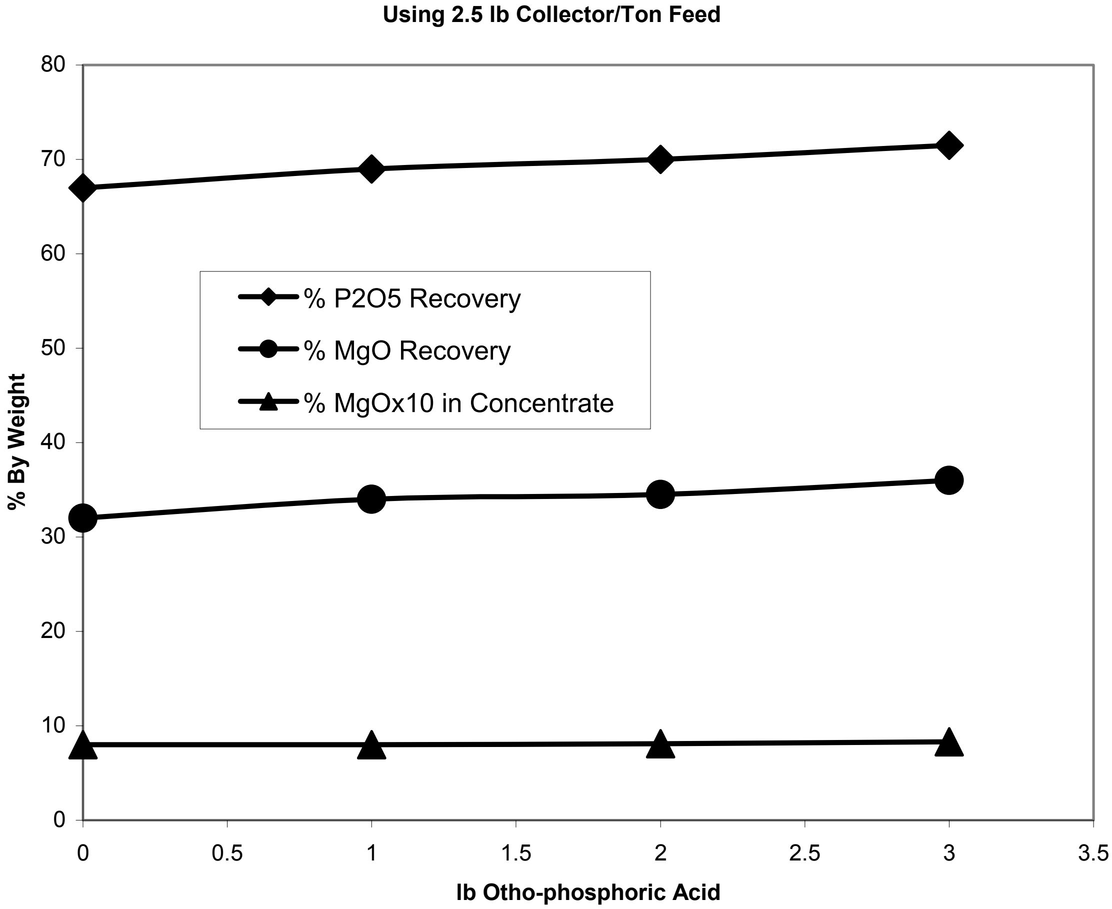


Figure 27. Flotation Concentrate Grade/Recovery Using Various OPA Levels.

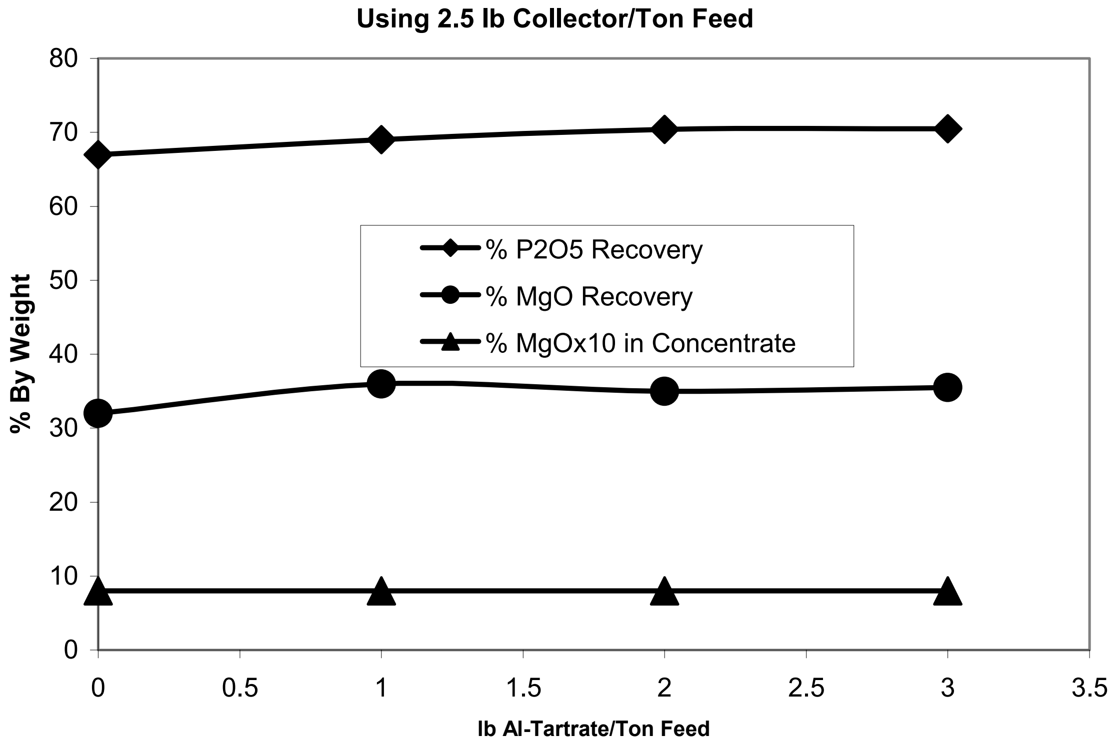


Figure 28. Flotation Concentrate Grade/Recovery Using Various Tartrate Levels.

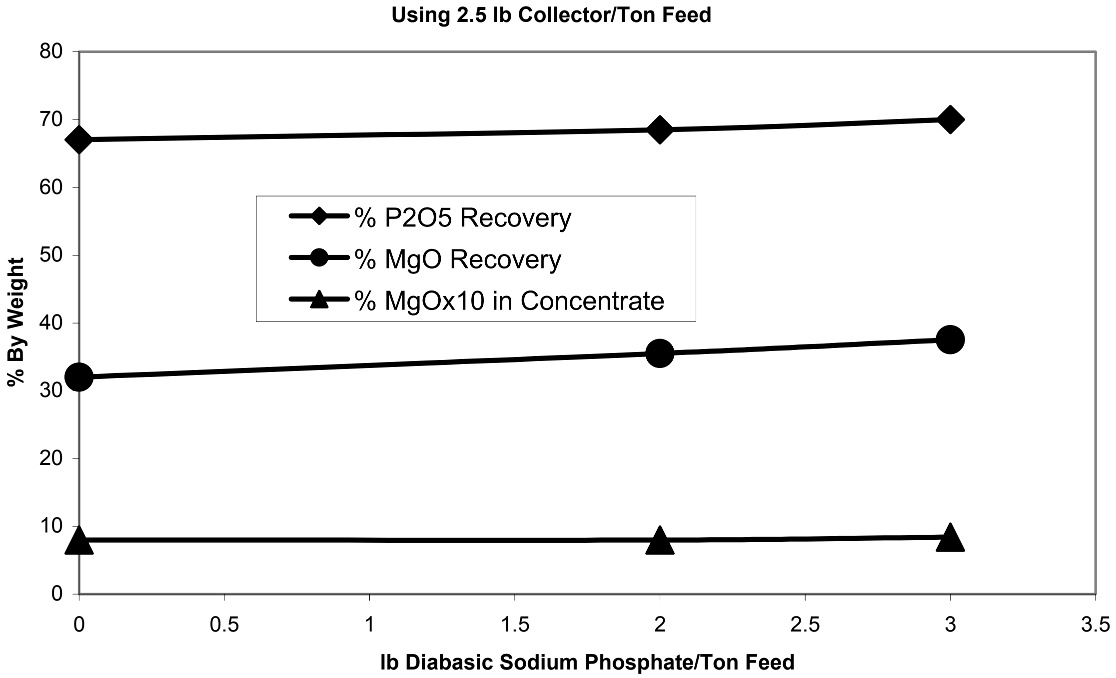


Figure 29. Flotation Concentrate Grade/Recovery Using Various DSHP Levels.

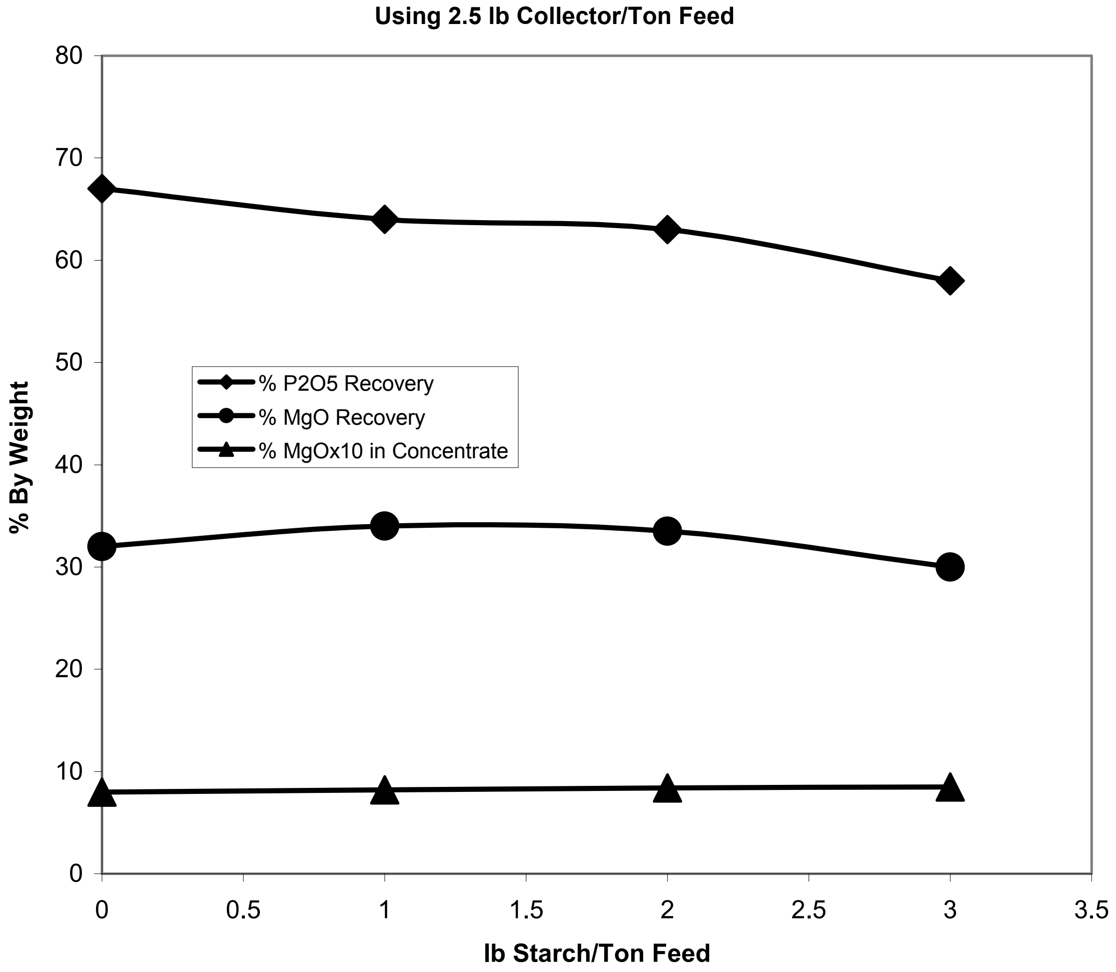


Figure 30. Flotation Concentrate Grade/Recovery Using Various Starch Levels.

Figure 31 presents flotation performance curves using 3 lbs. of starch per ton of feed with various Sulfonate OA-5R collector levels at pH = 5.5-6.0. Comparing the Figure 31 curves with the Figure 22a curves wherein no depressant was used also illustrates the small negative effects on flotation performance when starch was used.

Figure 32 presents flotation performance curves using 1 lb. of Alizarin Red S per ton of feed as a potential phosphate depressant with various collector levels at pH = 5.5-6.0. Comparing the Figure 32 curves with the Figure 22a curves again shows the negative effects on flotation performance when ARS was used. A small but noticeable depression of dolomite by ARS was indicated. Also, the ARS caused a reddish discoloration of the flotation product waters because of reaction with calcium ions. Since ARS is a laboratory specialty chemical, probably not readily available in bulk quantity, its use in flotation most probably would be highly prohibitive. Based upon laboratory reagent catalog pricing, it is estimated that ARS would cost more than $30 per pound.

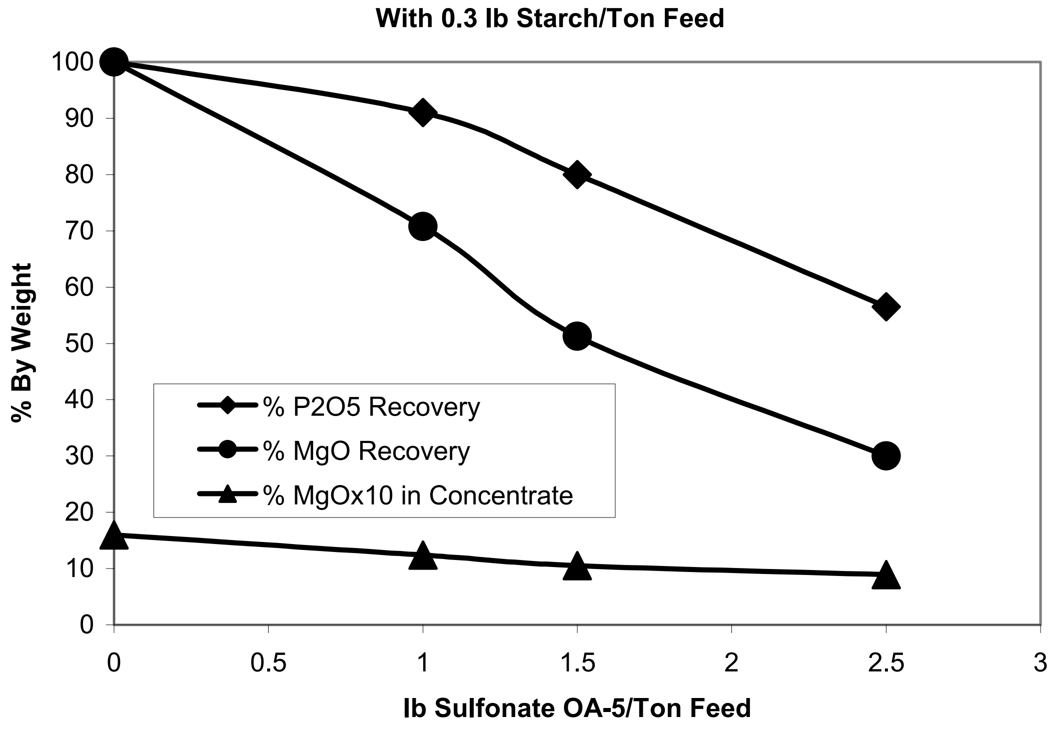


Figure 31. Flotation Concentrate Grade/Recovery Using Various OA-5 Levels.

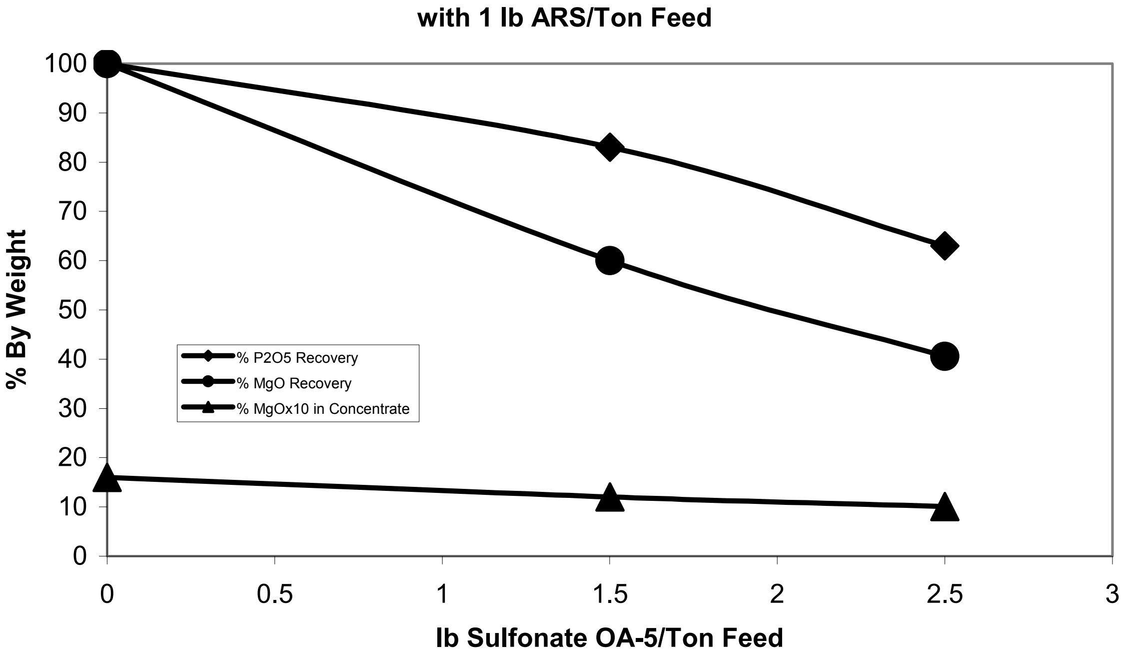


Figure 32. Flotation Concentrate Grade/Recovery Using Various OA-5 Levels.

Figures 33a and 33b present flotation performance curves using fluosilicic acid as the phosphate depressant at pH = 5.5-6.0 and pH = 4.1-4.6, respectively, using various Sulfonate OA-5R collector levels. FSA levels used were 1.0 lb. and 1.5 lb. per ton of feed to obtain the desired conditioning/flotation pH ranges.

The curves shown in Figure 33a, using FSA at pH = 5.5-6.0, are very similar to the Figure 22a results wherein sulfuric acid was used to control the pH at 5.5-6.0. The curves shown in Figure 33b, using more FSA to yield pH = 4.1-4.6, indicate that better selectivity was obtained at the lower pH range. The best results are summarized as follows:

			Phosphate Concentrate		
Figure	Test	Depressant	% MgO	MgO/P_2O_5	% Recov. P_2O_5
33b	39	FSA	0.91	.033	85.4
33b	38	FSA	1.04	.038	94.2

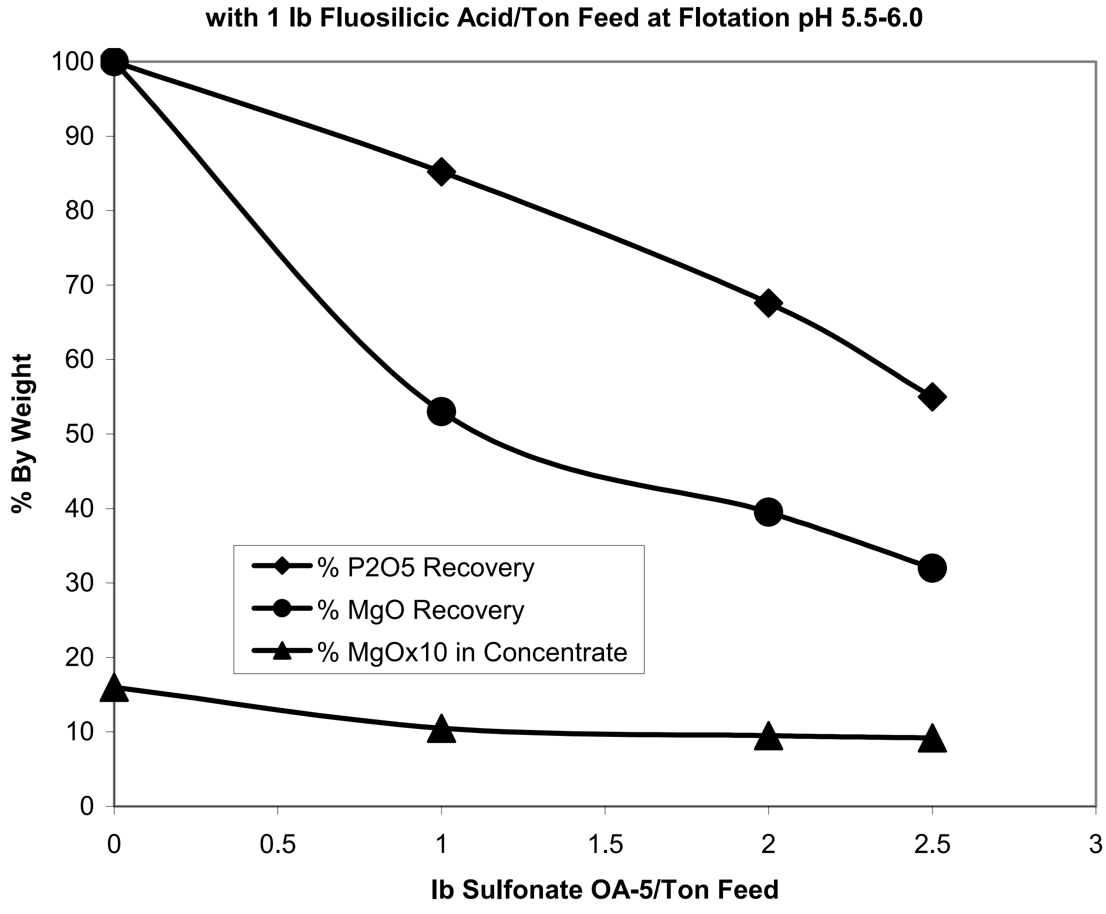


Figure 33a. Flotation Concentrate Grade/Recovery Using Various OA-5 Levels.

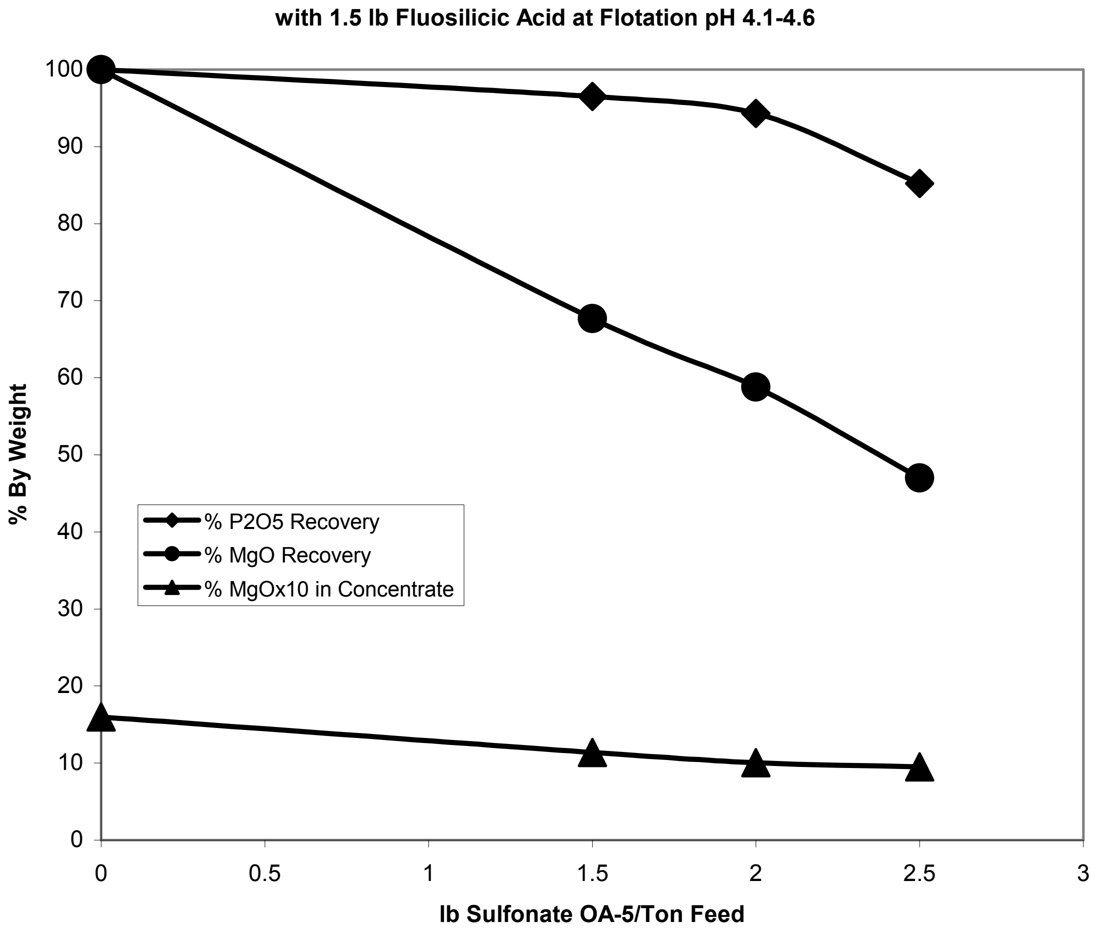


Figure 33b. Flotation Concentrate Grade/Recovery Using Various OA-5 Levels.

Figure 34 compares concentrate % MgO vs. % P_2O_5 recovery curves for all tests using sulfuric acid with tests using FSA at the various pH ranges investigated. The superior selectivity obtained using FSA at the 4.1-4.6 pH range is apparent; however, the results are inferior to those previously obtained using STPP, DPA, SHMP or TSPP as the phosphate depressant at pH = 5.5-6.0. Controlling flotation pH at levels lower than about 5.0 was more difficult during lab tests and is considered to be impractical, especially for feed samples containing lime rock and/or seashells in addition to dolomite.

Finally, Figure 35 presents a concentrate % MgO vs. % P_2O_5 recovery diagram for all dolomite flotation tests performed with and without phosphate depressant additions. The superior selectivity of STPP, SHMP and TSPP to all other depressants is illustrated by the three boundary curves.

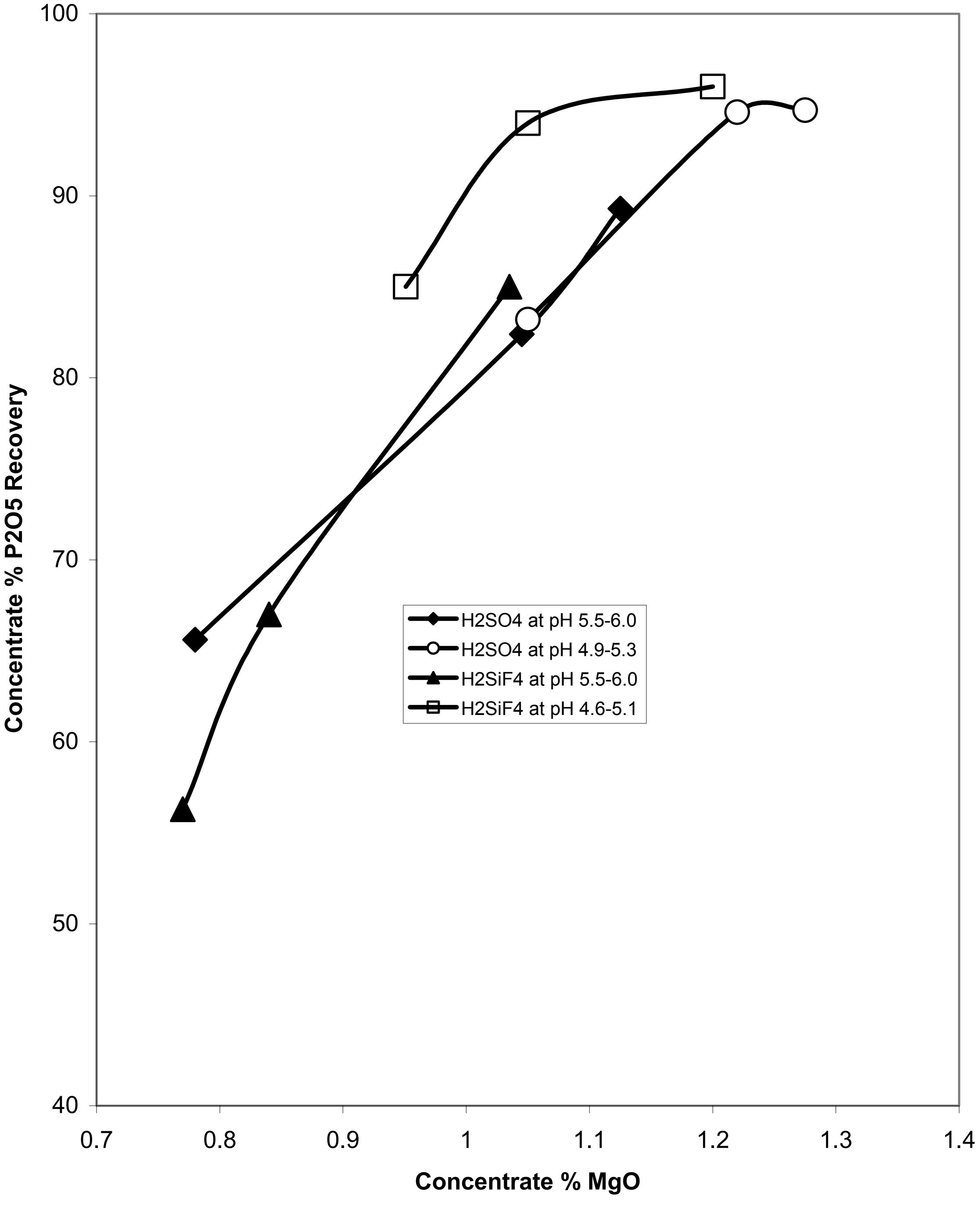


Figure 34. Flotation Concentrate Grade/Recovery Using Different pH Modifiers.

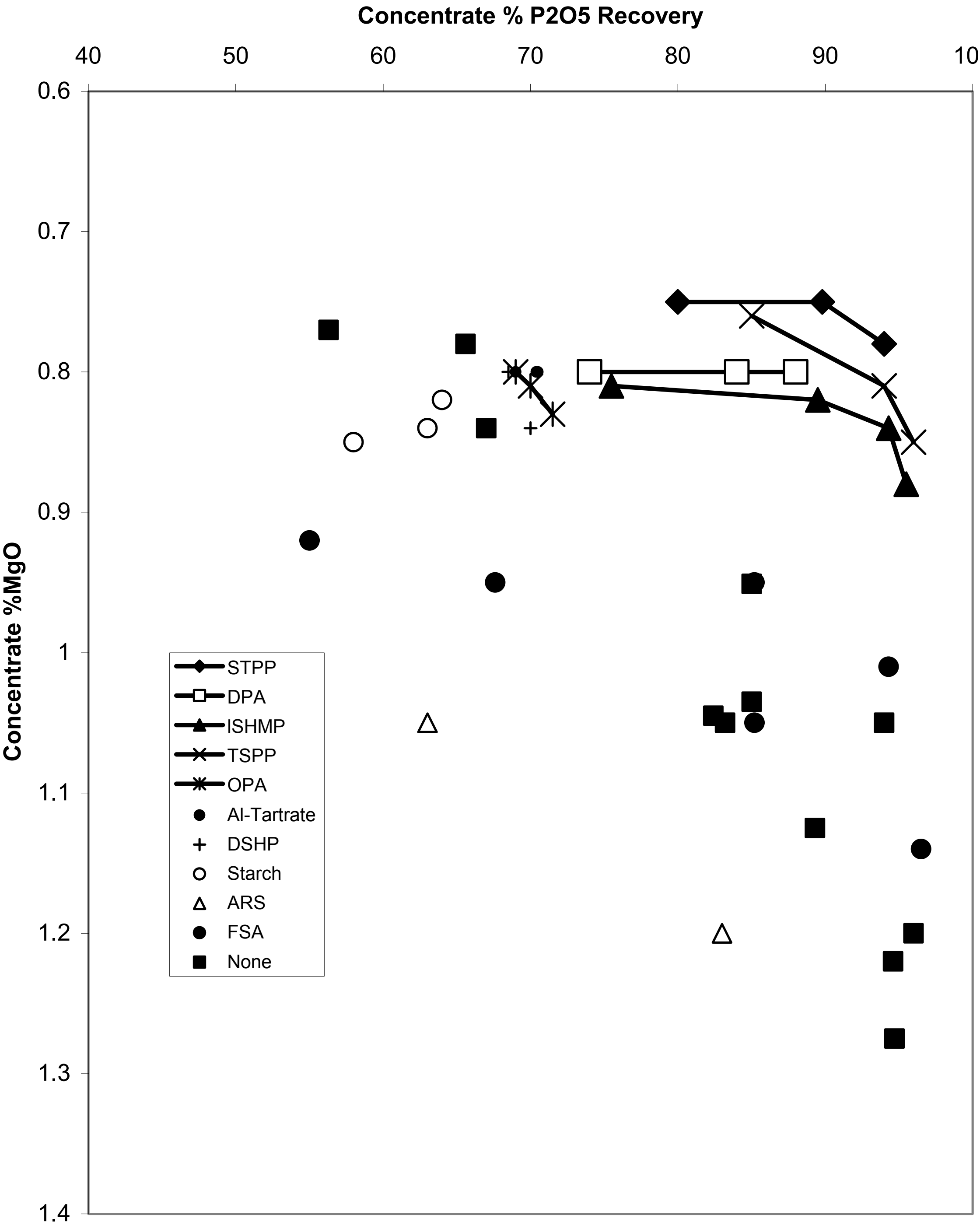


Figure 35. Flotation Concentrate Grade/Recovery for All Test Depressants.

DOLOMITE AND SILICA FLOTATION USING SELECTED PHOSPHATE DEPRESSANTS

Three tests were performed in which dolomite was initially floated at pH = 5.5-6.0 using Sulfonate OA-5R plus oil with each of the three most promising phosphate depressants, followed by dewatering/washing of the phosphatic cell product to pH = 6.8-6.9 and cationic flotation of silica, using Custamine 738, to yield final phosphate concentrates containing at least 30% P_2O_5 and less than 1% MgO ($MgO/P_2O_5 = <.031$). STPP, SHMP and TSPP were the selected phosphate depressants used. Amine flotation of silica was excellent, and no obvious detrimental effects from the traces of residual dolomite stage flotation reagents was observed. Amine flotation P_2O_5 recoveries exceeded 97% for each of the three tests. The three flotation material balances and reagent levels used are presented in Table 17. Phosphate concentrates were produced analyzing 30.46-31.33% P_2O_5, 1.44-2.61% insol, 0.80-0.91% MgO and MgO/P_2O_5 ratio = .026-.030 at 86.9-92.1 overall % P_2O_5 recovery.

Table 17. Dolomite/Silica Flotation Using Various Phosphate Depressants.

Test	Reagent	lb/TOF	Product	% Wt.	MgO/P_2O_5
A1	Dolo. Flot.				
	H2SO4	3.20	Dolo. Tail.	12.9	0.354
	STPP	2.00	Silica Tail.	11.6	0.020
	OA-5R	2.50	Phos. Conc.	75.5	0.026
	Ph.Oil	1.25	Flot. Feed	100.0	0.055
	Silica Flot.				
	Custamine 738	0.70			
	Diesel	0.10			
A2	Dolo. Flot.				
	H2SO4	3.40	Dolo. Tail.	15.0	0.295
	STPP	1.50	Silica Tail.	10.7	0.021
	OA-5R	2.50	Phos. Conc.	74.3	0.026
	Ph.Oil	1.25	Flot. Feed	100.0	0.060
	Silica Flot.				
	Custamine 738	0.60			
	Diesel	0.10			
A3	Dolo. Flot.				
	H2SO4	3.40	Dolo. Tail.	10.4	0.491
	STPP	2.00	Silica Tail.	10.3	0.022
	OA-5R	2.50	Phos. Conc.	79.3	0.030
	Ph.Oil	1.25	Flot. Feed	100.0	0.061
	Silica Flot.				
	Custamine 738	0.70			
	Diesel	0.10			

Table 17 (Cont.). Dolomite/Silica Flotation Using Various Phosphate Depressants.

Test	Product	% P_2O_5	% Insol	% MgO	% Dist. P_2O_5	% Dist. MgO
A1						
	Dolo. Tail.	18.94	5.82	6.70	9.2	58.5
	Silica Tail.	4.87	84.20	0.10	2.1	0.7
	Phos. Conc.	31.33	1.44	0.80	88.7	40.8
	Flot. Feed	26.65	11.61	1.47	100.0	100.0
A2						
	Dolo. Tail.	20.70	4.39	6.10	11.8	60.1
	Silica Tail.	3.31	89.21	0.07	1.3	0.7
	Phos. Conc.	30.78	2.00	0.81	86.9	39.2
	Flot. Feed	26.33	11.70	1.53	100.0	100.0
A3	Dolo. Tail.	17.12	6.00	8.40	6.8	53.8
	Silica Tail.	2.76	91.08	0.06	1.1	0.4
	Phos. Conc.	30.46	2.61	0.93	92.1	45.8
	Flot. Feed	26.26	12.07	1.61	100.0	100.0

DOLOMITE FLOTATION USING VARIOUS SULFONATE COLLECTORS WITH STPP

In addition to Sulfonate OA-5R collector used for all previously described tests, the following three sulfonated tall oil soaps were tested using STPP phosphate depressant and test conditions paralleling Test 1A (Table 17): Sulfonate OA-5U (B.I.T. Manufacturing, Inc.), CC-6621-55B (exp. lab.) (Custom Chemicals), and CCS-505 (Custom Chemicals).

The additional three flotation material balances and reagent levels used are presented in Table 18 for comparison with Test 1A (Table 17). The flotation balances indicate that using any of these alternative collectors resulted in selective separation of dolomite from phosphate, however their collecting strengths were less than when Sulfonate OA-5R was used. Phosphate concentrates were produced analyzing 30.60-30.94% P_2O_5, 1.35-1.96% insol, 0.92-1.11% MgO and MgO/P_2O_5 ratio = .030-.036 at 91.6-93.7 overall % P_2O_5 recovery. Sulfonate CCS-505 was considered to yield the best overall dolomite/phosphate separation and to be the "strongest" of the three alternative collectors. All of the sulfonate collectors including Sulfonate OA-5R are sold as 50% aqueous solutions.

Table 18. Dolomite/Silica Flotation Using Sulfonated Tall Oils with STPP.

Test	Reagent	lb/TOF	Product	% Wt.	MgO/P_2O_5
A4	Dolo. Flot.				
	H_2SO_4	3.20	Dolo. Tail.	8.3	0.478
	STPP	2.00	Silica Tail.	10.7	0.036
	OA-5U	2.50	Phos. Conc.	81.0	0.036
	Ph.Oil	1.25	Flot. Feed	100.0	0.060
	Silica Flot.				
	Custamine 738	0.70			
	Diesel	0.10			
A5					
	Dolo. Flot.				
	H_2SO_4	3.00	Dolo. Tail.	9.7	0.517
	STPP	2.00	Silica Tail.	10.5	0.039
	Sulf.6621-55B	2.50	Phos. Conc.	79.8	0.032
	Ph.Oil	1.25	Flot. Feed	100.0	0.062
	Silica Flot.				
	Custamine 738	0.70			
	Diesel	0.10			
A6					
	Dolo. Flot.				
	H_2SO_4	3.00	Dolo. Tail.	10.5	0.491
	STPP	2.00	Silica Tail.	11.2	0.033
	CCS-505	2.50	Phos. Conc.	78.3	0.030
	Ph.Oil	1.25	Flot. Feed	100.0	0.062
	Silica Flot.				
	Custamine 738	0.70			
	Diesel	0.10			

Table 18 (Cont.). Dolomite/Silica Flotation Using Sulfonated Tall Oils with STPP.

Test	Product	% P_2O_5	% Insol	% MgO	% Dist. P_2O_5	% Dist. MgO
A1						
	Dolo. Tail.	17.36	5.81	8.30	5.4	43.1
	Silica Tail.	2.24	91.91	0.08	0.9	0.6
	Phos. Conc.	30.60	1.35	1.11	93.7	56.3
	Flot. Feed	26.47	11.40	1.60	100.0	100.0
A2						
	Dolo. Tail.	17.01	4.53	8.80	6.2	51.5
	Silica Tail.	2.04	89.80	0.08	0.8	0.6
	Phos. Conc.	30.84	1.96	0.99	93.0	47.9
	Flot. Feed	26.47	11.43	1.65	100.0	100.0
A3	Dolo. Tail.	17.72	4.01	8.70	7.0	55.5
	Silica Tail.	3.30	88.54	0.11	1.4	0.6
	Phos. Conc.	30.94	1.75	0.92	91.6	43.9
	Flot. Feed	26.46	11.71	1.64	100.0	100.0

EFFECT OF MgO CONTENT AND PRELIMINARY ECONOMICS

Summary

The dolomite flotation test results obtained for several rodmilled, deslimed pebble phosphate samples are presented in this section. The principal objectives of the testwork were:

(1) To determine the phosphate concentrate quality and % P_2O_5 recovery obtained for the pebble samples as a function of the process feed % MgO.

(2) To obtain preliminary ballpark reagent cost estimates for flotation processing of the various pebble samples.

Selected flotation test data reported in Progress Report No. 6 are included in this report for comparison with the recent test data for the three additional processed pebble samples.

Four IMC/Agrico pebble samples from the Four Corners reserves have been processed using the procedures described in Progress Report No. 6. The samples were obtained from the Noralyn Metallurgical Laboratory storage piles. Pebble sample MgO contents ranged from about 1.5-4.6%. Flotation feeds were prepared from each sample by wet rodmilling and desliming to produce -48+325 mesh feeds. The four flotation feed samples contained 73-77% recovery of the original pebble P_2O_5 content and analyzed about 1.0%, 1.6%, 2.3+% and 2.9+% MgO. Sulfonated oleic acid collector and STPP phosphate depressant were used to process each sample.

The 1.0% and 1.6% MgO feed samples responded readily to dolomite flotation. Phosphate concentrates analyzed 0.6-0.8% MgO at 90-96% P_2O_5 recovery. The 2.3+% MgO feed sample yielded phosphate concentrates analyzing about 1.1-1.2% MgO at 74-89% P_2O_5 recovery. The 2.9+% MgO sample was more difficult to process and yielded phosphate concentrates analyzing about 1.5% MgO at 89-92+% P_2O_5 recovery.

STPP levels required for effective phosphate depression ranged from 1-3 lbs. per ton of flotation feed. Sulfonate OA-5R collector levels required ranged from 1.5-2.5 lbs. per ton of flotation feed. The failure of the flotation process to produce phosphate concentrates containing <1.0% MgO from the 2.3+% and 2.9+% MgO feeds was attributed to the inability to float enough of the -48+65 mesh dolomite particles from these two samples. The need for grinding these two pebble samples to at least -65 mesh was recognized in order to reduce phosphate concentrate MgO contents to 1.0% or less. Without using finer grinding, the process is assumed to be capable of producing phosphate concentrates containing 1.0% MgO or less from pebble-derived flotation feeds containing <1.8-2.0% MgO.

Size/assay analyses were obtained for each flotation feed sample and for selected phosphate concentrates analyzing >1.0% MgO. The -65 mesh concentrate fractions analyzed 0.8+-1.0+% MgO and comprised about 65-77+% weight of the total concentrates produced.

Cationic flotation of silica from selected dolomite flotation cell underflow products succeeded in producing 30-31+% P_2O_5 final phosphate concentrates containing 0.8-1.6% MgO. Cationic flotation P_2O_5 recovery exceeded 97% for each sample processed.

Reagent costs for dolomite flotation from the three feed samples, analyzing 1.0-2.3+% MgO, ranged from $1.78-$2.77 per ton of feed and from $1.87-$3.11 per ton of phosphate concentrate. Cationic flotation of silica from the selected dolomite cell underflow samples cost an additional $0.18 per ton of feed and $0.19-$0.26 per ton of final phosphate concentrate.

Laboratory Testwork

Description of High-MgO Pebble Samples

Three more Four Corners mine pebble samples, containing about 1.5%, 3.5% and 4.5% MgO, were obtained from IMC/Agrico for grinding, desliming and dolomite flotation. Chemical analyses for these samples, plus the 2.5% MgO sample (B) described above are summarized as follows:

Table 19. Analyses of Dolomitic Pebble Samples.

Sample	Weight, lb.	P_2O_5	Insol	MgO	MgO/P_2O_5
A	16	26.18	12.98	1.54	0.059
B	97	25.77	9.55	2.56	0.099
C	12	24.63	9.03	3.54	0.144
D	23	22.98	7.68	4.60	0.200

Treatment of Pebble Samples

Each bulk pebble sample was batch rodmilled (wet) in stages to -48 mesh and deslimed by decanting over a 325 mesh screen. The grinding/sizing material balances and chemical analyses of the products are listed in Table 20. Grinding and desliming produced flotation feeds containing about 1.0%, 1.6%, 2.3+% and 2.9+% MgO at 73-77% P_2O_5 recovery in the feeds and 53-55% rejection of MgO in the slime fractions. Standard wet-dry size-assay analyses for each -48+325 mesh flotation feed fraction are presented in Table 21.

Table 20. Material Balances for Various Rodmilled Phosphate Pebble Samples.

Product	% Wt.	% P_2O_5	% Insol	% MgO
48/325 Mesh Feed	73.1	25.58	16.59	0.96
-325 Mesh Slime	26.9	25.51	6.27	2.94
Total Pebble, Sample A	100	25.56	13.82	1.49
48/325 Mesh Feed	73.0	26.52	11.80	1.60
-325 Mesh Slime	27.0	22.17	5.42	5.20
Total Pebble, Sample B	100	25.35	10.07	2.57
48/325 Mesh Feed	72.5	26.42	10.62	2.24
-325 Mesh Slime	27.5	19.94	4.85	6.98
Total Pebble, Sample C	100	24.63	9.03	3.54
48/325 Mesh Feed	70.8	25.23	9.81	2.80
-325 Mesh Slime	29.2	17.51	4.87	8.40
Total Pebble	100	22.97	8.37	4.43

Table 21. Size/Assay Analyses of Rodmilled Pebble Feed Samples.

Tyler Mesh	% Wt.	% P_2O_5	% Insol	% MgO
SAMPLE A:				
+65	23.7	25.57	17.36	0.87
65/100	27.0	25.27	17.99	0.92
100/150	17.7	25.22	18.26	0.97
150/200	11.9	26.07	15.19	0.99
200/325	13.2	26.66	12.96	1.10
-325	6.5	27.17	9.23	1.43
Total	100	25.73	16.32	0.99
SAMPLE B:				
+65	23.7	27.61	12.34	1.30
65/100	27.9	27.03	12.62	1.60
100/150	17.4	26.74	13.00	1.70
150/200	12.0	27.23	11.22	1.60
200/325	12.6	27.92	9.99	1.60
-325	6.4	26.81	6.92	2.50
Total	100	27.23	11.75	1.60
SAMPLE C:				
+65	26.1	27.25	9.97	2.04
65/100	27.4	25.63	10.80	2.43
100/150	16.9	25.58	10.74	2.52
150/200	11.7	26.97	9.71	2.36
200/325	12.4	26.98	8.39	2.36
-325	5.5	26.51	4.65	3.31
Total	100	26.41	9.82	2.37
SAMPLE D:				
+65	26.4	25.71	8.64	2.73
65/100	26.6	25.05	9.83	2.86
100/150	16.7	25.03	10.86	2.70
150/200	11.4	25.20	8.96	2.88
200/325	12.6	25.08	4.97	3.28
-325	6.3	23.40	8.11	4.93
Total	100	25.13	8.86	2.98

Results and Discussion

Dolomite Flotation at Various Depressant and Collector Levels

Each of the four -48+325 mesh rodmilled pebble samples was subjected to multiple dolomite flotation tests using STPP as the phosphate depressant and Sulfonate

OA-5R as the dolomite collector. Flotation pH range was 5.5-6.0. Feed conditioning and flotation times were the same as described previously. Reagent levels used and flotation test results are presented in Tables 22a, 22b, 22c and 22d for pebble samples A, B, C and D, respectively.

Table 22a. Dolomite Flotation Using Various STPP Levels—Sample A.

Test	OA-5,lb/TOF	STPP, lb/tof	H_2SO_4, lb/TOF	Product	% Wt.
A6	2.5	None	3.4	Dolo. Tail.	25.7
				Phos. Conc.	74.3
				Flot. Feed	100.0
A4	2.5	1	3.4	Dolo. Tail.	16.5
				Phos. Conc.	83.5
				Flot. Feed	100.0
A2	2.5	2	3.6	Dolo. Tail.	7.4
				Phos. Conc.	92.6
				Flot. Feed	100.0
A7	2.5	3	3.6	Dolo. Tail.	6.3
				Phos. Conc.	93.7
				Flot. Feed	100.0
A3	1.5	None	3.2	Dolo. Tail.	12.7
				Phos. Conc.	87.3
				Flot. Feed	100.0
A5	1.5	1	3.2	Dolo. Tail.	6.3
				Phos. Conc.	93.7
				Flot. Feed	100.0
A1	1.5	2	3.6	Dolo. Tail.	5.0
				Phos. Conc.	95.0
				Flot. Feed	100.0

Table 22a (Cont.). Dolomite Flotation Using Various STPP Levels—Sample A.

Test	Product	Concentrate Analysis			% Distribution	
		% P_2O_5	% Insol	% MgO	P_2O_5	MgO
A6	Dolo. Tail.	29.00	3.85	1.86	28.4	50.0
	Phos. Conc.	25.31	19.91	0.65	71.6	50.0
	Flot. Feed	26.25	15.78	0.96	100.0	100.0
A4	Dolo. Tail.	26.85	6.15	2.59	16.8	45.3
	Phos. Conc.	26.22	17.72	0.62	83.2	54.7
	Flot. Feed	26.32	15.81	0.95	100.0	100.0
A2	Dolo. Tail.	22.06	7.31	5.48	6.3	41.4
	Phos. Conc.	26.11	17.73	0.63	93.7	58.6
	Flot. Feed	25.81	16.96	0.99	100.0	100.0
A7	Dolo. Tail.	21.05	11.88	5.14	5.0	33.7
	Phos. Conc.	26.74	16.59	0.67	95.0	66.3
	Flot. Feed	26.39	16.29	0.95	100.0	100.0
A3	Dolo. Tail.	27.89	3.33	2.49	13.5	34.0
	Phos. Conc.	25.96	18.02	0.71	86.5	66.0
	Flot. Feed	26.20	16.15	0.94	100.0	100.0
A5	Dolo. Tail.	22.99	7.82	4.78	5.5	30.6
	Phos. Conc.	26.50	16.46	0.73	94.5	69.4
	Flot. Feed	26.28	15.91	0.98	100.0	100.0
A1	Dolo. Tail.	19.66	10.00	6.32	3.8	33.0
	Phos. Conc.	26.06	17.32	0.68	96.2	67.0
	Flot. Feed	25.74	16.95	0.97	100.0	100.0

Table 22b. Dolomite Flotation Using Various STPP Levels—Sample B.

Test	OA-5,Lb/Tof	STPP, Lb/tof	H_2SO_4, lb/tof	Product	% Wt.
B2	2.5	None	3.4	Dolo. Tail.	33.6
				Phos. Conc.	66.4
				Flot. Feed	100.0
B3	2.5	1	3.4	Dolo. Tail.	22.1
				Phos. Conc.	77.9
				Flot. Feed	100.0
B1	2.5	2	3.6	Dolo. Tail.	13.4
				Phos. Conc.	86.6
				Flot. Feed	100.0
B4	2.5	3	3.4	Dolo. Tail.	10.8
				Phos. Conc.	89.2
				Flot. Feed	100.0

Table 22b (Cont.). Dolomite Flotation Using Various STPP Levels—Sample B.

Test	Product	Concentrate Analysis			% Distribution	
		% P_2O_5	% Insol	% MgO	P_2O_5	MgO
B2	Dolo. Tail.	26.86	2.72	3.30	34.1	68.1
	Phos. Conc.	26.28	16.07	0.78	65.9	31.9
	Flot. Feed	26.47	11.58	1.63	100.0	100.0
B3	Dolo. Tail.	23.35	4.80	4.60	19.7	64.5
	Phos. Conc.	27.01	13.07	0.72	80.3	35.5
	Flot. Feed	26.20	11.24	1.58	100.0	100.0
B1	Dolo. Tail.	19.50	6.34	6.50	10.0	58.0
	Phos. Conc.	27.18	12.68	0.73	90.0	42.0
	Flot. Feed	26.15	11.83	1.50	100.0	100.0
B4	Dolo. Tail.	17.09	6.85	7.20	7.1	52.3
	Phos. Conc.	27.17	12.02	0.80	92.9	47.7
	Flot. Feed	26.09	11.46	1.49	100.0	100.0

Table 22c. Dolomite Flotation Using Various STPP Levels—Sample C.

Test	OA-5, lb/TOF	STPP, lb/TOF	H_2SO_4, lb/TOF	Product	% Wt.
C2	2.5	1	3.6	Dolo. Tail.	27.2
				Phos. Conc.	72.8
				Flot. Feed	100.0
C1	2.5	2	3.6	Dolo. Tail.	15.4
				Phos. Conc.	84.6
				Flot. Feed	100.0
C3	2.5	3	3.6	Dolo. Tail.	13.9
				Phos. Conc.	86.1
				Flot. Feed	100.0
C6	3.5	1	3.4	Dolo. Tail.	30.3
				Phos. Conc.	69.7
				Flot. Feed	100.0
C5	3.5	2	3.4	Dolo. Tail.	19.1
				Phos. Conc.	80.9
				Flot. Feed	100.0
C4	3.5	3	3.4	Dolo. Tail.	14.6
				Phos. Conc.	85.4
				Flot. Feed	100.0

Table 22c (Cont.). Dolomite Flotation Using Various STPP Levels—Sample C.

Test	Product	Concentrate Analysis			% Distribution	
		% P_2O_5	% Insol	% MgO	P_2O_5	MgO
C2	Dolo. Tail.	23.68	2.53	5.90	24.6	67.2
	Phos. Conc.	27.18	10.40	1.07	75.4	32.8
	Flot. Feed	26.23	9.32	2.38	100.0	100.0
C1	Dolo. Tail.	17.65	3.30	8.98	10.5	59.2
	Phos. Conc.	27.41	9.44	1.13	89.5	40.8
	Flot. Feed	25.91	8.50	2.33	100.0	100.0
C3	Dolo. Tail.	17.10	5.11	9.00	8.8	52.3
	Phos. Conc.	28.49	8.74	1.32	91.2	47.7
	Flot. Feed	26.91	8.24	2.39	100.0	100.0
C6	Dolo. Tail.	24.02	3.64	5.28	27.3	69.0
	Phos. Conc.	27.69	12.69	1.04	72.7	31.0
	Flot. Feed	26.58	9.94	2.32	100.0	100.0
C5	Dolo. Tail.	20.08	4.26	6.62	14.5	56.0
	Phos. Conc.	28.04	11.26	1.22	85.5	44.0
	Flot. Feed	26.52	9.92	2.25	100.0	100.0
C4	Dolo. Tail.	17.60	5.12	7.79	9.7	50.0
	Phos. Conc.	27.84	10.90	1.33	90.3	50.0
	Flot. Feed	26.35	10.06	2.28	100.0	100.0

Table 22d. Dolomite Flotation Using Various STPP Levels—Sample D.

Test	OA-5, lb/TOF	STPP, lb/TOF	H_2SO_4, lb/TOF	Product	% Wt.
D3	2.5	None	3.6	Dolo. Tail.	39.4
				Phos. Conc.	60.6
				Flot. Feed	100.0
D2	2.5	1	3.6	Dolo. Tail.	23.7
				Phos. Conc.	76.3
				Flot. Feed	100.0
D1	2.5	2	3.6	Dolo. Tail.	17.6
				Phos. Conc.	82.4
				Flot. Feed	100.0
D4	2.5	3	3.6	Dolo. Tail.	13.8
				Phos. Conc.	86.2
				Flot. Feed	100.0
D5	3.5	2	3.6	Dolo. Tail.	19.0
				Phos. Conc.	81.0
				Flot. Feed	100.0
D6	4.5	2	3.6	Dolo. Tail.	24.4
				Phos. Conc.	75.6
				Flot. Feed	100.0
D10	5.5	1	3.6	Dolo. Tail.	47.5
				Phos. Conc.	52.5
				Flot. Feed	100.0
D7	5.5	2	3.6	Dolo. Tail.	28.7
				Phos. Conc.	71.3
				Flot. Feed	100.0
D9	5.5	3	3.6	Dolo. Tail.	23.1
				Phos. Conc.	76.9
				Flot. Feed	100.0
D8	6.5	2	3.6	Dolo. Tail.	37.2
				Phos. Conc.	62.8
				Flot. Feed	100.0

Table 22d (Cont.). Dolomite Flotation Using Various STPP Levels—Sample D.

Test	Product	Concentrate Analysis			% Distribution	
		% P_2O_5	% Insol	% MgO	P_2O_5	MgO
D3	Dolo. Tail.	23.33	2.95	5.49	37.0	73.2
	Phos. Conc.	25.85	14.20	1.30	63.0	26.8
	Flot. Feed	24.86	9.76	2.95	100.0	100.0
D2	Dolo. Tail.	19.61	2.94	7.61	18.7	60.8
	Phos. Conc.	26.50	11.81	1.52	81.3	39.2
	Flot. Feed	24.87	9.72	2.96	100.0	100.0
D1	Dolo. Tail.	14.62	3.77	10.20	10.3	59.1
	Phos. Conc.	27.22	10.92	1.50	89.7	40.9
	Flot. Feed	25.00	9.66	3.03	100.0	100.0
D4	Dolo. Tail.	13.06	3.75	11.40	7.3	54.1
	Phos. Conc.	26.70	10.89	1.54	92.7	45.9
	Flot. Feed	24.82	9.91	2.90	100.0	100.0
D5	Dolo. Tail.	16.54	2.67	9.36	12.5	59.7
	Phos. Conc.	27.03	11.15	1.48	87.5	40.3
	Flot. Feed	25.03	9.54	2.98	100.0	100.0
D6	Dolo. Tail.	18.74	2.57	8.12	18.2	66.9
	Phos. Conc.	27.12	11.96	1.30	81.8	33.1
	Flot. Feed	25.07	9.67	2.96	100.0	100.0
D10	Dolo. Tail.	24.49	2.59	4.85	46.0	75.9
	Phos. Conc.	26.01	14.81	1.35	54.0	24.1
	Flot. Feed	25.29	9.00	3.03	100.0	100.0
D7	Dolo. Tail.	20.06	3.22	7.52	22.9	70.4
	Phos. Conc.	27.17	12.13	1.28	77.1	29.6
	Flot. Feed	25.13	9.57	3.07	100.0	100.0
D9	Dolo. Tail.	20.12	2.85	7.28	18.4	57.3
	Phos. Conc.	26.80	11.19	1.62	81.6	42.7
	Flot. Feed	25.26	9.27	2.93	100.0	100.0
D8	Dolo. Tail.	22.65	2.91	6.00	33.3	72.6
	Phos. Conc.	26.80	12.99	1.34	66.7	27.4
	Flot. Feed	25.25	9.24	3.07	100.0	100.0

Sample A

This flotation feed sample, analyzing about 1.0% MgO, was very responsive to dolomite flotation using either 2.5 or 1.5 lbs. of collector and 1.0-3.0 lbs. of STPP per ton of feed. Figures 36 and 37 present graphs showing concentrate % MgO, % recovery of

P_2O_5 and % recovery of MgO as a function of STPP level employed. Figure 36 shows that when 2.5 lbs./ton of collector were used, 2-3 lbs./ton of STPP depressant were required to yield phosphate concentrates containing 0.63-0.67% MgO (MgO/P_2O_5 = .024-.025) at 93.7-95.0% recovery of P_2O_5 (Table 3a; tests A2 and A7). Figure 37 shows that when only 1.5 lbs./ton of collector was used, 1-2 lbs./ton of STPP depressant was required to yield phosphates containing 0.68-0.73% MgO (MgO/P_2O_5 = .026-.027) at 94.5-96.2% recovery of P_2O_5 (Table 22a; tests A1 and A5).

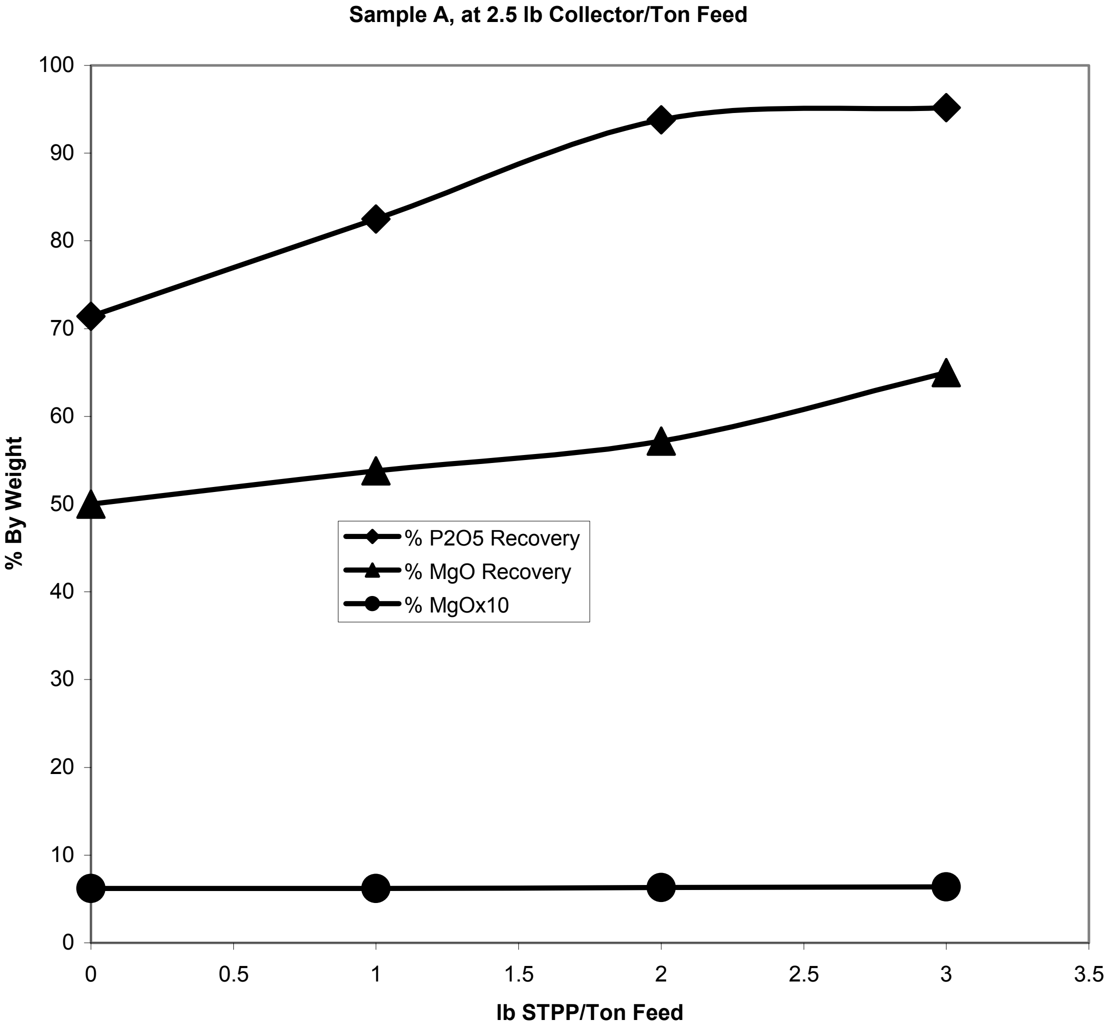


Figure 36. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

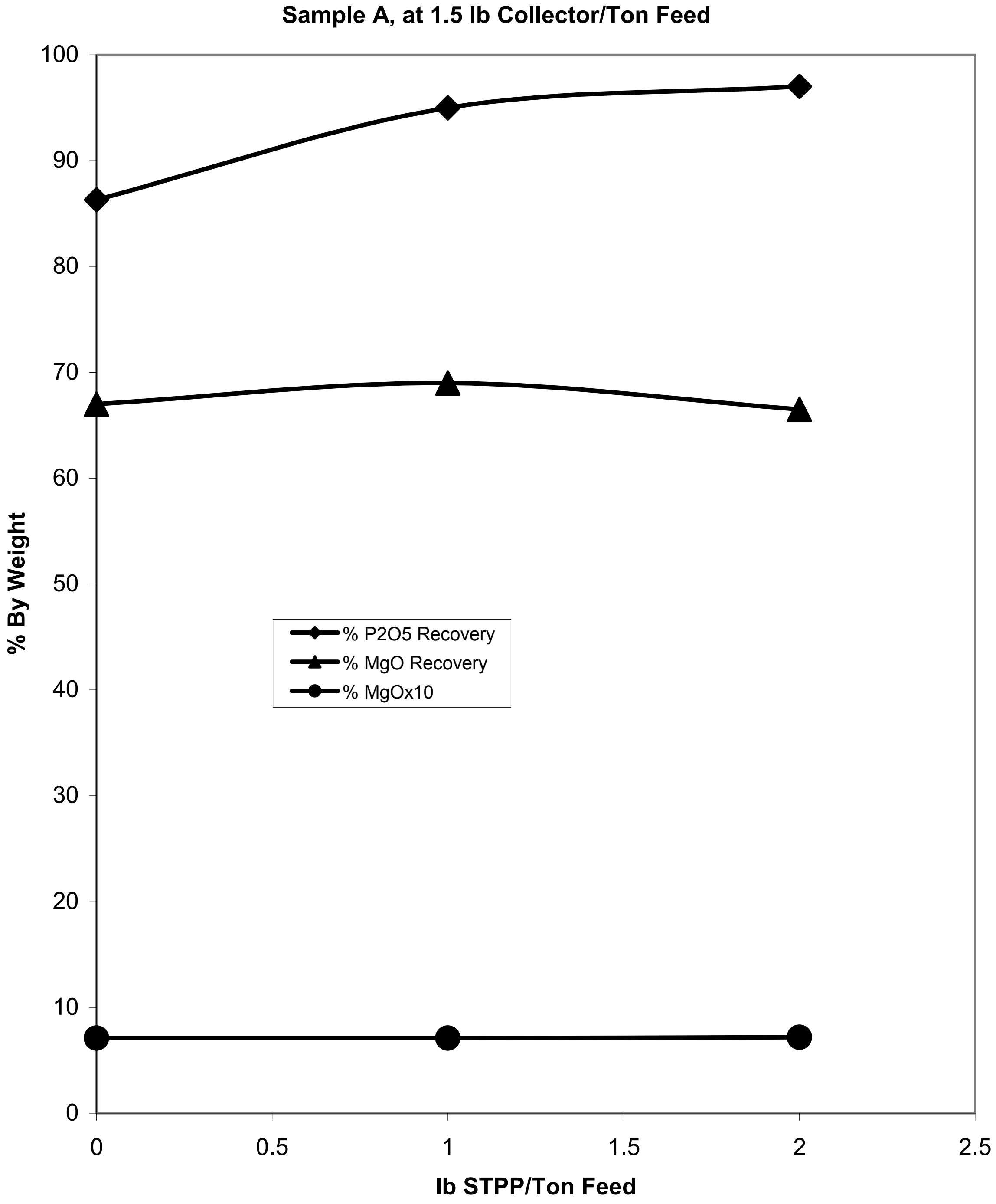


Figure 37. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Sample B

This very responsive flotation feed sample, analyzing about 1.5-1.6% MgO, was previously shown in Progress Report No. 6 and in Figure 38 to require 2-3 lbs./ton of STPP depressant, using 2.5 lbs./ton of collector, to produce phosphate concentrates containing 0.73-0.80% MgO (MgO/P_2O_5 = .027-.029) at 90.0-92.9% recovery of P_2O_5 (Table 3b; Tests B1 and B4).

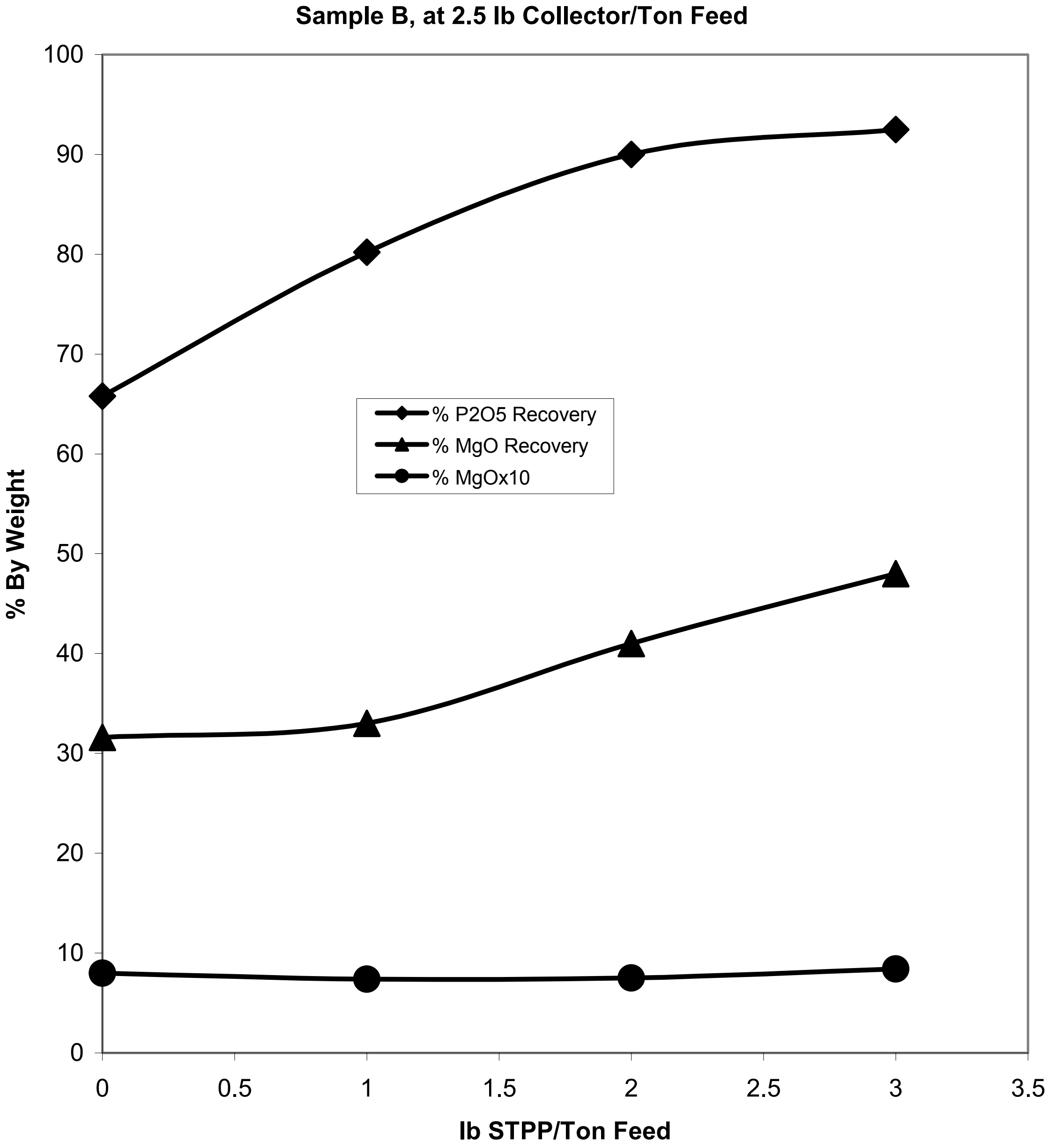


Figure 38. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Sample C

This flotation feed sample, analyzing about 2.3-2.4% MgO, was more difficult to process than samples A and B. No concentrates were obtained analyzing less than 1.0% MgO. Figure 39 shows that when 1-2 lb./ton of STPP were used with 2.5 lb./ton of collector, phosphate concentrates were obtained containing 1.07-1.13% MgO (MgO/P_2O_5 = .039-.041) at 75.4-89.5% recovery of P_2O_5 (Table 22c; Tests C2 and C1).

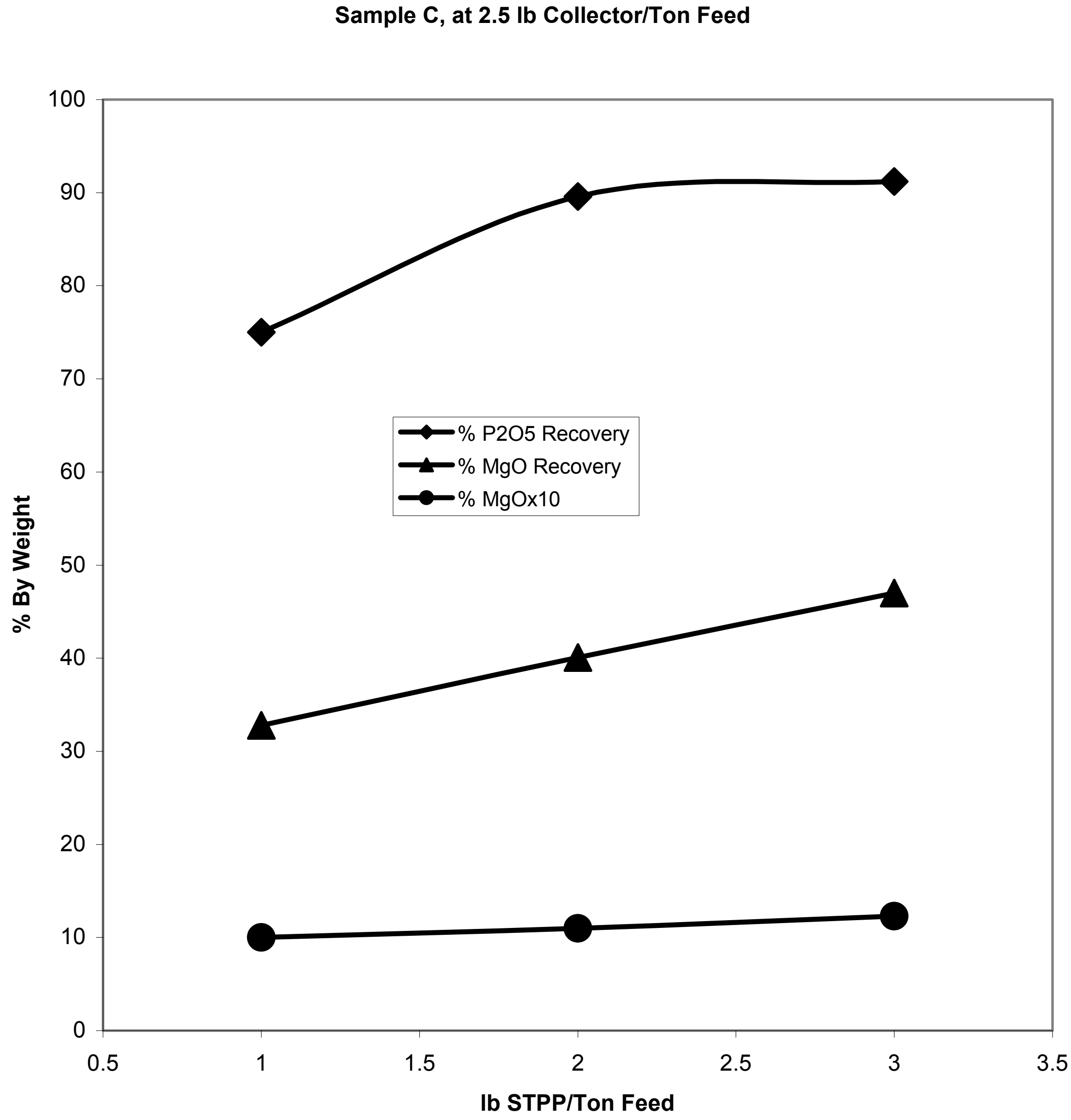


Figure 39. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

As shown in Figure 40, using 1-2 lbs./ton of STPP with 3.5 lbs./ton of collector did not produce concentrates containing significantly lower % MgO. Concentrates containing 1.04-1.22% MgO (MgO/P_2O_5 = .037-.043) were obtained at 72.7-85.5% recovery of P_2O_5 (Table 22c; Tests C6 and C5).

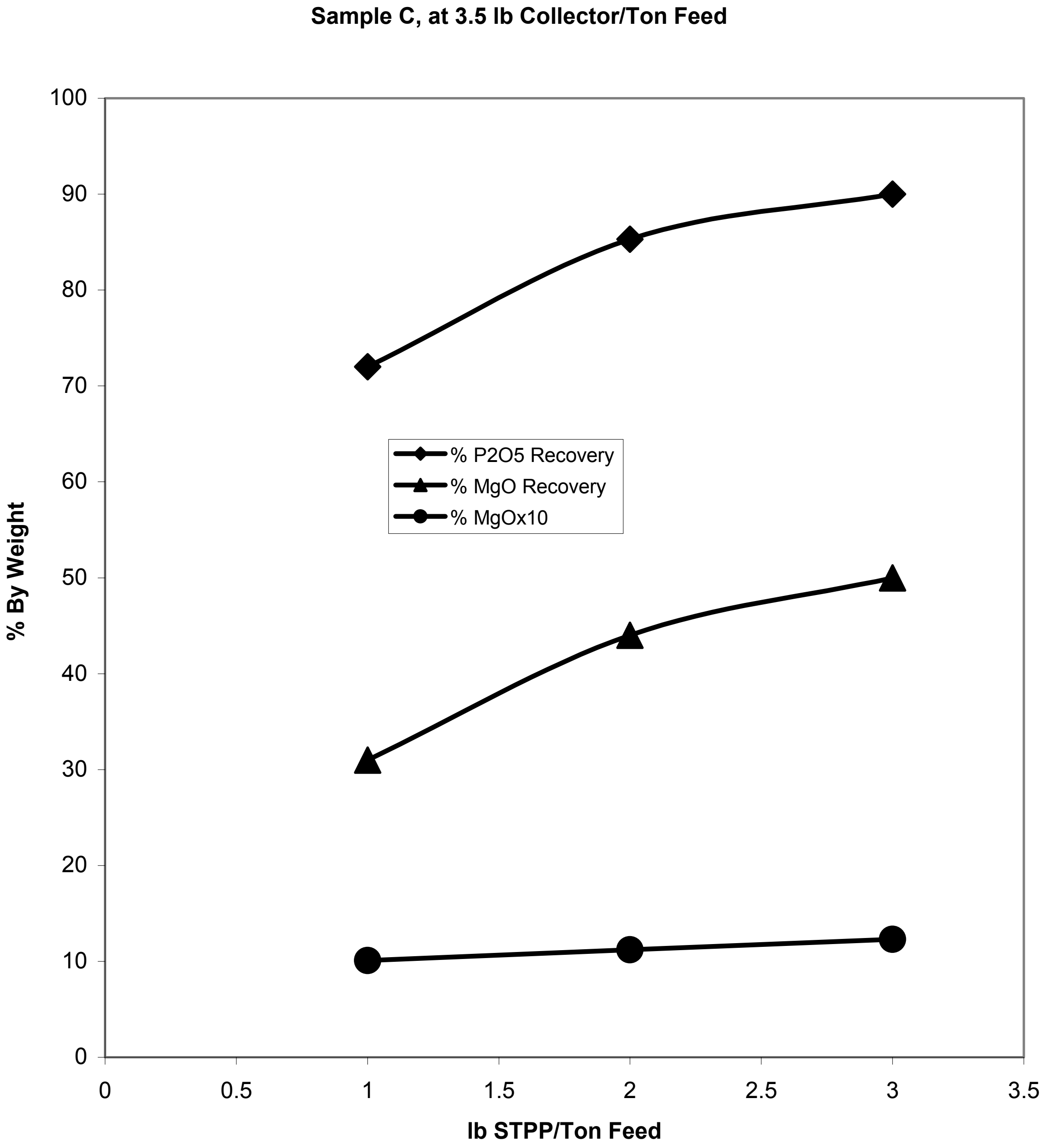


Figure 40. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Sample D

This high-MgO flotation feed sample, analyzing about 2.9-3.0% MgO, was very difficult to process compared to the previous three samples. Figure 41 shows that when 2-3 lb./ton of STPP depressant was used with 2.5 lb./ton of collector, the phosphate concentrates analyzed 1.50-1.54% MgO (MgO/P_2O_5 = .055-.058) at 89.7-92.7% recovery of P_2O_5 (Table 22d; Tests D1 and D4).

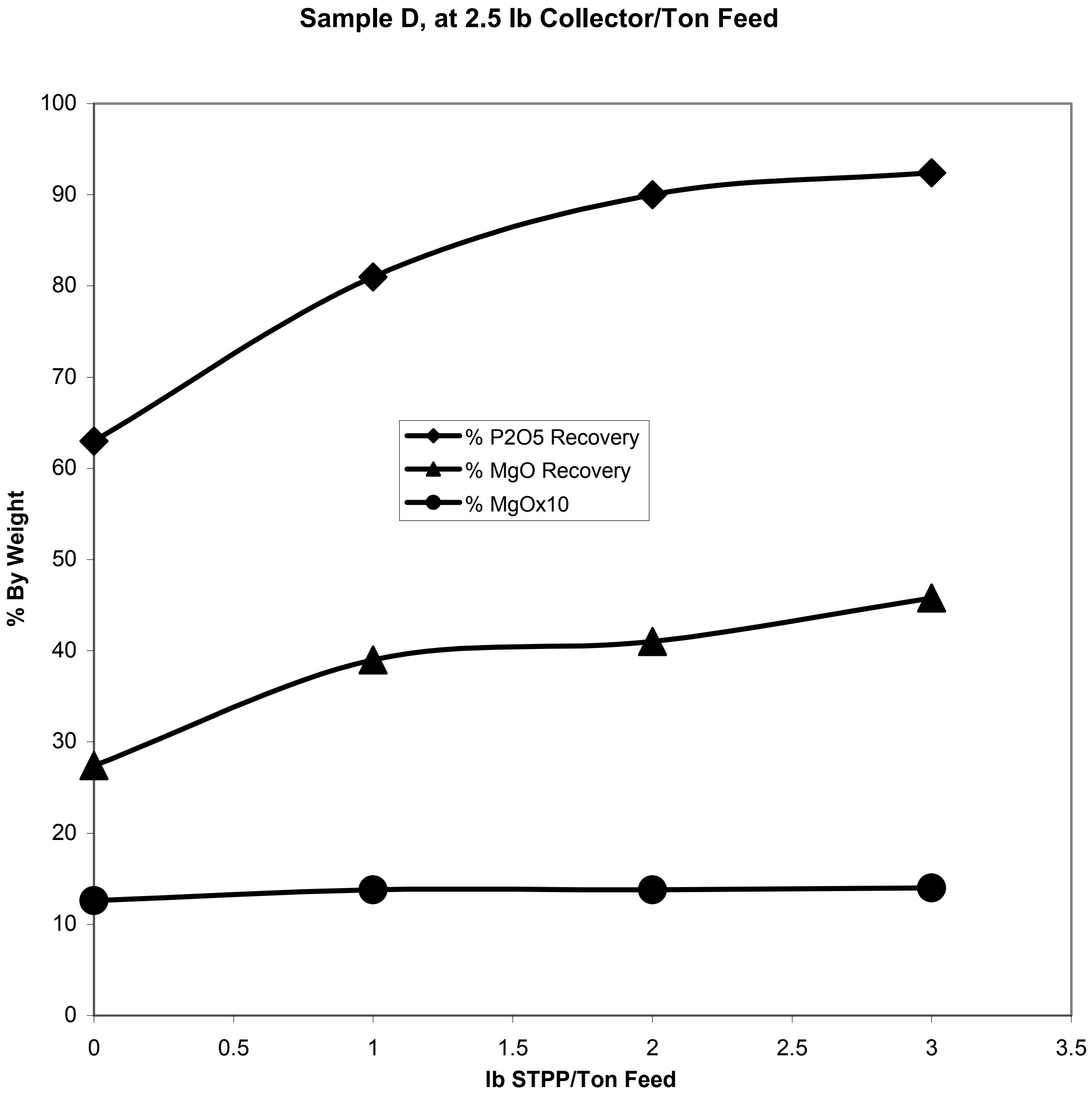


Figure 41. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

As shown in Figure 42, using 2-3 lbs./ton of STPP depressant with 5.5 lbs./ton of collector produced phosphate concentrates analyzing 1.28-1.62% MgO (MgO/P_2O_5 = .047-.060) at 77.1-81.6% recovery of P_2O_5 (Table 22d; Tests D7 and D9). Using this very high collector level appeared to promote the flotation of more fine (-100 mesh) phosphate particles instead of floating more of the +65 mesh dolomite particles. Flotation selectivity was not easily maintained using excessive collector level.

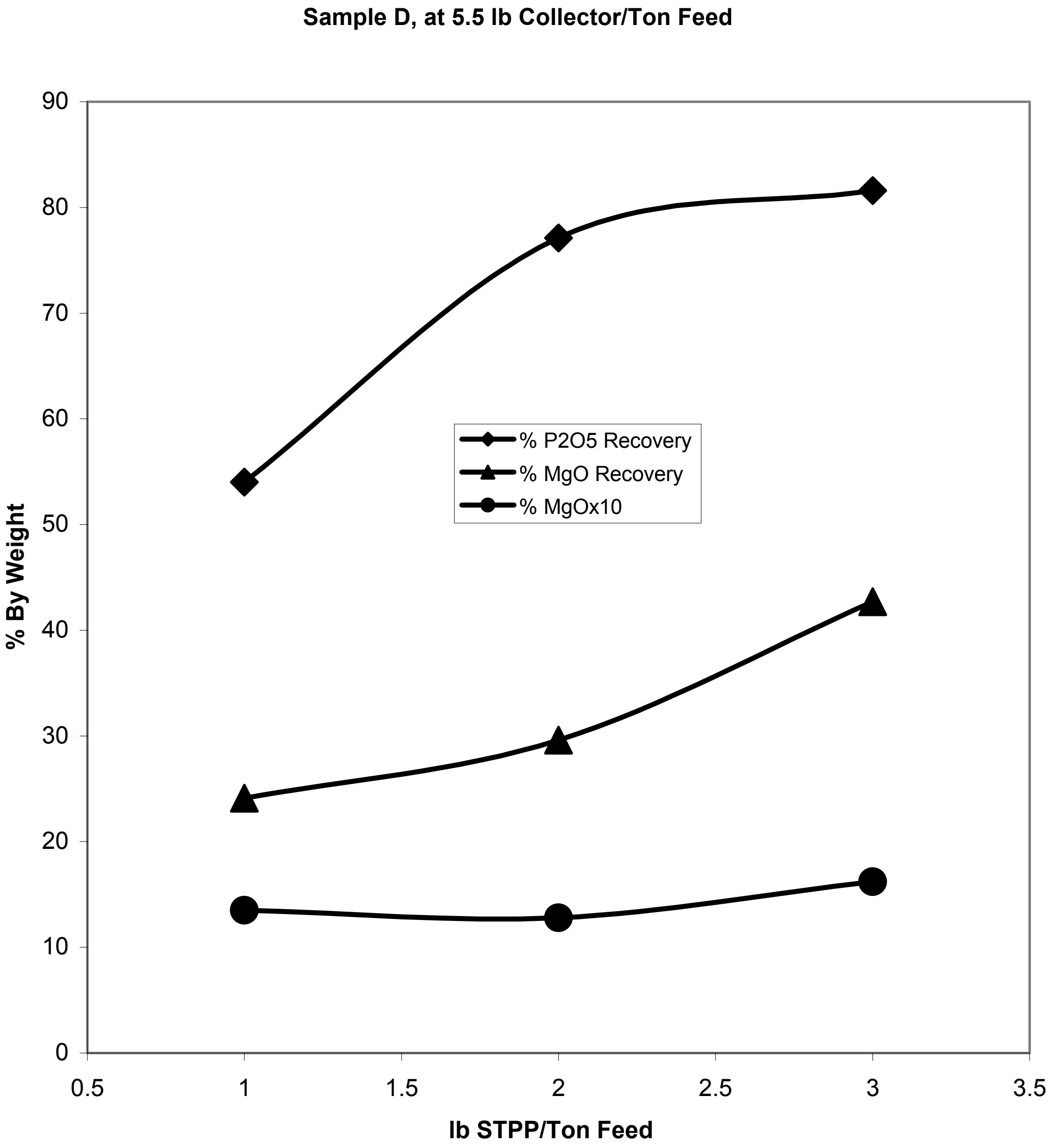


Figure 42. Flotation Concentrate Grade/Recovery Using Various STPP Levels.

Size/Assay Analyses of Selected Phosphate Concentrates

Size/assay analyses were performed on four selected samples of flotation concentrate derived from pebble samples C and D. These concentrates contained about 1.1-1.5% MgO. Table 23 shows that the -100 mesh fraction of each concentrate analyzed only 0.58-0.68% MgO, and the total -65 mesh fractions analyzed 0.84-.07% MgO, illustrating the problem of floating the coarsest dolomite particles. Microscopic examination of the +65 mesh concentrate size fractions, after staining the dolomite particles with Titan Yellow, revealed some locked phosphate/dolomite; however the majority of the stained dolomite appeared to be present as essentially free particles. Finer grinding of the pebble samples C and D to -65 mesh is probably required in order to produce phosphate concentrates analyzing 1.0% MgO or less using reasonable reagent levels.

Table 23. Size/Assay Analyses for Selected Flotation Concentrate Samples.

Sample	Tyler Mesh	% Wt.	% P_2O_5	% Insol	% MgO
Pebble C	+65	29.3	27.39	10.06	1.59
Test C1	65/100	29.8	26.96	11.52	1.24
	-100	40.9	28.72	11.50	0.64
	Total	100.0	27.81	11.08	1.10
Pebble C	+65	30.5	27.43	10.32	1.62
Test C5	65/100	30.5	26.97	11.52	1.37
	-100	39.0	28.08	12.01	0.62
	Total	100.0	27.55	11.34	1.15
Pebble D	+65	34.6	27.36	8.99	1.91
Test D7	65/100	30.8	27.84	11.03	1.15
	-100	34.6	27.75	14.27	0.58
	Total	100.0	27.64	11.45	1.21
Pebble D	+65	30.2	26.73	8.90	2.22
Test D1	65/100	29.2	27.24	10.89	1.62
	-100	40.6	28.71	11.05	0.68
	Total	100.0	27.68	10.36	1.44

Dolomite and Quartz Flotation from Feed Samples

Laboratory two-stage flotation tests were performed on each of the feeds derived from all four pebble samples. Dolomite was initially floated using Sulfonate OA-5R plus oil at pH = 5.5-6.0 and STPP as the phosphate depressant. Cell underflows were dewatered, washed and subjected to silica flotation at pH = 6.8-7.1 using Custamine 738 to yield final phosphate concentrates containing at least 30% P_2O_5. Results are presented in Table 24.

Table 24. Dolomite/Silica Flotation Material Balances for Various Pebbles.

Test	Reagents	lb./ton f Pro	Product	% Wt.
Sample A, A1	H_2SO_4	3.60	Dolo. Tail.	10.3
	STPP	2.00	Silica Tail.	14.6
	OA-5R	2.50	Phos. Conc.	75.1
	Ph.Oil	1.25	Flot. Feed	100.0
	Custamine 738	0.70		
	Diesel	0.10		
Sample A, A2	H_2SO_4	3.60	Dolo. Tail.	5.3
	STPP	2.00	Silica Tail.	14.8
	OA-5R	1.50	Phos. Conc.	79.9
	Ph.Oil	0.75	Flot. Feed	100.0
	Custamine 738	0.70		
	Diesel	0.10		
Sample B, A1	H_2SO_4	3.20	Dolo. Tail.	12.9
	STPP	2.00	Silica Tail.	11.6
	OA-5R	2.50	Phos. Conc.	75.5
	Ph.Oil	1.25	Flot. Feed	100.0
	Custamine 738	0.70		
	Diesel	0.10		
Sample C, A1	H_2SO_4	3.40	Dolo. Tail.	16.5
	STPP	2.00	Silica Tail.	8.7
	OA-5R	2.50	Phos. Conc.	74.8
	Ph.Oil	1.25	Flot. Feed	100.0
	Custamine 738	0.70		
	Diesel	0.10		
	Dolo. Flot.			
Sample D, A1	H_2SO_4	3.40	Dolo. Tail.	18.7
	STPP	3.00	Silica Tail.	8.4
	OA-5R	3.50	Phos. Conc.	72.9
	Ph.Oil	1.25	Flot. Feed	100.0
	Custamine 738	0.70		
	Diesel	0.10		

Table 24 (Cont.). Dolomite/Silica Flotation for Various Pebbles.

Test	Product	Concentrate Analysis			% Distribution	
		%P_2O_5	% Insol	% MgO	P_2O_5	MgO
Sample A, A1	Dolo. Tail.	24.61	8.75	3.74	9.7	39.4
	Silica Tail.	1.69	90.60	0.05	1.0	1.0
	Phos. Conc.	31.02	1.76	0.79	89.3	59.6
	Flot. Feed	26.08	15.45	0.99	100.0	100.0
Sample A, A2	Dolo. Tail.	21.18	10.56	5.34	4.3	28.0
	Silica Tail.	2.97	94.56	0.09	1.7	1.0
	Phos. Conc.	30.52	2.45	0.89	94.0	71.0
	Flot. Feed	25.95	16.51	1.00	100.0	100.0
Sample B, A1	Dolo. Tail.	18.94	5.82	6.70	9.2	58.5
	Silica Tail.	4.87	84.20	0.10	2.1	0.7
	Phos. Conc.	31.33	1.44	0.80	88.7	40.8
	Flot. Feed	26.65	11.61	1.47	100.0	100.0
Sample C, A1	Dolo. Tail.	18.42	4.80	9.00	11.4	60.0
	Silica Tail.	3.57	88.13	0.10	1.2	0.4
	Phos. Conc.	31.12	2.39	1.31	87.4	39.6
	Flot. Feed	26.63	10.25	2.47	100.0	100.0
Sample D, A1	Dolo. Tail.	15.7	5.02	10.49	11.6	61.4
	Silica Tail.	4.23	85.89	0.14	1.4	0.3
	Phos. Conc.	30.36	2.30	1.68	87.0	38.3
	Flot. Feed	25.42	9.83	3.20	100.0	100.0

Sample A yielded phosphate concentrates analyzing 30.52-31.02% P_2O_5, 2.97-1.69% insol, 0.89-0.79% MgO and MgO/P_2O_5 ratio = .029-.025 at 94.0-89.7% overall P_2O_5 recovery. Sample B yielded a phosphate concentrate analyzing 31.33% P_2O_5, 1.44% insol, 0.80% MgO and MgO/P_2O_5 ratio = .026 at 88.7% overall P_2O_5 recovery. Sample C yielded a phosphate concentrate analyzing 31.12% P_2O_5, 2.39% insol, 1.31% MgO and MgO/P_2O_5 = .042 at 87.4% overall P_2O_5 recovery. Sample D yielded a phosphate concentrate analyzing 30.36% P_2O_5, 2.30% insol, 1.68% MgO and MgO/P_2O_5 ratio = .055 at 87% overall P_2O_5 recovery. Amine flotation recovery of P_2O_5 exceeded 97% for all four samples processed.

Preliminary Flotation Reagent Cost Estimates

Dolomite flotation reagent costs were calculated for processing of the four pebble samples. Costs were obtained for two selected tests for each pebble sample. The costs are presented in Table 25 as $/ton of feed and $/ton of concentrate for each of the eight selected tests.

Table 25. Dolomite Flotation Reagent Cost Estimates for Selected Tests.

Test	Reagent Name	Lb./TOF	$/Lb.	$/TOF	$/TOC
SAMPLE A: Conc. Ratio = 1.080; 0.63% MgO and 93.7% Recov. P_2O_5					
A2	Sulfuric Acid	3.6	0.02	0.072	0.078
	STPP	2.0	0.43	0.860	0.929
	Sulfonate OA-5R	2.5	0.49	1.225	1.323
	Philflo Oil	1.25	0.15	0.188	0.203
	Total	9.35	--	2.345	2.533
SAMPLE A: Conc. Ratio = 1.053; 0.68% MgO and 96.2% Recov. P_2O_5					
A1	Sulfuric Acid	3.6	0.02	0.072	0.076
	STPP	2.0	0.43	0.860	0.905
	Sulfonate OA-5R	1.5	0.49	0.735	0.774
	Philflo Oil	0.75	0.15	0.113	0.119
	Total	7.85	--	1.780	1.874
SAMPLE B: Conc. Ratio = 1.155; 0.73% MgO and 90.0% Recov. P_2O_5					
B1	Sulfuric Acid	3.6	0.02	0.072	0.083
	STPP	2.0	0.43	0.860	0.993
	Sulfonate OA-5R	2.5	0.49	1.225	1.415
	Philflo Oil	1.25	0.15	0.188	0.217
	Total	9.35	--	2.345	2.708

Table 25 (Cont.). Dolomite Flotation Reagent Cost Estimates for Selected Tests.

Test	Reagent Name	Lb./TOF	$/Lb.	$/TOF	$/TOC
SAMPLE B: Conc. Ratio = 1.121; 0.80% MgO and 92.9% Recov. P_2O_5					
B4	Sulfuric Acid	3.4	0.02	0.068	0.076
	STPP	3.0	0.43	1.290	1.446
	OA-5R	2.5	0.49	1.225	1.373
	Philflo Oil	1.25	0.15	0.188	0.211
	Total	10.15	--	2.771	3.106
SAMPLE C: Conc. Ratio = 1.182; 1.13% MgO and 89.5% Recov. P_2O_5					
C2	Sulfuric Acid	3.6	0.02	0.072	0.085
	STPP	2.0	0.43	0.860	1.017
	Sulfonate OA-5R	2.5	0.49	1.225	1.448
	Philflo Oil	1.25	0.15	0.188	0.222
	Total	9.35	--	2.345	2.772
SAMPLE C: Conc. Ratio = 1.435; 1.04% MgO and 72.7% Recov. P_2O_5					
C6	Sulfuric Acid	3.4	0.02	0.068	0.097
	STPP	1.0	0.43	0.430	0.617
	Sulfonate OA-5R	3.5	0.49	1.715	2.461
	Philflo Oil	1.25	0.15	0.188	0.270
	Total	9.15	--	2.401	3.445
SAMPLE D: Conc. Ratio = 1.235; 1.50% MgO and 89.7% Recov. P_2O_5					
D1	Sulfuric Acid	3.6	0.02	0.072	0.087
	STPP	2.0	0.43	0.860	1.044
	Sulfonate OA-5	2.5	0.49	1.225	1.487
	Philflo Oil	1.25	0.15	0.188	0.228
	Total	9.35	--	2.345	2.846
SAMPLE D: Conc. Ratio = 1.214; 1.48% MgO and 87.5% Recov. P_2O_5					
D5	Sulfuric Acid	3.6	0.02	0.072	0.089
	STPP	2.0	0.43	0.860	1.062
	Sulfonate OA-5R	3.5	0.49	1.715	2.118
	Philflo Oil	1.25	0.15	0.188	0.232
	Total	10.35	--	2.835	3.501

For sample A, the total reagent costs ranged from $1.78-$2.35/ton of flotation feed and $1.87-$2.53/ton of phosphate concentrate analyzing <0.7% MgO. For sample B, the costs ranged from $2.35-$2.77/ton of flotation feed and $2.71-$3.11/ton of phosphate concentrate analyzing <0.9% MgO.

For sample C, the total reagent costs ranged from \$2.35-\$2.40/ton of flotation feed and \$2.77-\$3.45/ton of phosphate concentrate analyzing 1.0-1.1+% MgO. Since concentrates derived from sample D contained >1.4% MgO at >85% P_2O_5 recovery, calculated reagent costs were considered to be irrelevant at the present time.

In order to produce final phosphate concentrates analyzing >30% P_2O_5, amine flotation of silica from the dolomite flotation cell underflow is required. Reagent requirements for this final flotation stage were about 0.7 lbs. of Custamine 738 and 0.1 lb. of diesel fuel per ton of original dolomite flotation feed. For Custamine 738 at \$0.24/lb. and diesel fuel at \$0.15/lb., the reagent cost for silica flotation to produce >30% P_2O_5 and <3% insol would be about \$0.18/ton of feed or \$0.19-\$0.26/ton of final phosphate concentrate.

ADSORPTION STUDIES

Summary

Previous tests have shown that several phosphatic reagents performed effectively as phosphate depressants during the anionic flotation of dolomite from Florida phosphate ores. The depressants included sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), sodium hexametaphosphate (SHMP) and disodium hydrogen phosphate (DSHP). Further tests were conducted and measure mineral solubility at various pH levels and depressant adsorption in an attempt to ascertain the fundamental reasons for the depressants effectiveness observed during the reported flotation testwork. Florida phosphate and dolomite concentrates prepared by electrostatic separation (1995-96) of IMC/Agrico feed and hand-picked, comminuted and deslimed dolomite pebbles were used for the current testwork.

Chemical analyses were performed on the two "pure" mineral samples. The phosphate mineral concentrate analyzed 32.4% P_2O_5, 4.7% insol, 0.4% MgO and 46.1% CaO. The dolomite mineral concentrate analyzed 1.6% P_2O_5, 4.4% insol, 17.6% MgO and 29.9% CaO. The phosphate concentrate contained about 27.2% weight of +35 mesh particles, whereas the dolomite concentrate contained only 0.2% weight of +35 mesh particles. Surface areas for the phosphate and dolomite, as measured by the University of Florida, were reported to be 11.8 sq. meters/g and 6.9 sq. meters/g, respectively.

Dissolution of dolomite and phosphate from 25% solids tap water slurries was determined for the approximate pH range of 4.0-7.5 using sulfuric acid for pH regulation. Using a 5-minute contact time, dolomite released many more Ca and Mg ions into solution compared to phosphate. About 2 ppm or less of P_2O_5, Ca, or Mg ions were released from the phosphate at a pH as low as 5.0-5.5. More than 115 ppm of Ca ion and 25 ppm of Mg ion were released from dolomite in the same pH range. The Ca and/or Mg ions caused finely dispersed precipitates to form by reaction with STPP, TSPP, SHMP and DSHP in solution.

A series of depressant adsorption tests was performed using de-ionized water solutions and tap water solutions of STPP, TSPP, SHMP, DSHP and orthophosphoric acid with the previously described phosphate and dolomite mineral samples. Slurries containing 25 g of mineral solids and 75 g of water were tested at natural pH and at moderately acid pH levels using sulfuric acid as the pH regulator. P_2O_5 analyses were performed on the various depressant solutions before and after 2-minute contact with either the phosphate or dolomite mineral. The original contact solutions contained 0.21 g of selected depressant per liter during initial adsorption tests. “Adsorption" does not necessarily denote that ionic or precipitate adsorption actually occurred and resulted in deletion of all of the P_2O_5 from the various depressant solutions tested.

Using de-ionized water depressant solutions of STPP, TSPP, SHMP and DSHP, a greater adsorption or depletion of P_2O_5 from solution was obtained by contact with dolomite as compared to phosphate. Adsorption of P_2O_5 on dolomite ranged from about 0.06-0.16 mg/g of mineral. Adsorption of P_2O_5 on phosphate ranged from about 0.02-0.06 mg/g of mineral. Adsorption of P_2O_5 was not significant (less than 0.02 mg/g) on phosphate when orthophosphoric acid was used as the potential phosphate depressant. Using the turbid tap water depressant solutions of STPP, TSPP, SHMP and DSHP, adsorption or depletion of P_2O_5 from solution was somewhat erratic. Adsorption of P_2O_5 ranged from about 0.02-0.10 mg/g of each mineral. Using orthophosphoric acid, adsorption of P_2O_5 was again less than 0.02 mg/g of mineral. It is not known whether chemical adsorption of various depressant anions, physical adsorption of extremely fine Ca and/or Mg precipitates with depressant anions, or both mechanisms occurred. Additional adsorption tests were performed using phosphate and dolomite with de-ionized water solutions containing 0.41 g and 0.61 g of STPP per liter. All other test conditions and procedures remained the same as the original test series. The higher STPP content solutions yielded test results similar to the initial tests using 0.21 g of STPP depressant per liter.

LABORATORY TESTWORK

Description of "Pure" Mineral Samples

The phosphate mineral sample used for the depressant adsorption and ion solubility testwork was prepared by multiple-pass freefall electrostatic separation of -20+200 mesh IMC/Agrico unsized feed obtained from the Ft. Green plant. The dolomite "pure" mineral sample prepared for parallel testwork was obtained by hand-picking dolomite pebble from IMC/Agrico's Four Corners plant storage piles located at the Noralyn metallurgical laboratory. The dolomite sample was stage rodmilled (wet), screened and deslimed to yield a -35+200 mesh product for single-pass electrostatic separation to lower the siliceous mineral content. Preheat temperature for all electrostatic separations was about 275° F.

Chemical analyses for the phosphate and dolomite concentrates revealed the following compositions:

Product	% P_2O_5	% Insol	% MgO	% CaO
Phosphate	32.41	4.74	0.40	46.11
Dolomite	1.63	4.43	17.60	29.95

Approximately 33 pounds of "pure" phosphate and 12 pounds of "pure" dolomite were produced for solubility and adsorption testwork. The phosphate was multi-colored (ivory, brown, tan, and black) and the dolomite was yellowish tan in color. Specific gravity, as measured by methanol/water displacement, was 2.91 for the phosphate and 2.70 for the dolomite. Surface area measurements were performed on the phosphate and dolomite samples by the University of Florida. Results were 11.8 sq. meters/g for the phosphate and 6.9 sq. meters/g for the dolomite. Alizarin Red S staining of the phosphate and dolomite samples showed the absence of limerock (calcite) in either mineral sample.

Titan Yellow staining of the phosphate sample revealed the presence of a very small amount of dolomite particles.

Dry screen analyses of the two mineral samples showed the following particle size distributions:

Tyler	Phosphate		Dolomite	
Mesh	% Wt.	Cum. % Wt.	% Wt.	Cum. % Wt.
+35	27.2	27.2	0.2	0.2
35/48	26.4	53.6	29.8	30.0
48/65	27.1	80.7	28.3	58.3
65/100	14.3	95.0	21.3	79.6
100/150	3.6	98.6	11.6	91.2
150/200	1.1	99.7	6.2	97.4
-200	0.3	100.0	2.6	100.0
Total	100.0	---	100.0	---

RESULTS AND DISCUSSION

Dissolution of Phosphate and Dolomite at Various Slurry pH Levels

A series of laboratory tests was performed wherein multiple 25 g phosphate mineral / 75 g tap water slurries were adjusted to various acidic pH levels by dropwise additions of 10% sulfuric acid with stirring for 1 minute. Sulfuric acid required to obtain the reported acidic pH levels ranged from 2-9 drops (.0042-.0381g 100% H_2SO_4). Each initial slurry pH was measured and recorded at this time. Each slurry was allowed to settle for 4 additional minutes and the final pH at the liquid-solid interface was measured and recorded. Each supernatant liquid phase was decanted into a plastic sample bottle for chemical analyses (ppm P_2O_5, Ca and Mg). The procedure was repeated using dolomite in place of phosphate as the test mineral, and the decanted liquid phase was analyzed for ppm Ca and ppm Mg. The tap water used for these tests was also analyzed for ppm P_2O_5, Ca, and Mg to supply background data for comparisons. The various pH readings and liquid phase chemical analyses were summarized as follows:

Mineral/Water System	Initial pH	Final pH	Solution Analysis, ppm P_2O_5	Ca	Mg
Tap Water	7.25	7.25	0.12	122.98	25.98
Phosphate	7.05	7.05	0.27	124.76	26.78
and Tap Water	5.80	5.95	0.73	120.10	28.56
	5.05	5.36	1.19	122.24	28.05
	3.85	4.40	9.30	175.70	31.54
Dolomite	7.48	7.49	N.A.	138.16	35.52
and Tap Water	6.50	6.54	N.A.	172.13	35.17
	5.84	6.02	N.A.	187.07	45.22
	5.40	5.92	N.A.	253.87	60.28
	3.92	5.75	N.A.	325.60	65.31

For purposes of clarity, graphs of the above data are presented in Figures 43a, 43b and 43c for phosphate and in Figures 44a and 44b for dolomite. In these figures, the open circle point represents the tap water pH and the respective ion contents measured in ppm. The triangular points represent the initial slurry pH and the solid circle points represent the five minute final slurry pH.

Figure 43a shows that only about 1 ppm P_2O_5 was dissolved from the phosphate mineral at pH = 5.0-5.5, and that lowering the pH to about 4.0-4.5 resulted in about 9 ppm P_2O_5 being dissolved. Figure 1b shows that very little Ca was dissolved at pH = 5.0-5.5, and that dissolution of about 50-53 ppm of Ca was obtained when the solution pH was lowered to 4.0-4.5. Figure 43c illustrates that less than 2 ppm Mg was dissolved at pH = 5.0-5.5, and less than about 5 ppm of Mg was dissolved when the solution pH was lowered to 4.0-4.5. A significant part of the Ca and Mg dissolved from the phosphate sample was probably derived from the small amount of dolomite impurity present in the sample.

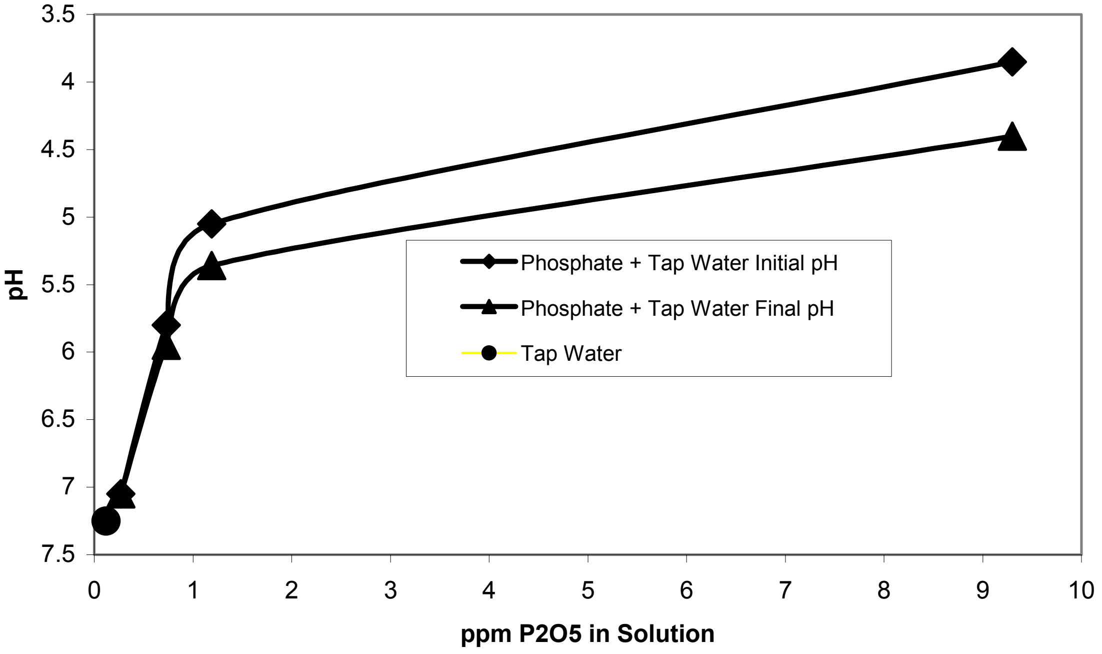


Figure 43a. P_2O_5 Solubilized from Phosphate in Tap Water at Various pH Levels.

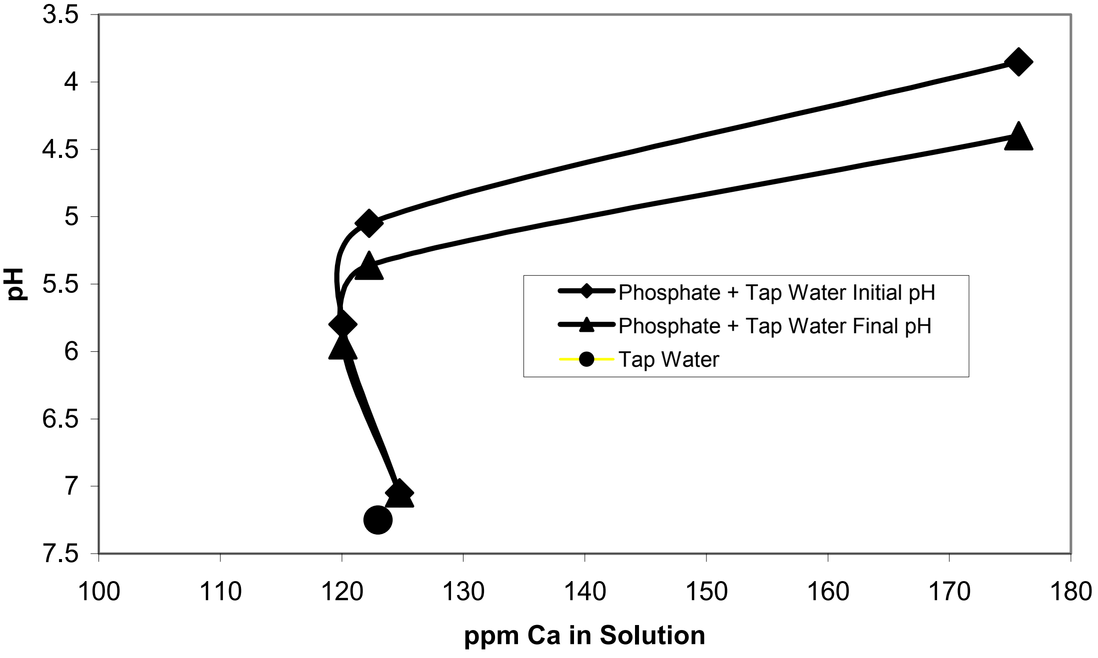


Figure 43b. Ca Solubilized from Phosphate in Tap Water at Various pH Levels.

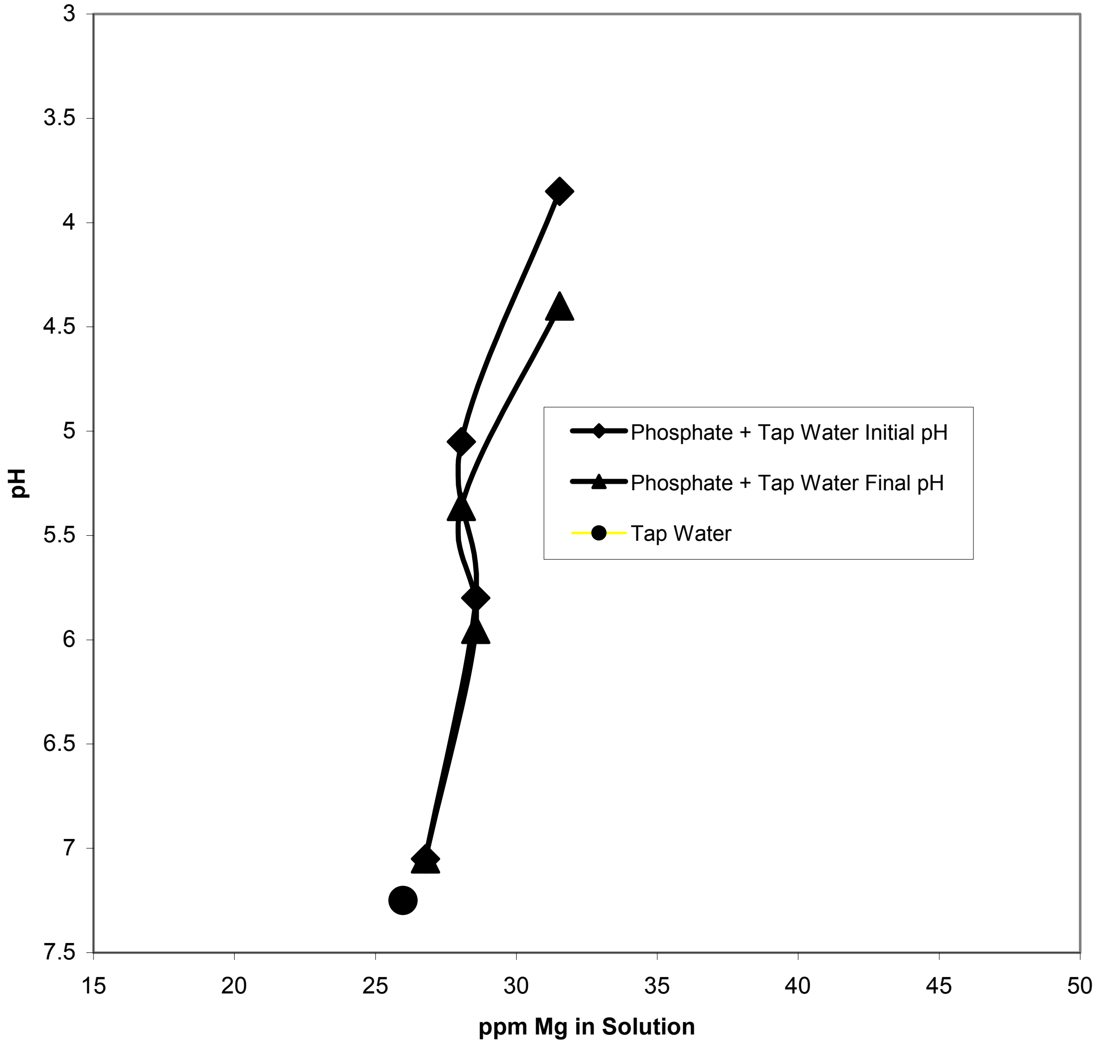


Figure 43c. MgO Solubilized from Phosphate in Tap Water at Various pH Levels.

Figure 44a shows that 15 ppm of Ca was dissolved from the dolomite mineral in the pH range of about 6.5-7.5 and increased to about 64 ppm of Ca dissolved when the pH was lowered to about 6.0. Further lowering of the pH to the 5.5-6.0 ranges increased the dissolution of Ca to about 130 ppm, and even further lowering of the initial pH to slightly under 4.0 caused an additional dissolution of Ca to exceed 200 ppm.

Figure 44b shows that about 9 ppm of Mg was dissolved from the dolomite mineral sample at a pH of about 6.5-7.5 and increased to about 19 ppm of Mg dissolved when the pH was lowered to about 6.0. Further lowering of the pH to the 5.4-5.9 range increased the dissolution of Mg to about 34 ppm, and even further lowering of the initial pH to just under 4.0 resulted in the dissolution of about 39 ppm of MgO.

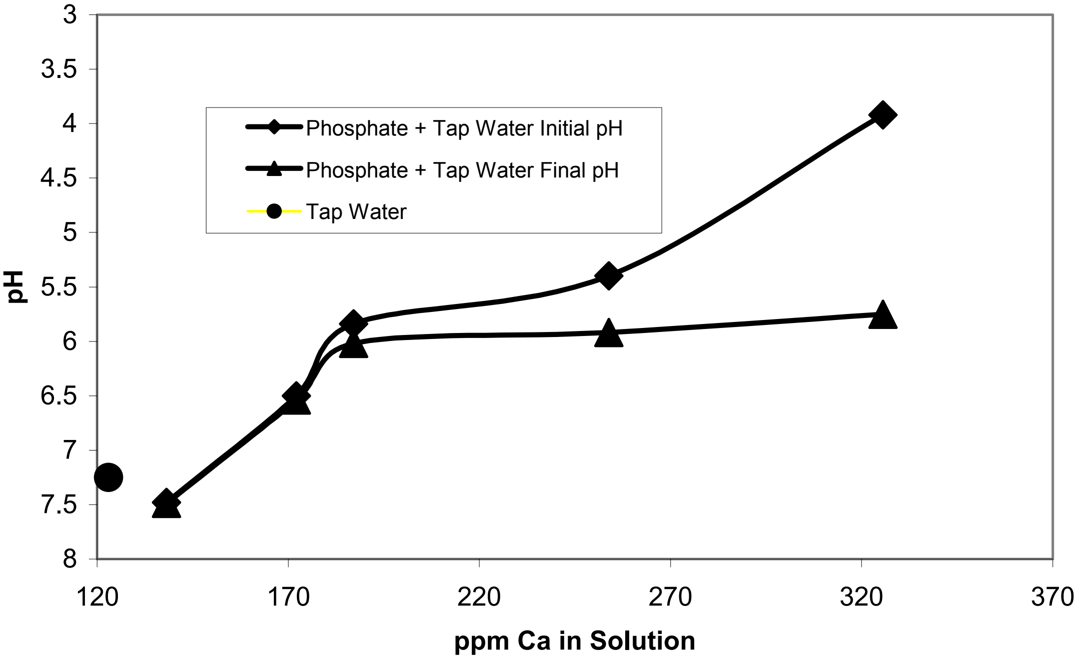


Figure 44a. Ca Solubilized from Phosphate in Tap Water at Various pH Levels.

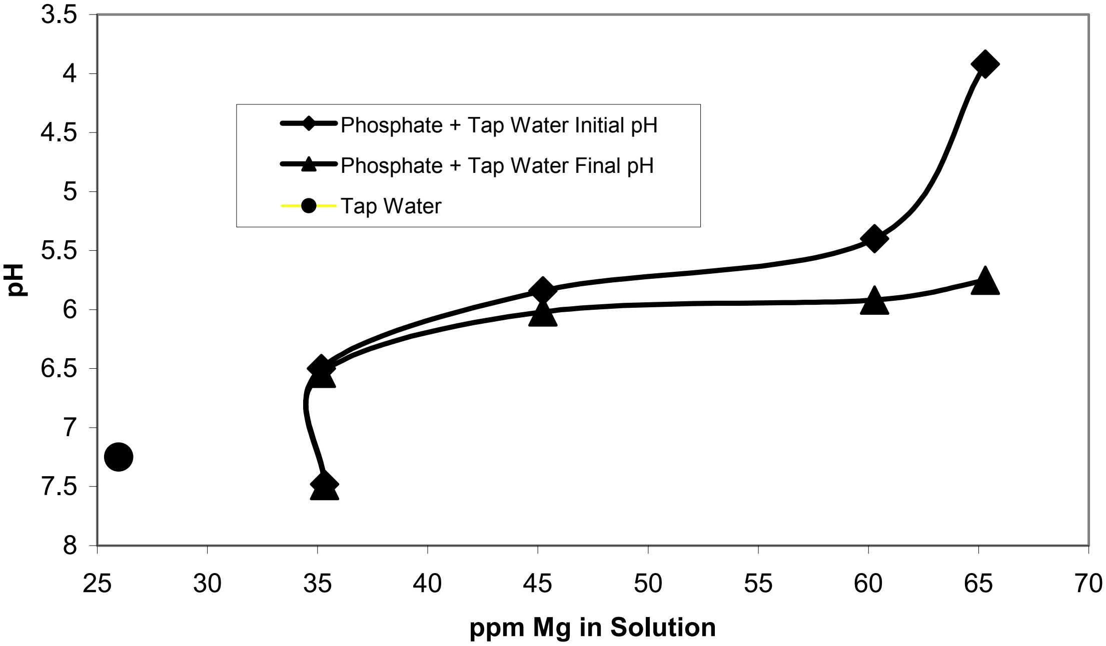


Figure 44b. MgO Solubilized from Phosphate in Tap Water at Various pH Levels.

It is apparent from these crude dissolution tests that significant quantities of Ca and Mg ions were released from dolomite, but not from phosphate, at a slurry pH range of 5.0-

6.0 commonly used for the flotation separation of the two minerals. These cations can react with various phosphatic depressants including STPP, SHMP, TSPP, DSHP and with fatty acid type collectors thereby affecting flotation performance by precipitation from solution as well as adsorption on mineral surfaces. Also, very little dissolution of P_2O_5 from phosphate was observed unless the slurry pH was reduced to about 4.0-4.5 or lower.

Adsorption of Phosphatic Depressants on Phosphate and Dolomite

A series of phosphatic depressant adsorption tests was attempted using STPP, TSPP, SHMP, DSHP and orthophosphoric acid depressants with more of the same phosphate and dolomite products used for the solubility testwork. Each test was performed in duplicate. Dropwise additions of 10% H_2SO_4 were used for slurry pH adjustments. Slurries were prepared for each test using 25 g of mineral and 75 g of depressant solution. Both tap water and de-ionized water were used for the preparation of 1 liter batches of depressant solution. Each stock solution contained 0.21 g/liter of phosphatic depressant (100% basis). These stock solutions, containing approximately 210 ppm of depressant, were similar to the concentrations used during flotation of dolomite from phosphate as described in previous sections. The stock solutions using tap water, except for orthophosphoric acid, turned cloudy shortly after preparation. These solutions were prepared fresh for the phosphate and for the dolomite tap water tests series. The stock solutions prepared using de-ionized water were clear.

Each 100 g slurry containing the selected depressant was stirred for 1 minute while adjusting the pH by dropwise sulfuric acid addition. The adjusted slurry was allowed to stand for 1 additional minute, the final pH recorded, and the supernatant liquid phase decanted into a plastic bottle for chemical analysis for ppm of P_2O_5. The 2 minute total contact time was the same as was used for conditioning time for flotation tests described previously. The adsorption test results using phosphate and dolomite with de-ionized water are shown in Figure 45. Parallel tests using tap water are shown in Figure 46.

The Figure 45 data indicates that the adsorption of each depressant P_2O_5 was greater on dolomite (open symbols) than on phosphate (solid symbols) over the entire pH range tested when de-ionized water was used. Adsorption of P_2O_5 on dolomite ranged from about 0.06-0.16 mg/g of mineral, whereas adsorption of P_2O_5 on phosphate ranged from about 0.02-0.06 mg/g of mineral. Figure 46 illustrates that when tap water was used, the data points show more random distribution of P_2O_5 adsorption on dolomite and phosphate using the various depressants. Adsorption of P_2O_5 when orthophosphoric acid was used ranged from about -0.02 to 0.0l mg/g of mineral. This reagent did not perform as a selective phosphate depressant during flotation tests previously reported. The other depressants showed that adsorption of P_2O_5 ranged from about 0.02-0.11 mg/g of mineral when tap water was used. The relatively high levels of Ca and Mg ions present in the tap water that caused complexing and/or precipitation of P_2O_5 in the various depressant solutions appeared to interfere with adsorption of P_2O_5 on the mineral surfaces. SHMP showed the most consistent adsorption character using either de-ionized or tap water. This depressant was observed to be slower to cause stock solution turbidity when dissolved in tap water compared to the other effective depressants used for flotation.

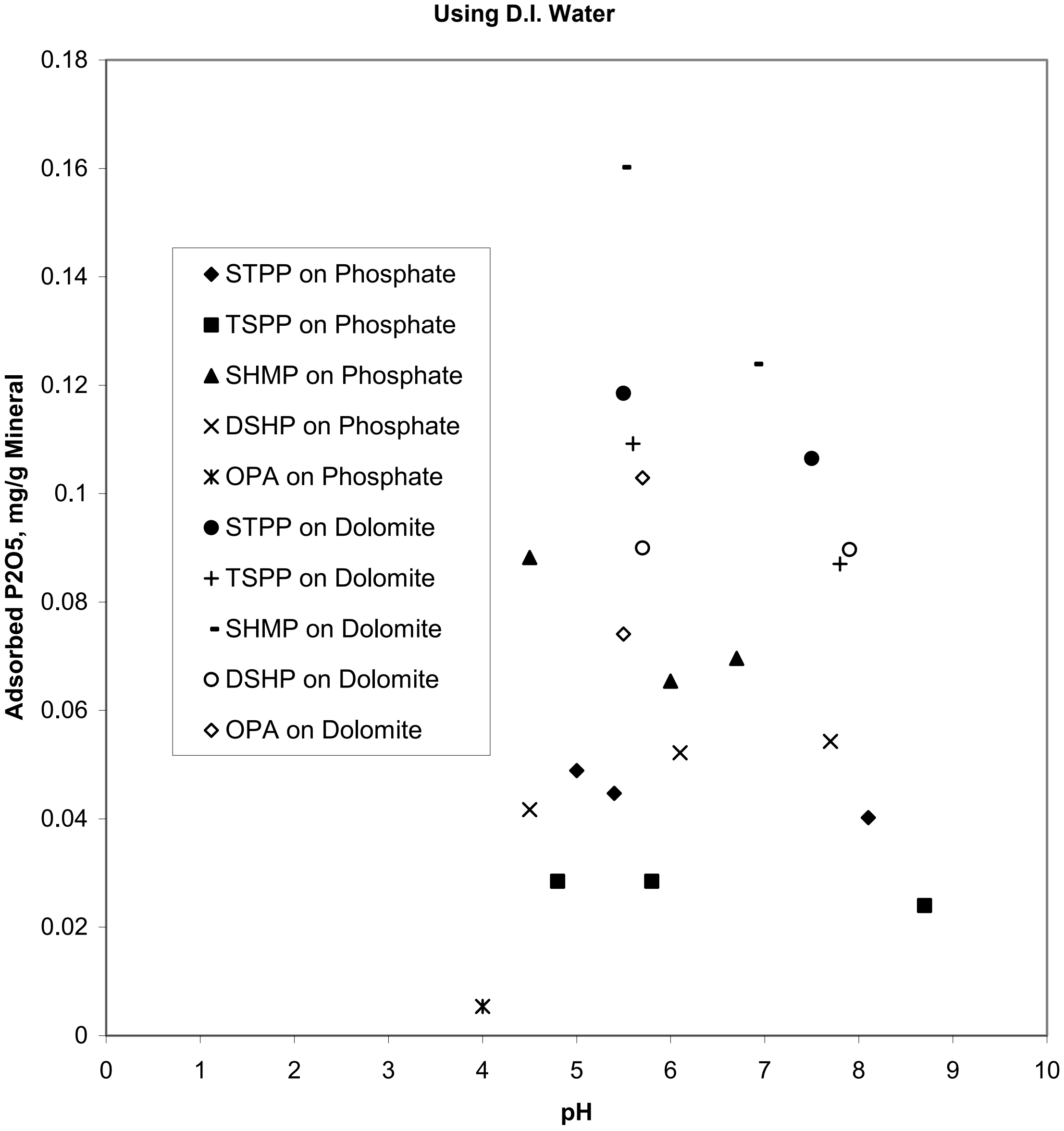


Figure 45. P_2O_5 Adsorption on Phosphate and Dolomite from Phosphate Depressant Solutions at Different pH Levels.

The overall test results do not explain that adsorption of P_2O_5 as complex ions, or as nearly colloidal precipitates of Ca and/or Mg compounds formed by hard water reaction with the various depressants, produced the results obtained. The effects of the phosphatic reagents, referred to as depressants, on electrical charge magnitude, sign and/or distribution on the phosphate and dolomite mineral surfaces at different pH levels is unknown. A more detailed fundamental study, probably including zeta potential determinations, is considered necessary to understand the mechanisms responsible for improved selectivity obtained during anionic flotation of dolomite from phosphate when various phosphatic depressants or "selectivity enhancers" were used.

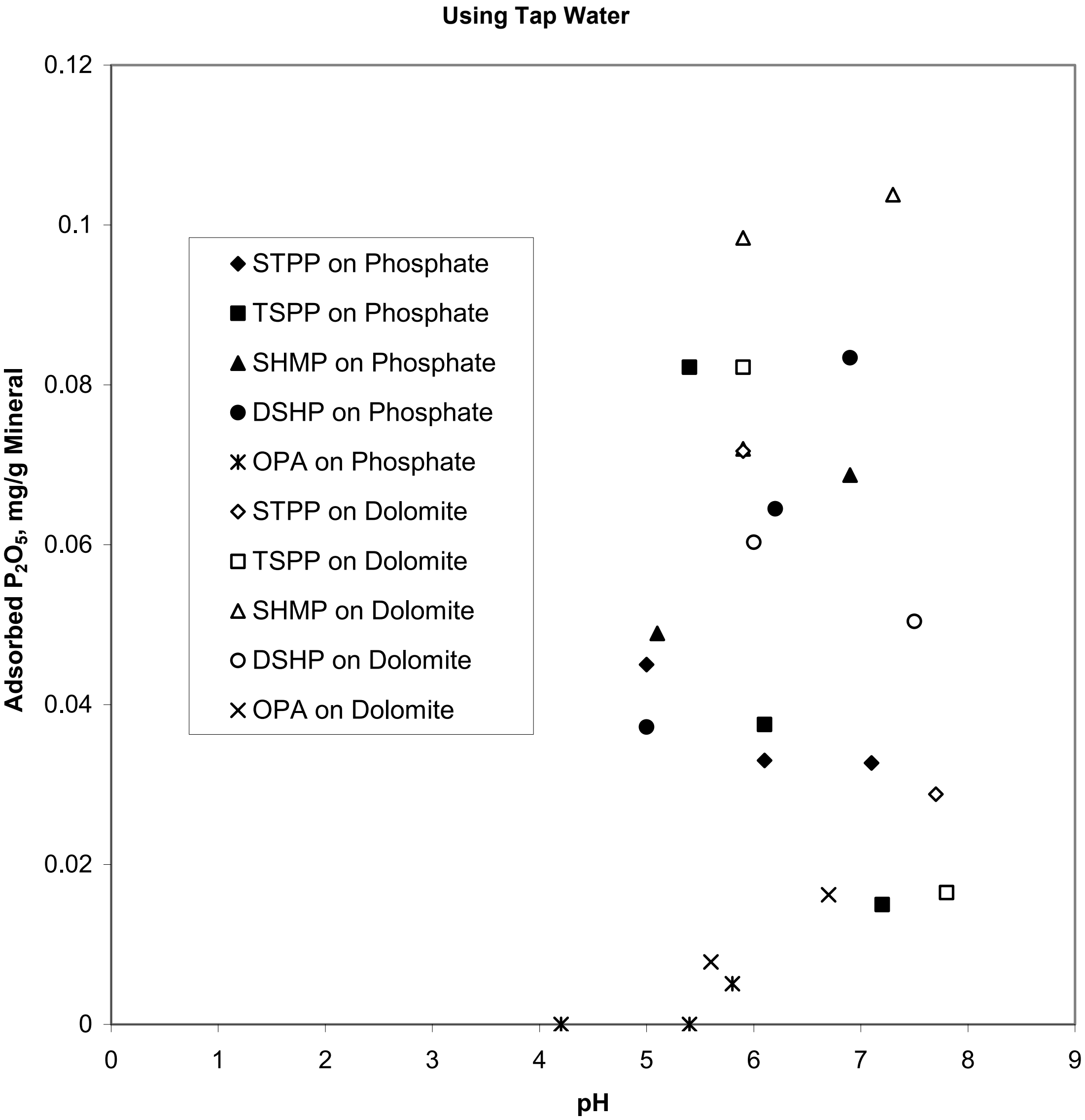


Figure 46. P_2O_5 Adsorption on Phosphate and Dolomite from Phosphate Depressant Solutions at Different pH Levels.

An analytical procedure was developed by FIPR's analytical laboratory for P_2O_5 analysis of adsorption test liquid samples. The procedure consisted of hot digestion of 10ml. of sample liquid with 2ml. of modified aqua regia containing 60% nitric acid, 20% hydrochloric acid and 20% de-ionized water. Conversion of tripolyphosphate, hexametaphosphate, pyrophosphate, etc. to PO_4 ions for accurate detection was the objective of this digestion procedure.

Standard deviations of ppm of P_2O_5 in solution after mineral contact were calculated for each set of repeat adsorption tests presented in Tables 1-4. Results were as follows:

Water	Mineral	Std. Dev., ppm P_2O_5
De-ionized	Phosphate	2.0
Tap	Phosphate	6.4
De-ionized	Dolomite	2.9
Tap	Dolomite	5.5

These data indicate that a better degree of reproducibility resulted when de-ionized water, instead of tap water, was used with either phosphate or dolomite.

A final set of adsorption tests was performed on phosphate and dolomite using de-ionized water stock solutions containing 0.41g per liter (SS-2) and 0.61g per liter (SS-3) of STPP. The test results are illustrated in Figure 47 along with the previous test results using 0.21g per liter (SS-1) of STPP. Figure 47 shows that adsorption of P_2O_5 ranged from about 0.05-0.13 mg/g of dolomite and only -0.02 to 0.05 mg/g of phosphate. Generally, very little change in P_2O_5 adsorption resulted from using the higher concentration STPP stock solutions.

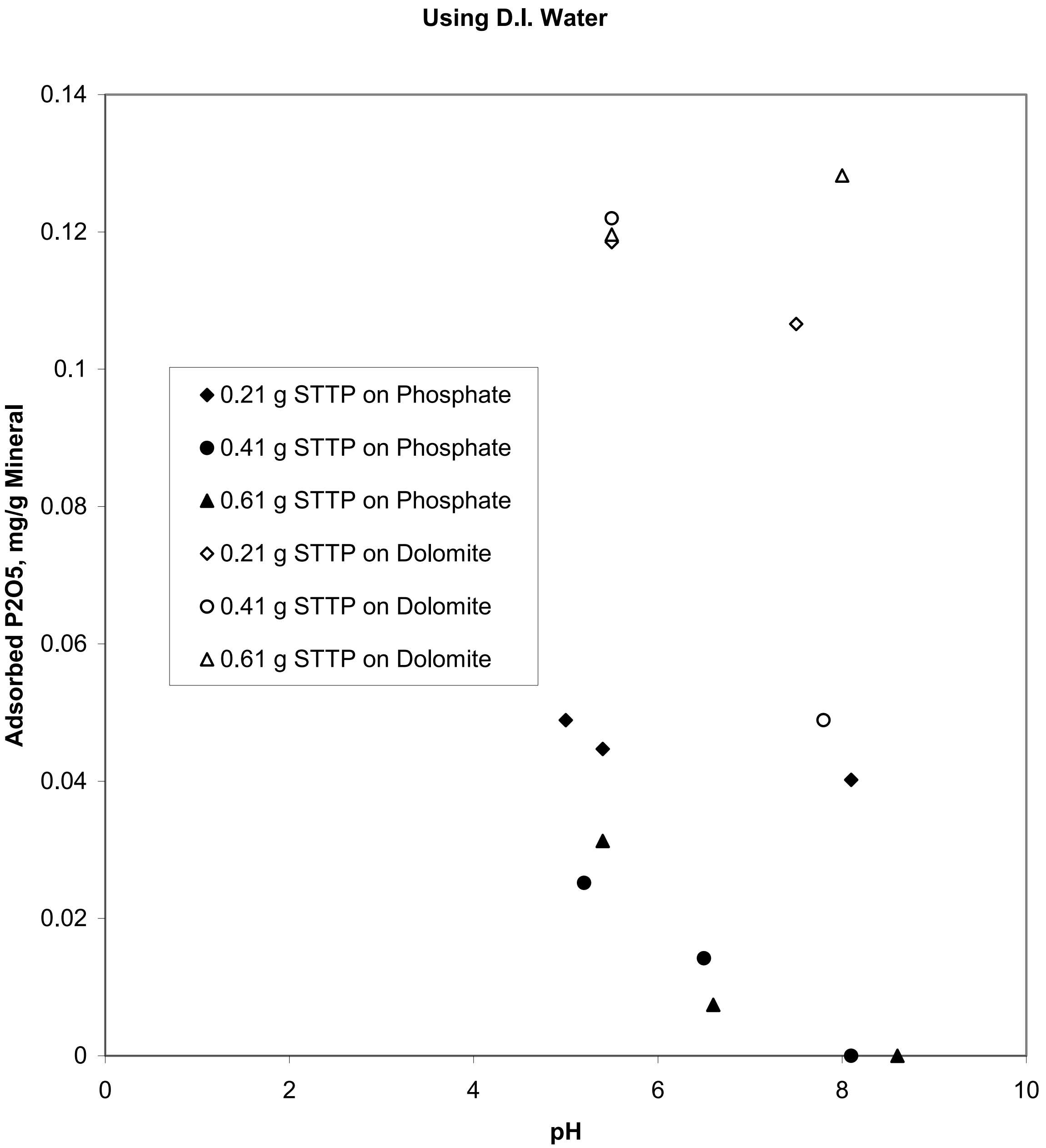


Figure 47. P_2O_5 **Adsorption on Phosphate and Dolomite from Various STPP Solutions at Different pH Levels.**

PART III. DEVELOPMENT OF THE REVERSE CRAGO PROCESS

DEVELOPMENT OF THE REVERSE CRAGO PROCESS

INTRODUCTION

In the conventional Double Float (Crago) process, more than 20% by weight of the sands present in the feed are floated twice, first by fatty acid and then by amine. The Crago process is therefore somewhat inefficient in terms of collector usage. However, there were a number of reasons for the phosphate industry to endorse the process enthusiastically: (1) fatty acid was much cheaper than amine so that anionic flotation followed by amine flotation made more economic sense than otherwise, (2) desliming was not sophisticated, leaving significant amount of clay in the flotation feed so that amine usage would have been prohibitive had silica been floated first, and (3) the ore was high in grade, so the adsorption of fatty acid on silica was tolerable compared with that on phosphate in the rougher flotation stage. The situation is quite different today: (a) the amine price is approximately twice that of fatty acid compared to nearly 10 times in the 1950s; (b) the washers have been upgraded to reduce the fine slimes in the flotation feed; and (c) the BPL content in the currently-mined phosphate matrices is about half that in the past.

There are two primary reasons why the Crago process has never been seriously challenged. First, the Crago is operator-friendly, making it the easiest to control concentrate grade. Another reason is this conventional wisdom about amine flotation: Amine flotation requires clean feed and deep well water. Therefore, one would need more sophisticated desliming devices, and utilize more deep aquifer water in order to float silica first. To some extent, this conventional wisdom is true. But, we could use our knowledge about amine flotation to overcome this problem.

Actually, our knowledge about amine flotation is far beyond the conventional wisdom. For example, we know that amines are more selective than fatty acids. Another important phenomenon is that amine adsorbs instantaneously on sand.

The fact that amine is more selective in floating silica than fatty acid in floating phosphate is demonstrated in the following figures. Figure 48 (Somasundaran and Gruber 1999) indicates that fatty acid adsorption on silica is significant.

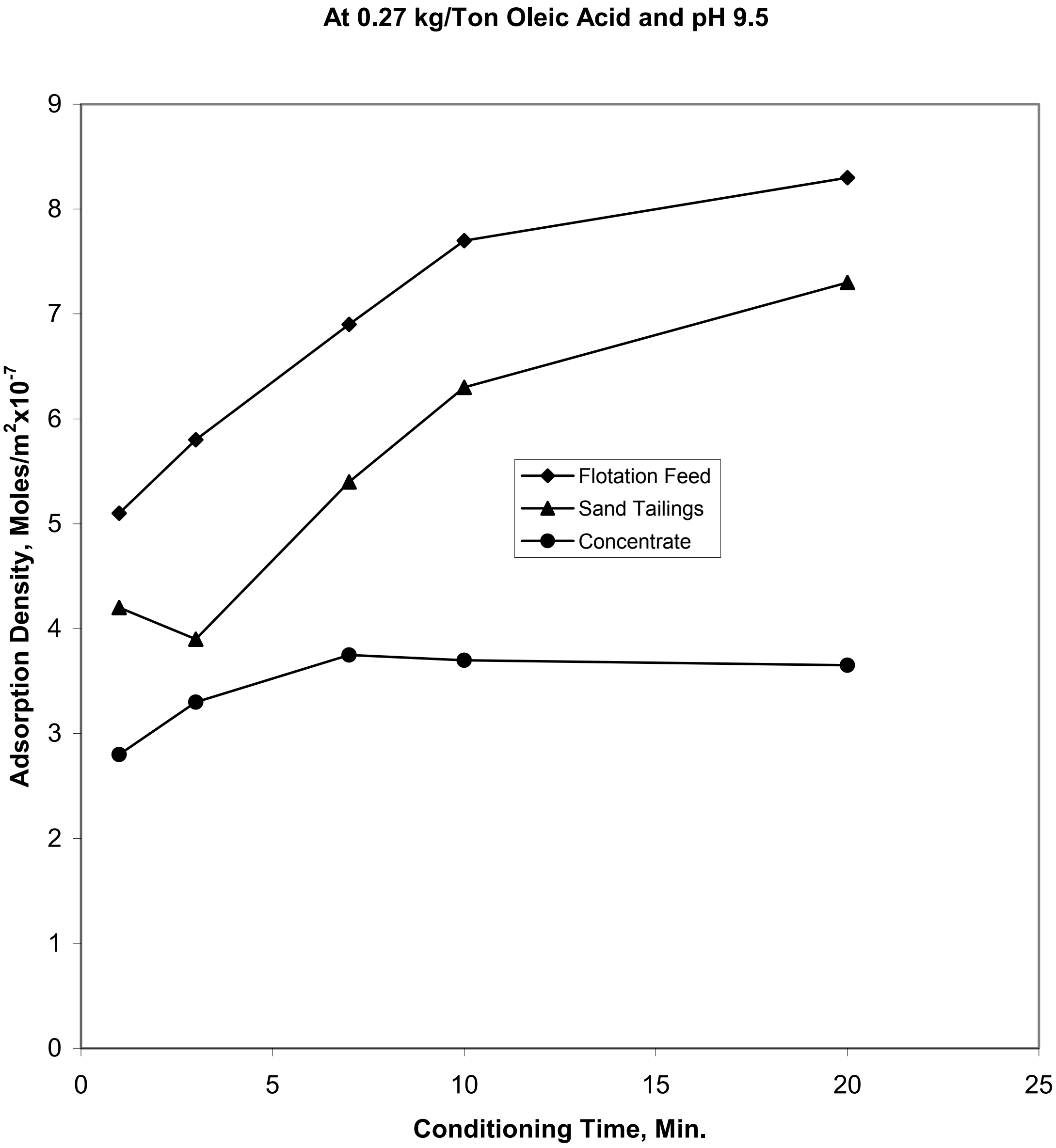


Figure 48. Kinetics of Oleic Acid Adsorption.

Figure 49 (Somasundaran and Moudgil 1988) shows that amine can float more than 95% of silica from pH 3 to 12, while phosphate flotation by amine is minimal within this pH range.

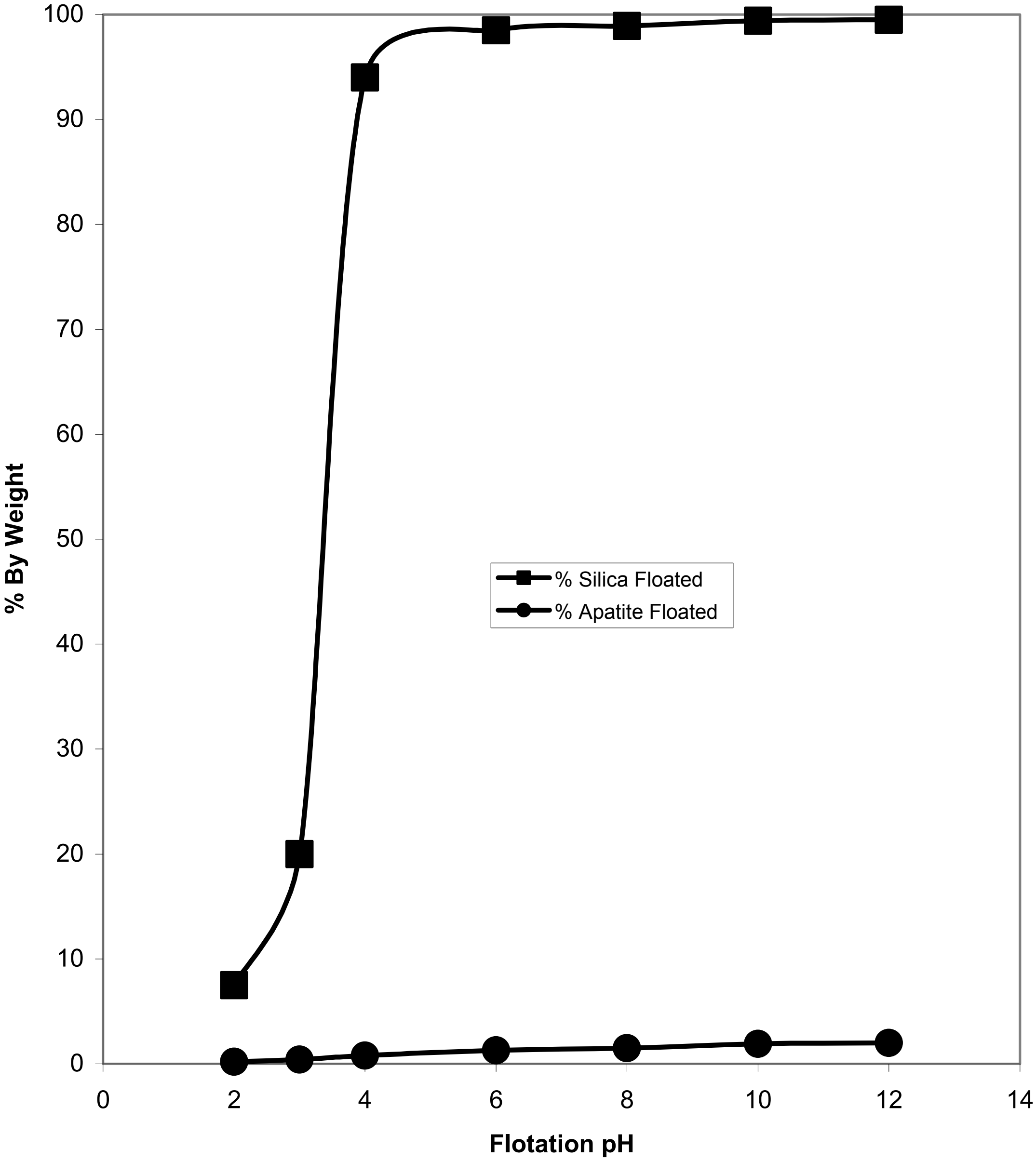


Figure 49. Flotation Recovery of Apatite and Silica with Dodecylammonium Chloride at Different pH Levels.

Figure 50 (Somasundaran and Moudgil 1988) shows that at near neutral pHs, there is big difference in zeta potential between silica and phosphate. Therefore, it is ideal to separate silica from phosphate at neutral pHs. It is a well known fact that neutral pH is not an ideal condition for fatty acids to adsorb on phosphate. That leaves you only one option: floating silica first.

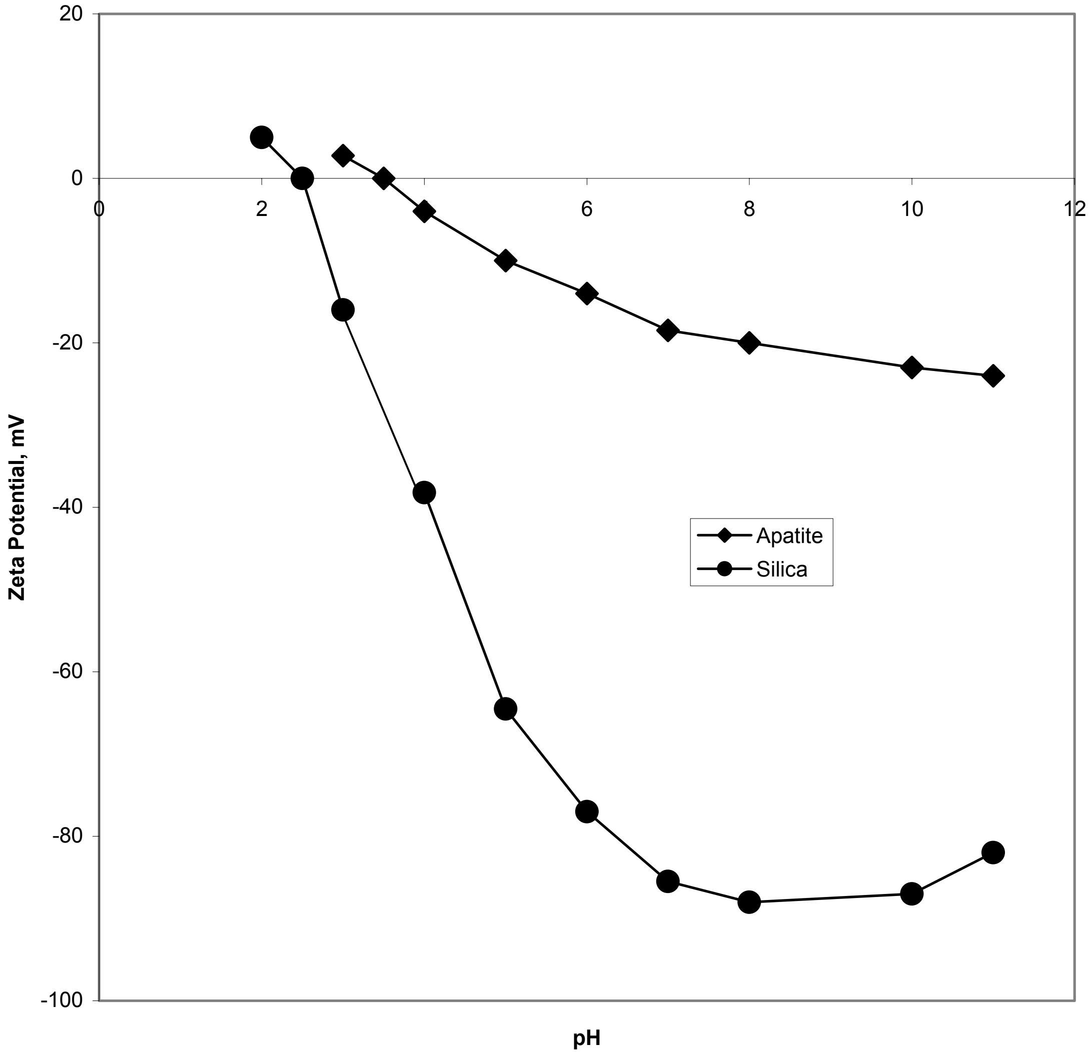


Figure 50. Effect of pH on Zeta Potential of Silica and Apatite.

Since amine adsorbs on silica very rapidly, the effect of clay on amine consumption may be reduced by adding amine stagewise or in any flotation cells. Flotation is conducted in a series of banks of flotation cells. Each bank consists of four to six cells. In the conventional process, all the amine is added as one dose in the first flotation cell. If we add a small amount of amine in the first cell, this cell not only acts as a flotation machine, but also as a desliming device. Since no conditioning is required, the number of conditioners currently used for flotation may be reduced by floating silica first. Because amine flotation is conducted at neutral pH, pH modifier consumption would be significantly reduced by floating silica first. Finally and perhaps more importantly, since amine is more selective than fatty acid, collector efficiency should be dramatically improved by floating silica first.

In recognition of these changed conditions, FIPR has developed the Reverse Crago process, an amine-fatty acid flotation flowsheet. In this process, fine sand is first floated with a minimal consumption of amine condensate by adding amine stepwise, so that phosphate loss could be minimized without using a depressant. The concentrate from prefloat is then floated with a surfactant/fatty acid blend as a phosphate collector. Figure 51 shows the general flowsheet for relatively fine feeds. For flotation feeds with a significant amount of coarse (+35 mesh) phosphate, a scavenging flotation may be added to improve the recovery with some additional reagents. The flowsheet with scavenging is shown in Figure 52.

The idea of floating silica first was advocated and tested by Clint Hollingsworth in the 1960s (Hollingsworth and Sapp 1961). However, the Hollingsworth process requires recycling both middlings from the amine flotation circuit and the tails from the fatty acid flotation. Therefore, the process is does not simply the existing flotation process.

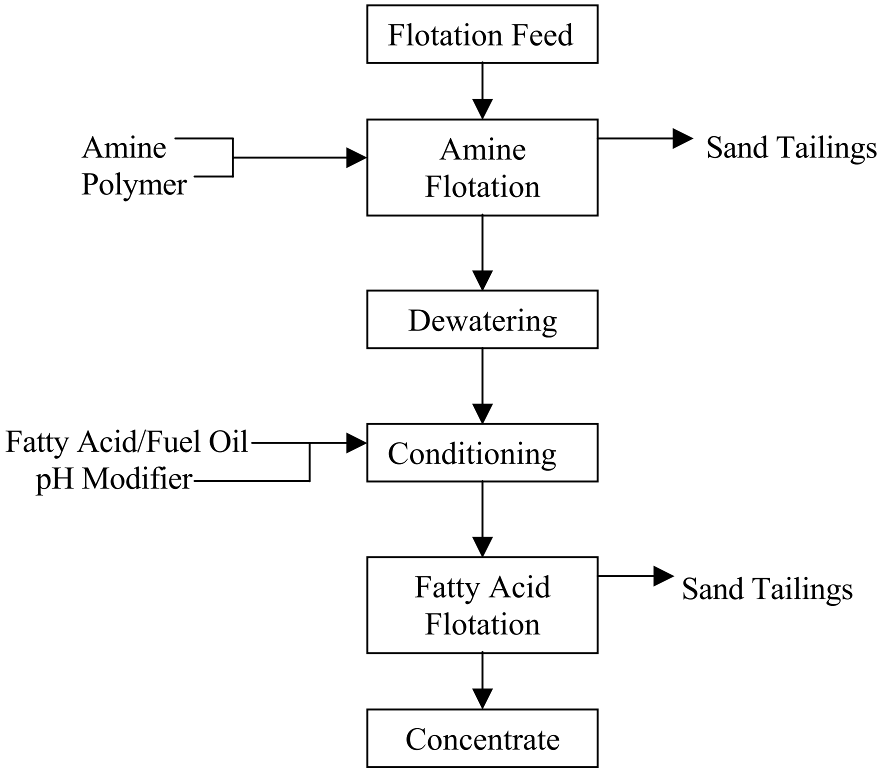


Figure 51. The Basic Reverse Crago Flowsheet.

Benefits of the amine-fatty acid flotation process include:

1. Reduced flotation reagent cost because only a single mineral is floated in each step.

2. Maximized phosphate recovery and improved concentrate grade because phosphate is in an inferior position to compete with fine sands for adsorption of amine, and coarse silica is not easy to float in the second stage.
3. Reduced energy cost due to the elimination of acid wash circuit.
4. Simplified flowsheet since it is a non-sizing and non-scrubbing process.
5. Minimized inorganic chemicals consumption, particularly sulfuric acid.

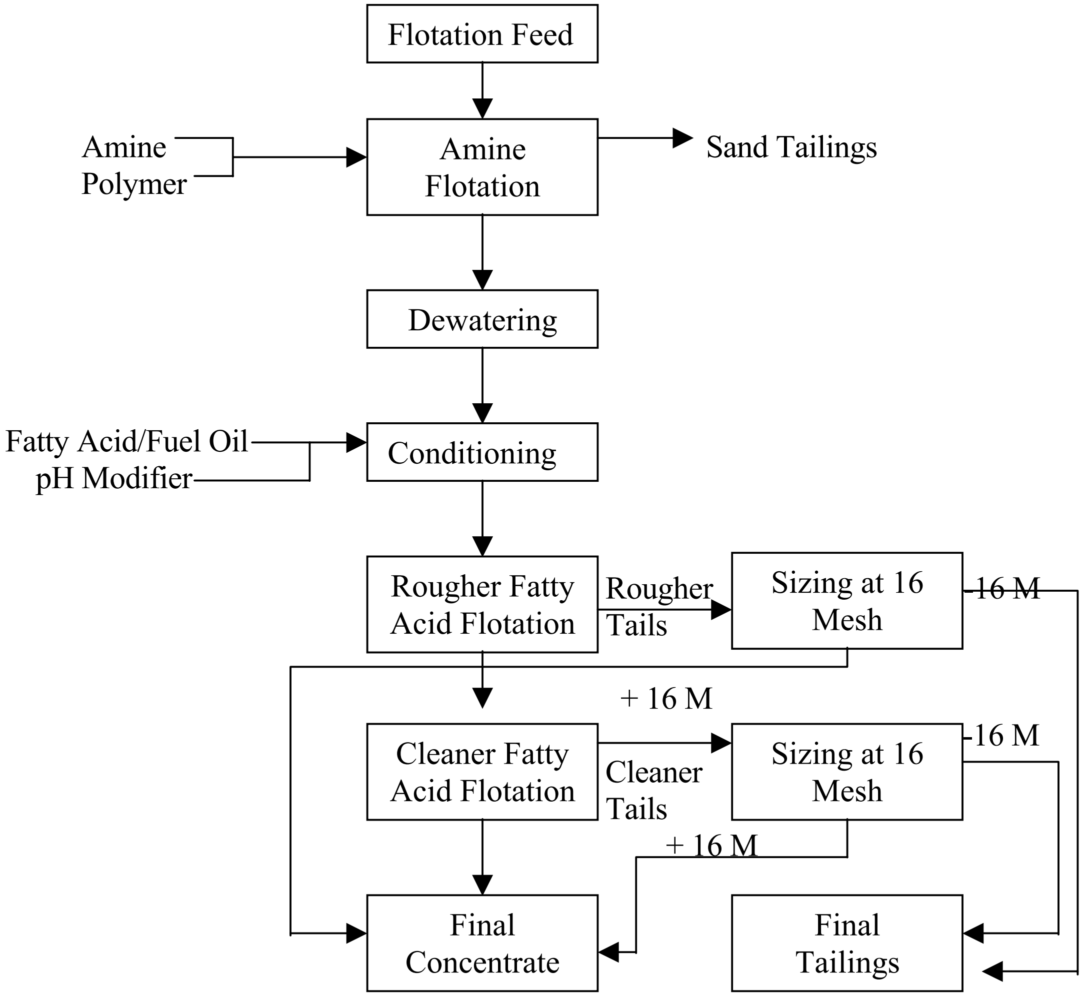


Figure 52. An Alternate Flowsheet of the Reverse Crago Process.

MATERIALS AND EXPERIMENTAL PROCEDURE

FLOTATION FEEDS

Most of the flotation feeds tested with this process were the same as those with the All-Cationic process. A coarse (+35 mesh) feed was also prepared by screening one of the feeds tested. Tables 26 and 27 show size distribution and the basic chemical properties of the four feeds.

FLOTATION REAGENTS

Flotation reagents used in the prefloat step included an amine condensate with or without diesel. The reagent scheme in the fatty acid flotation stage included a blend of fatty acid/surfactant/fuel oil with soda ash as the pH modifier. Table 28 lists the prices of the major reagents used.

FIRST STAGE—AMINE FLOTATION

A wet feed of 600 g (approximately 500 g dry weight) was placed in a standard Denver flotation cell. After tap water was added to the desired level, amine and diesel (which was not used on some feeds) were added, and the feed was agitated for about 5 seconds. Upon opening the air valve more tap water was added to obtain a flotation slurry of 18-20% solids. Additional collector was added after about 20 seconds of first-step flotation. Amine flotation was conducted at natural pH. It should be pointed out that the time interval between the two steps of collector addition varied with different feeds.

SECOND STAGE—FATTY ACID FLOTATION

The amine flotation rougher concentrate (cell product) was subjected to the standard fatty acid flotation. After being adjusted to 70-72% solids and pH 9.1-9.3, the feed slurry was conditioned for 60 seconds with the collector—a mixture of fatty acid, surfactant and fuel oil. After conditioning, the slurry was transferred into a Denver flotation cell, adjusted to 18-20% solids, and floated to completion at 1200 RPM. In order to reduce secondary slime generation, some feeds were conditioned for less than 60 seconds. Flotation could also be conducted at natural or slightly acidic pHs to improve concentrate grade.

THIRD STAGE—SCAVENGING FLOTATION

For those feeds containing more coarse (+35 mesh) material, a scavenging flotation step was added to clean the +35 mesh fraction of fatty acid flotation tail thus maximizing the recovery of coarse phosphates. In this case, the fatty acid flotation tails were first screened at 35 mesh, and the +35 mesh fraction was then subjected to scavenging flotation using the same reagent scheme as the second stage flotation. The collector dosage and flotation pH varied with different feeds. Sizing of the scavenging tails was also beneficial for the feeds containing significant amount of +14 mesh material.

Table 26. Size (Mesh) Distribution (Wt. %) of the Flotation Feeds.

Sample ID	+20	20/28	28/35	35/150	-150
Plant A Fine	1.3	3.3	10.2	83.7	1.5
Plant A Coarse	4.7	6.1	15.6	73.1	0.5
Plant B	3.0	3.1	7.8	82.6	3.5
Plant C #1	3.1	4.5	13.3	76.5	2.6
Plant C #2	1.4	4.3	12.7	79.6	2.0
Coarse Feed	>35m 100	---	---	---	---

Table 27. Chemical Analysis of the Flotation Feeds.

Sample ID	% P_2O_5	% Insol
Plant A Fine	9.26	70.60
Plant A Coarse	9.44	70.45
Plant B	5.43	83.49
Plant C #1	8.60	74.86
Plant C #2	6.77	79.75
Coarse Feed	13.82	?????

Table 28. Reagent Prices.

Reagent Name	Cost, $/lb
Azamine 36A	0.24
Diesel Fuel	0.15
Fatty Acid Blend	0.17
Soda Ash	0.07
Fuel Oil	0.07

RESULTS AND DISCUSSION

PERFORMANCE OF THE REVERSE CRAGO ON DIFFERENT FEEDS

Results on Plant A Unsized Fine Feed

It may be seen from Table 29 that increasing amine dosage in the first flotation stage improved concentrate grade but with some sacrifice in recovery. Concentrate insol could be significantly reduced by conducting fatty acid flotation at lower pHs.

Table 29. Performance of the Reverse Crago Precess on Plant A Unsized Fine Feed.

Reagent Dosages, lb/ton feed	Fraction	Wt.%	P_2O_5%	Insol %	P_2O_5 Recovery
Amine0.18;Diesel 0.1	Amine Tails	34.0	0.90	98.20	3.0
Blend FA 0.6;FO 0.35	FA Tails	33.8	0.91	97.57	2.9
	Concentrate	32.2	**30.32**	**7.34**	**94.1**
Amine0.20;Diesel 0.1	Amine Tails	42.9	1.17	96.38	4.8
Blend FA 0.6;FO 0.35	FA Tails	26.0	0.79	96.99	2.1
	Concentrate	31.1	**30.62**	**6.23**	**93.1**
Amine0.22;Diesel 0.2	Amine Tails	49.7	0.69	97.46	3.3
Blend FA 0.6;FO 0.35	FA Tails	19.4	0.79	96.96	1.5
	Concentrate	31.0	**31.20**	**5.18**	**95.2**
Amine0.20;Diesel 0.1	Amine Tails	43.6	0.86	97.32	3.7
Blend FA 0.5;FO 0.35	FA Tails	25.8	1.27	96.28	3.3
	Concentrate	30.6	**30.57**	**5.40**	**93.0**
Amine0.22;Diesel 0.2	Amine Tails	56.3	0.88	96.93	4.9
Blend FA 0.6;FO 0.35	FA Tails	13.8	1.39	94.93	1.9
Lower pH	Concentrate	29.9	**31.40**	**4.40**	**93.2**

Table 30. Reagent Cost for Plant A Unsized Fine Feed.

Reagent	Flotation Step	Price $/lb	Dose lb/TOC	Cost $/TOC
Amine-Custamine 738	Amine	0.24	3.0	0.72
Diesel	Flotation	0.15	0.35	0.05
Blend Fatty Acid	Fatty Acid	0.17	2.00	0.34
Soda Ash	Flotation	0.07	1.70	0.12
Fuel Oil		0.07	1.20	0.08

It should be pointed out that the total reagent cost takes into account the slime effect. If a desliming stage (which could be a simple rinsing-decanting exercise) is added, the total reagent cost should be lower.

Results on Plant A Unsized Coarse Feed

Table 31 shows flotation results for the coarse feed. Amine consumption is significantly higher on the coarse feed than that on the fine feed. Such satisfactory results on a coarse flotation feed without any sizing, depressants or scavenging circuits have never been achieved even on the laboratory scale.

Table 31. Performance of the Reverse Crago Process on Plant A Unsized Coarse Feed.

Reagent Dosages lb/ton feed	Fraction	Wt.%	P_2O_5%	Insol %	P_2O_5 Recovery
Amine0.35;Diesel 0	Amine Tails	55.4	0.78	95.91	4.2
Blend FA 0.6;FO 0.35	FA Tails	15.2	2.20	91.48	3.3
	Concentrate	29.4	**31.80**	**4.24**	**92.5**
Amine0.32;Diesel 0	Amine Tails	54.2	0.63	97.54	3.3
Blend FA 0.6;FO 0.35	FA Tails	15.9	2.96	89.85	4.6
	Concentrate	19.9	**31.87**	**4.17**	**92.1**
Amine0.27;Diesel 0	Amine Tails	34.4	0.48	98.01	1.6
Blend FA 0.6;FO 0.35	FA Tails	35.3	1.71	93.99	5.8
	Concentrate	30.3	**31.74**	**5.22**	**92.6**

Table 32. Reagent Cost for Plant A Unsized Coarse Feed.

Reagent	Flotation Step	Price, $/lb	Dose, lb/TOC	Cost, $/TOC
Amine-Custamine 738	Amine	0.24	4.0	0.96
Diesel	Flotation	0.15	0	0
Blend Fatty Acid	Fatty Acid	0.17	2.00	0.34
Soda Ash	Flotation	0.07	1.70	0.12
Fuel Oil		0.07	1.20	0.08

To improve the overall phosphate recovery, particularly the coarse phosphate, a scavenging step was added to the general flowsheet to float the fatty acid flotation tails. Table 33 shows that the scavenger increased phosphate recovery by about 3% for this particular feed. The amount of coarse fraction in the flotation feed determines whether a scavenging flotation is needed.

Table 33. Performance of the Reverse Crago Process on Plant A Unsized Coarse Feed with Scavenging the Fatty Acid Flotation Tails.

Reagent Dosages lb/ton feed	Fraction	Wt.%	P_2O_5%	Insol %	P_2O_5 Recovery
Amine0.30;Diesel 0	Amine Tails	45.9	0.47	97.7	2.1
Blend FA 0.6;FO 0.35	FA Tails	11.0	1.67	94.14	1.7
Blend FA 0.4;FO 0.3	Scavenger Tails	12.6	1.19	95.42	1.5
	Concentrate	30.5	**32.08**	**3.69**	**94.7**

Table 34. Reagent Cost for Plant A Unsized Coarse Feed with Scavenging.

Reagent	Flotation Step	Price, $/lb	Dose, lb/TOC	Cost, $/TOC
Custamine 738	Amine	0.24	4.0	0.96
Diesel	Flotation	0.15	0	0
Blend Fatty Acid	Fatty Acid	0.17	1.80	0.31
Soda Ash	Flotation	0.07	1.70	0.12
Fuel Oil		0.07	1.10	0.08
Blend Fatty Acid	Scavenger	0.17	1.20	0.2
Soda Ash	Flotation	0.07	0.85	0.06
Fuel Oil		0.07	0.80	0.06

Results on Plant B Feed without Desliming and Scavenging

Because of its coarseness and low grade, the Plant B feed was more difficult than the Plant A feeds, consuming more reagents, as shown in Tables 35 and 36.

Table 35. Average Reagent Costs for As-Received Plant B Feed.

Reagent	Flotation Step	Price, $/lb	Dose, lb/TOC	Cost, $/TOC
Custamine 738	Amine	0.24	4.56	1.09
Diesel	Flotation	0.15	0.00	0.00
Blend Fatty Acid	Fatty Acid	0.17	3.18	0.54
Soda Ash	Flotation	0.07	5.10	0.36
Fuel Oil		0.07	0.00	0.00

Table 36. Testing Results on the Plant B As-Received Flotation Feed.

Reagent Dosages lb/ton feed	Fraction	Wt. %	P_2O_5 %	Insol %	P_2O_5 Recovery
Amine (1)0.30; (2) 0.46	Amine Tails	60.3	0.58	98.4	6.0
Blend FA 0.53; FO 0	FA Tails	22.8	0.89	96.7	3.5
Hydrofluosilicic acid 0.13;	Float Conc.	15.6	31.74	8.3	84.3
FO 0	+16M Conc.	1.3	27.53	20.7	6.3
	Total Conc.	16.9	**31.40**	**9.3**	**90.6**
Amine (1)0.30; (2) 0.46	Amine Tails	60.4	0.58	98.4	5.9
Blend FA 0.53; FO 0	FA Tails	23.1	1.21	96.3	4.7
Hydrofluosilicic acid 0.13;	Float Conc.	14.8	32.49	7.3	81.0
FO 0	+16M Conc.	1.7	28.73	18.3	8.4
	Total Conc.	16.5	**32.09**	**8.5**	**89.4**
	Amine Tails	60.3	0.58	98.4	6.0
Amine (1)0.30; (2) 0.46	FA Tails	22.9	0.89	97.4	3.5
Blend FA 0.53; FO 0	Float Conc.	15.4	31.65	8.5	84.1
Hydrofluosilicic acid 0.13;	+16M Conc.	1.3	27.46	19.1	6.3
FO 0	Total Conc.	16.8	**31.31**	**9.3**	**90.5**

(1) and (2) stand for steps 1 and 2 of amine addition.

Results on Plant B Feed with Desliming and Scavenging

Again, Table 37 indicates that scavenging flotation is beneficial for relatively coarse flotation feeds. This table also shows that concentrate grade was significantly improved by adding a minimal amount of starch, but with some sacrifice in recovery.

By selecting the optimal performance as shown in Table 37, a cost estimate may be obtained, as shown in Table 38.

Table 37. Testing Results on the Plant B Feed with Desliming and Scavenging.

Reagent Dosages, lb/ton feed	Fraction	Wt. %	P_2O_5 %	Insol %	P_2O_5 Recovery
Amine 0.3;Diesel 0.1	Amine Tails	58.4	0.40	98.2	4.3
Blend FA 0.6; FO 0	FA Tails	16.5	0.32	98.3	1.0
	Scav.Tails	8.7	0.26	98.6	0.4
	Total Tails	83.6	0.35	98.1	5.6
	FA-Conc.	14.1	31.86	6.9	81.7
Blend FA 0.4;FO 0.14	Scav.-Conc.	2.0	29.71	13.2	10.8
for Scavenger	+14M Conc.	0.4	26.81	21.5	1.9
	Total Conc.	16.4	**31.58**	**7.4**	**94.4**
Amine0.32;Diesel 0.1	Amine Tails	48.3	0.23	98.8	1.9
Blend FA	FA Tails	23.5	0.40	98.3	1.6
0.53;FO0.47	Scav.Tails	11.3	0.83	97.1	1.6
	Total Tails	83.0	0.42	98.4	5.1
	FA-Conc.	13.7	32.50	6.6	77.0
Blend FA 0.3;FO 0.1	Scav.-Conc.	2.6	32.30	10.1	14.4
for Scavenger	+14M Conc.	0.7	29.20	16.8	3.5
	Total Conc.	17.0	**32.13**	**7.3**	**94.9**
Amine0.32;Diesel 0.1	Amine Tails	47.0	0.42	98.3	3.5
Blend FA0.53;FO	FA Tails	26.7	0.45	98.0	2.1
0.47	Scav.Tails	9.5	0.62	97.5	1.0
	Total Tails	83.3	0.46	98.3	6.6
	FA-Conc.	13.9	32.03	8.3	78.6
Blend FA 0.3;FO 0.1	Scav.-Conc.	2.4	30.61	9.8	12.8
for Scavenger	+14M Conc.	0.4	27.00	21.7	1.9
	Total Conc.	16.7	**31.26**	**8.5**	**93.4**
Amine0.34;Diesel 0.1	Total Tails	83.3	0.45	98.2	6.6
Blend FA0.53;FO 0	FA-Conc.	13.1	31.80	7.1	73.8
	Scav.-Conc.	3.1	31.56	7.3	17.2
Blend FA0.13;FO 0.1	+14M Conc.	0.5	27.0	20.9	2.4
for Scavenger	Total Conc.	16.7	**31.86**	**7.1**	**93.4**
Amine0.34;Diesel 0.1	Total Tails	83.4	0.53	98.1	8.3
Blend FA0.53;FO 0	FA-Conc.	13.9	31.55	5.8	77.8
	Scav.-Conc.	2.5	29.09	13.2	12.7
Blend FA0.15;FO 0.1	+14M Conc.	0.3	22.96	32.6	1.1
for Scavenger	Total Conc.	16.6	**31.83**	**6.3**	**91.7**
Amine 0.6;Diesel 0.6	Total Tails	84.7	0.61	97.9	9.5
Starch 0.2	FA-Conc.	10.5	33.24	4.9	63.4
Blend FA0.53;FO 0	Scav.-Conc.	4.1	32.05	8.1	23.9
Blend FA0.20;FO 0.1	+14M Conc.	0.6	28.16	18.4	3.2
for Scavenger	Total Conc.	15.3	**32.76**	**6.1**	**90.5**

Table 38. Reagent Cost Corresponding to Table 37.

Reagent	Flotation Step	Price, \$/lb	Dose, lb/TOC	Cost, \$/TOC
Amine-Custamine	Amine	0.24	2.04	0.49
738	Flotation	0.15	0.60	0.09
Diesel				
Blend Fatty Acid	Fatty Acid	0.17	3.18	0.54
Soda Ash	Flotation	0.07	3.00	0.21
Fuel Oil		0.07	1.80	0.13
Blend Fatty Acid	Scaveng-			
Soda Ash	ing Flotation	0.17	1.80	0.31
Fuel Oil		0.07	1.50	0.11
		0.07	1.26	0.09

Results on Plant C Feed #1

Tables 39 and 40 show material balance and reagent cost for Plant C Feed #1.

Table 39. Material Balance of Plant C Feed #1.

Test #	Fraction	Wt.%	P_2O_5%	Insol %	P_2O_5 Recovery
Test A	Amine Tails	56.8	0.26	98.45	1.7
	FA Tails	18.0	1.67	94.31	3.5
	Concentrate	25.2	**32.38**	**7.79**	**94.8**
Test B	Amine Tails	58.3	0.44	98.00	2.9
	FA Tails	14.8	0.61	97.31	1.1
	Concentrate	26.9	**31.41**	**11.67**	**96.0**
Test C	Amine Tails	62.4	0.38	98.31	2.8
	FA Tails	13.3	2.01	93.28	3.1
	Concentrate	24.3	**33.42**	**5.69**	**94.1**

Table 40. Average Reagent Cost for Plant C Feed #1.

Reagent	Flotation Step	Price, \$/lb	Dose, lb/TOC	Cost, \$/TOC
Custamine 738	Amine	0.24	1.98	0.475
Diesel	Flotation	0.15	0	
Blend Fatty Acid	Fatty Acid	0.17	2.92	0.496
Soda Ash	Flotation	0.07	1.81	0.13

Results on the Plant C Feed #2

Tables 41 and 42 show material balance and reagent cost for Plant C Feed #2.

Table 41. Material Balance of Plant C Feed #2.

Test Condition	Fraction	Wt.%	P_2O_5%	Insol %	P_2O_5 Recovery
Without Scavenger	Amine Tails	49.2	0.90	96.99	6.54
	FA Tails	30.5	0.63	97.83	2.84
	+16 M Conc.	1.1	---	---	--
	Total Conc.	20.3	**30.23**	**10.82**	**90.6**
With Scavenger	Amine Tails	56.9	0.51	97.87	4.36
	FA Tails	11.6	0.35	98.63	0.60
	Scav. Tails	11.6	1.26	95.75	2.19
	Total Conc.	**19.9**	**31.06**	**7.85**	**92.85**

Table 42. Average Reagent Cost for Plant C Feed #2 with Scavenging Flotation.

Reagent	Flotation Step	Price, $/lb	Dose, lb/TOC	Cost, $/TOC
Custamine 738	Amine	0.24	3.2	0.77
Diesel	Flotation	0.15	0	0
Blend Fatty Acid	Fatty Acid	0.17	4.90	0.83
Soda Ash	Flotation	0.07	2.4	0.17

Effects of Water Type

Tables 43 and 44 show the results on Plant C Feed #2. In these tests, amine circuit recycle water was used in the amine flotation step of the Reverse Crago process. The benefits of using amine recycle water are clearly seen in terms of both metallurgical performance and reagent costs.

Table 43. Material Balance of Plant C Feed #2.

Reagent Dosage	Fraction	Wt. %	P_2O_5%	Insol %	P_2O_5 Recovery
0.36 amine	Amine Tails	78.5	0.13	99.03	2.9
0.32 fatty acid blend	FA Tails	10.6	0.47	98.07	1.4
	FA Conc.	10.5	31.40	5.73	93.5
	16M Conc.	0.4	21.23	37.40	2.2
	Total Conc.	10.9	**31.01**	**6.83**	**95.7**
0.36 amine	Amine Tails	79.0	0.13	99.10	2.9
0.32 fatty acid blend	FA Tails	10.2	0.60	97.70	1.7
	FA Conc.	10.3	31.77	5.10	92.9
	16M Conc.	0.4	21.30	33.3	2.4
	Total Conc.	10.8	**31.38**	**6.10**	**95.4**

Table 44. Average Reagent Cost for the Plant C Feed #2 Using Amine Circuit Water.

Reagent	Flotation Step	Price, $/lb	Dose, lb/TOC	Cost, $/TOC
Custamine 738	Amine	0.24	1.98	0.475
Diesel	Flotation	0.15	0	
Blend Fatty Acid	Fatty Acid	0.17	2.92	0.496
Soda Ash	Flotation	0.07	1.81	0.13

Initial Feasibility Evaluation

Table 45 summarizes the flotation test results. In every case, flotation recoveries of over 90% were achieved at reagent costs of around $1.5 per ton of concentrate. In a typical industrial operation, flotation recovery is about 80% at reagent costs of over $2 per ton of concentrate.

Table 46 shows the phenomenal reduction in total chemicals usage by adopting the reverse Crago process. The first row was obtained by averaging data from two plants during a two-week period. The numbers for the reverse Crago process were averaged on the six feeds evaluated.

Table 45. Performance of the Reverse Crago Process on Different Feeds with Tap Water.

Feed ID	Conc. % P_2O_5	Conc.% Insol	%P_2O_5 Recov.	$/Ton Conc.
A1	31.10	6.23	93.1	1.41
A2	31.87	4.17	92.1	1.50
B	32.13	7.30	94.6	1.96
C1	33.42	5.69	94.1	1.10
C2	31.06	7.85	92.6	1.77
D	31.17	10.56	98.1	0.98

Table 46. Reagent Dosage Comparison between the Crago and Reverse Crago Processes.

	Dosage, Kg per Ton of Concentrate			
Process	Fatty Acid+Fuel Oil	Amine	Soda Ash	H_2SO_4
Crago	7.35	0.54	2.49	2.90
Reverse Crago	1.98	1.78	1.30	0

Dealing with the Clay (Slime) Problem

All the above results were generated using plant feeds with tap water. There was a concern that amine consumption would be economically prohibitive when slimy feed and plant recycled water are used. Therefore, more flotation tests were conducted for parallel comparison between Crago process and reverse Crago process using plant feed and plant water. Table 47 shows similar metallurgical performance on a low-grade (3.5% P_2O_5) fine feed.

Table 47. Flotation Performance Comparison between the Crago and Reverse Crago Processes Using Plant Water on a Plant Fine Feed.

Item	Crago Process	Reverse Crago
Concentrate %P_2O_5	30.04	30.32
Concentrate % insol	10.15	9.08
% P_2O_5 Recovery	84.94	84.49

However, the reagent consumption still made a big difference in terms of both total dosages and dollars (Table 48). In this case, the total reagent cost is significantly higher for the Reverse Crago process as well, compared with the previous tests using tap water.

Table 48. Reagent Consumption Comparison between the Crago and Reverse Crago Processes Using Plant Water on a Plant Fine Feed.

Reagent	Dosage, Kg/Ton Concentrate	
	Crago Process	Reverse Crago
Fatty acid/fuel oil	11.20	1.89
Amine	0.33	2.18
Polymer	----	0.15
Sodium silicate	1.17	----
Starch	1.87	----
Sulfuric acid	2.79	----
Soda ash	2.79	0.71
Total reagent usage	20.16	4.93
Total reagent cost	$3.95	$2.24

It should be understood that amine flotation is sensitive to clay in the feed and suspended solids in the water. It must also be recognized that amine is still more expensive than fatty acids. Therefore, the success of the Reverse Crago process depends solely on how the slime problem is handled. We have developed three techniques for this purpose: adding polymers in flotation water, adding amine stagewise, and adding amine continuously.

Figure 53 shows the effect of stagewise addition of amine. It may be seen that 0.45 kg of amine added stagewise was equivalent to about 0.90 kg of amine added as one dose in this test.

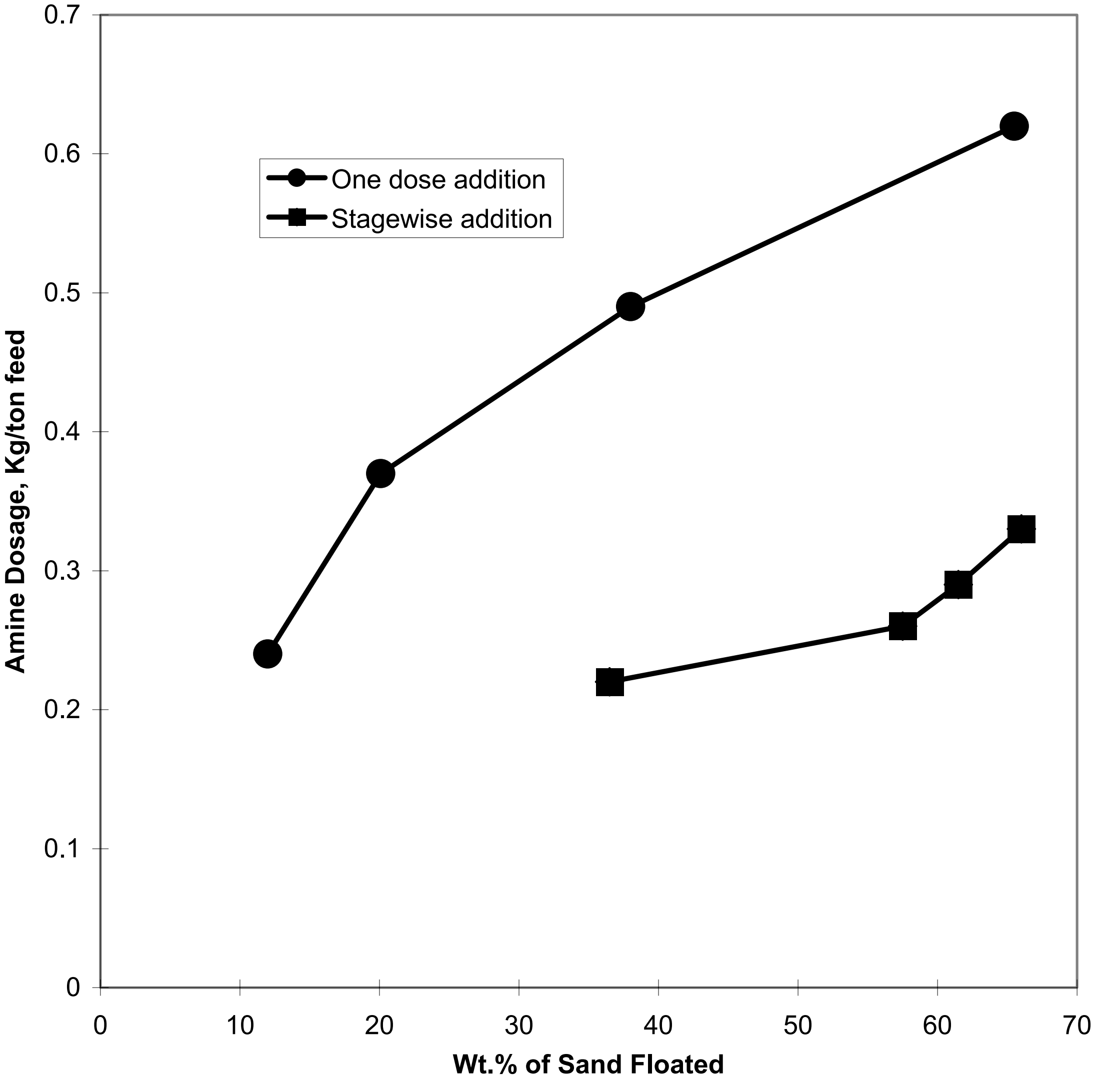


Figure 53. Comparison of One Dose Amine Addition with Stagewise Addition.

Another very effective way of reducing slime effect on amine consumption is to add a small amount of polymer in flotation feed. Figure 54 shows that the amine dosage could be reduced by as much as two thirds by adding the polymer for the same amount of silica floated. Here, 15 g of polymer had a tradeoff of 900 g of amine. This translates to a reagent saving of at least one dollar per ton of concentrate.

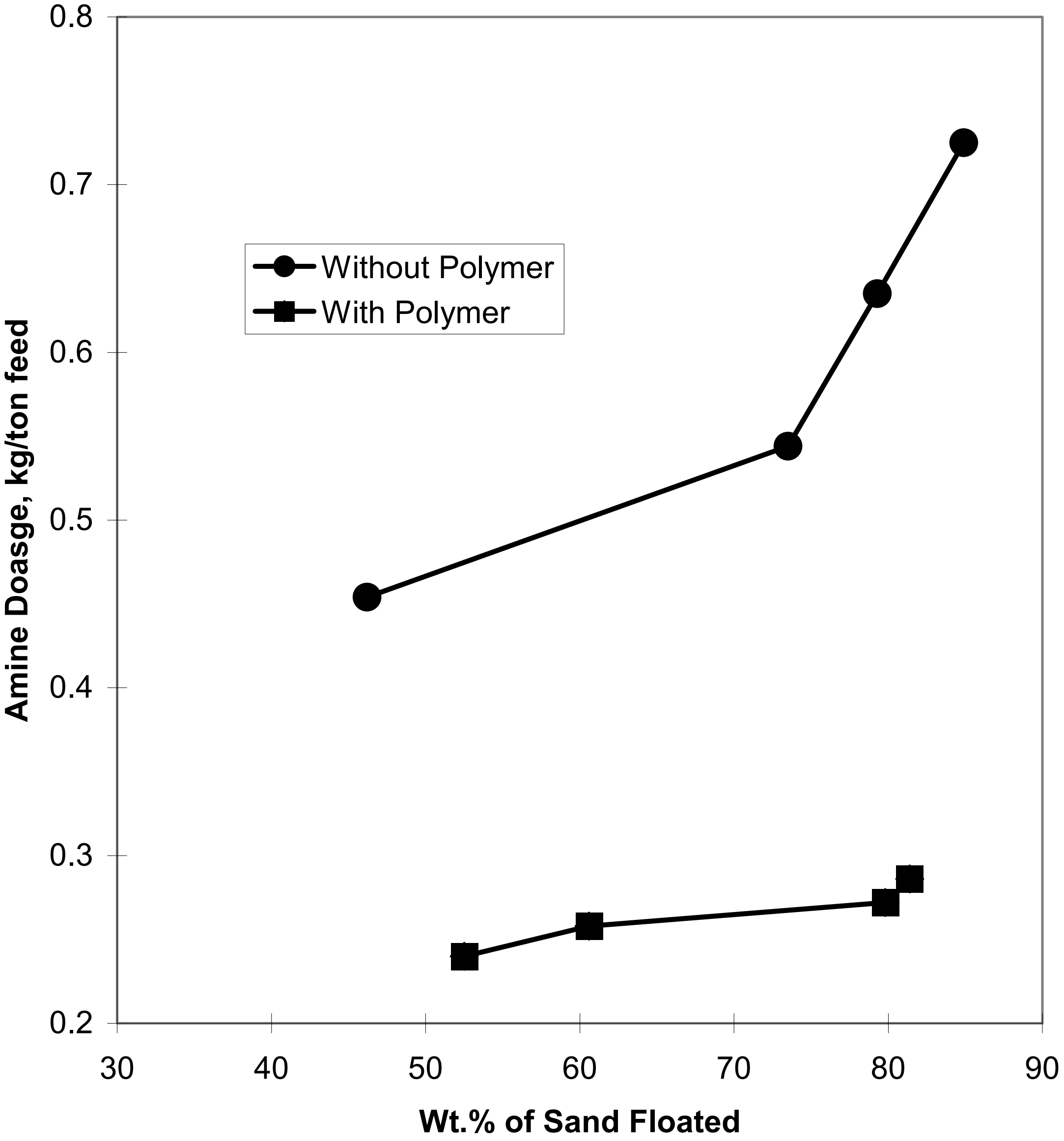


Figure 54. Effect of Polymer (0.014 Kg/Ton) on Amine Consumption and Wt. % of Sand Floated.

As is indicated in Figure 55, however, polymer could have a detrimental effect on amine flotation beyond certain concentration. Overdose of polymer not only reduces phosphate recovery to an unacceptable level, but also reduces the total amount of sand floated.

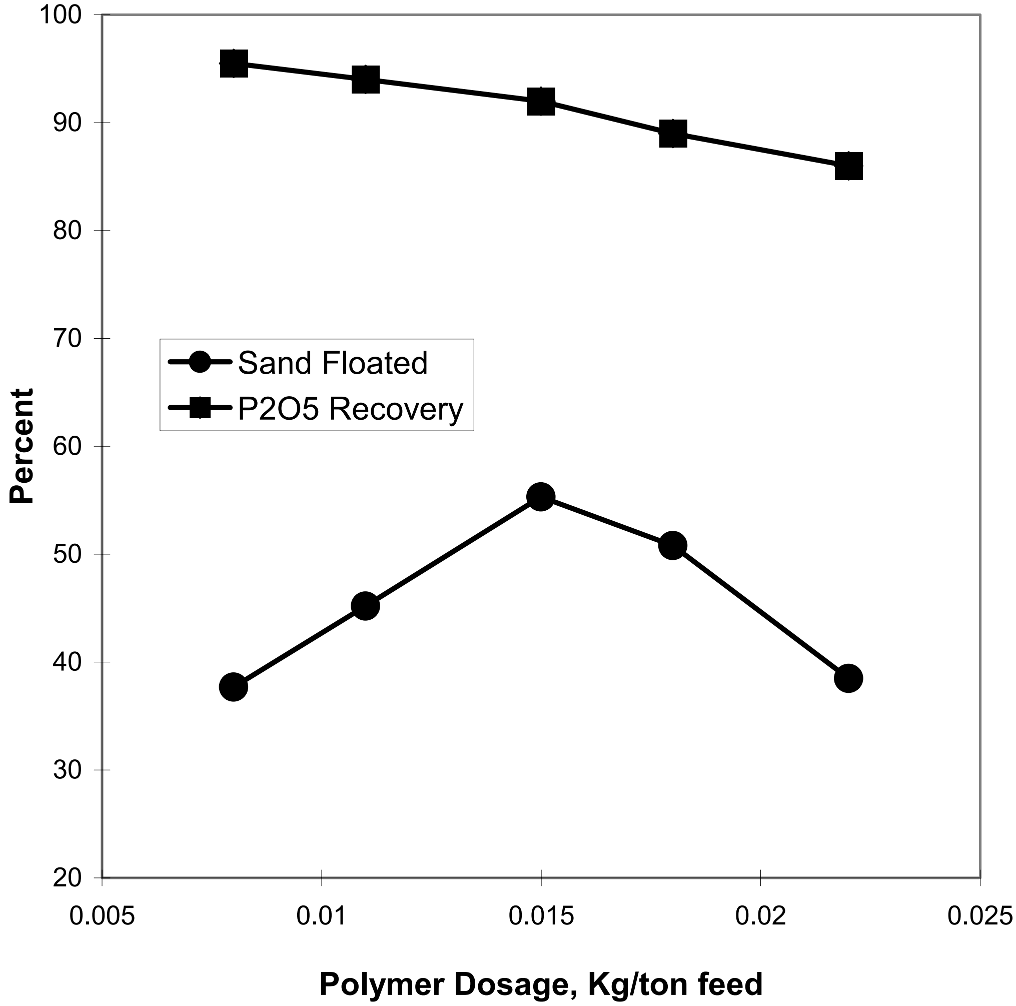


Figure 55. Effect of Polymer Dosage on Wt. % of Sand Floated and P_2O_5 Recovery at 0.23 Kg/Ton of Amine.

CONCLUSIONS

1. The Reverse Crago process is much more efficient than the Crago process.
2. The clay (slime) effect may be controlled using the following techniques:

   (a) Adding polymer in flotation feed
   (b) Adding amine stagewise
   (c) Adding amine continuously

3. The process would be more attractive in times of fatty acid shortage
4. The new process offers the following environmental benefits:

- Eliminating sulfuric acid usage in the amount of 60,000 tons per year
- Reducing soda ash usage by 20,000 tons per year
- Reducing organic reagents usage by up to 25,000 tons per year

The above numbers are calculated based on an annual production of 20 million tons of concentrate in Florida.

The Reverse Crago process also promises the following economic benefits:

- Reducing total reagent cost by a dollar per ton of product
- Improving flotation recovery by 2-5%
- Reducing number of conditioners by 50%
- Eliminating acid scrubbing circuit
- Reducing sizing equipment by 50-100%

PART IV. INVESTIGATION OF POLYMERS

INVESTIGATION OF POLYMERS

SUMMARY

One of the major current efforts by the Florida phosphate industry in reducing deep aquifer water consumption is to use 100% recycle water for flotation. This measure alone could save billions of gallons of deep well water annually. However, this also results in higher suspended solids (slimes) in flotation water, causing poor process performance, particularly for amine flotation. Polymers could play a major role in allowing the industry to use high-turbidity recycle water for amine flotation without compromising its impact on Florida economy. The enhancement of rougher flotation by polymers may also have potential. Most importantly, dramatic efficiency improvement may be realized by floating silica first. Adding polymer to flotation feed and/or water is perhaps the most economically viable way of reversing the Crago double float process, in order to reduce operating costs and increase phosphate recovery. This part presents both laboratory and pilot flotation data showing the effect of different polymers on collector dosage and flotation recovery. There appeared to be an optimal range of polymer concentration beyond which the benefits do not offset the drop in phosphate recovery. The effect of polymer is slime level-dependent. Pilot testing data show that the Reverse Crago process (floating silica first, followed by phosphate flotation) can outperform the Crago process.

INTRODUCTION

Water Consumption in Phosphate Flotation

One role polymer could play in phosphate flotation is to reduce deep well water consumption. The phosphate industry has set an impressive record in reducing aquifer water usage for phosphate flotation. In the 1970s, 3400 gallons of deep well water were required to produce one ton of flotation concentrate. This number was reduced to 1200 gallons in the 1980s. During the early 1990s, ground water usage was further cut to about 800 gallons. Now, many mines are going a step further, eliminating aquifer use entirely. Therefore, in the not too distant future, phosphate processing plants will be using aquifer water only for drinking purpose.

However, this battle was not a breeze, and it is far from over, all because of the clay (slime) problem. It is well known that amine flotation is very sensitive to clay in the feed or suspended solids in the flotation water. Suspended solids in the return water could be very high during rainy season or where clay settling ponds do not have enough capacity to allow the clays in processing water to settle out. In worst cases little sands could be floated even at high amine dosage, producing a product of high insol. Polymers have helped several phosphate mines overcome serious problems caused by poor return water quality.

ROLE OF POLYMERS IN THE REVERSE CRAGO PROCESS

The Florida Institute of Phosphate Research (FIPR) has conducted extensive laboratory testing to develop a more efficient process by reversing the Crago Double Float process (Zhang and others 1997). Polymer is the key to the success of this FIPR effort. The FIPR Reverse Crago process has substantial environmental benefits. If silica were floated first, there would be no need for the acid scrubbing circuit, thereby eliminating sulfuric acid usage in the amount of about 60,000 tons a year for the Florida phosphate industry. Since amine flotation does not need a pH modifier, soda ash (or other types of pH modifier) consumption is reduced by about half by floating silica first. Total organic reagent usage could also be reduced by hundreds of thousands of tons a year. Floating silica first also has significant economic benefits, including improving recovery, reducing the number of conditioners, eliminating acid scrubbers and wash boxes, and reducing sizing equipment.

Prior to FIPR's research, several attempts have been made to float silica first with success in both grade and recovery (Hollingsworth and Sapp 1961). But the reagent cost was economically prohibitive because of the higher amine consumption due to the effect of slime. The FIPR Reverse Crago process is novel in utilizing polymer to modify the amine flotation step.

EFFECT OF SLIME ON PHOSPHATE FLOTATION

Clay minerals and suspended solids in water have three major detrimental effects on flotation. They may form coating on the particles one wants to float, thus reducing selectivity. In worst cases when all the particles are coated with slime, nothing floats, no matter how much collector is added. Some slime particles are "friendlier" by just taking up excessive amounts of collector; one could still obtain a decent product but spend a dollar more for reagent per ton. These small particles also change the nature of flotation froth, with excessive foaming being most common, causing poor process performance. Polymers may offer the most promising solution to the clay problem.

BRIEF REVIEW ON POLYMER APPLICATIONS IN MINERAL PROCESSING

Polymer Uses as Depressants

Numerous polymers may be used as depressants and froth modifiers. Table 49 summarizes some typical applications of polymers as depressants.

Table 49. Some Examples of Polymer Use as Depressant.

Polymer Type	Minerals Depressed
Starch	Phosphate
Cationically modified polysaccharides	Silica
Cationically modified guar	Silica
Carboxymethyl cellulose (CMC)	Calcite, dolomite, apatite and talc
Polyphosphates	Siliceous gangue

A depressant must have functional groups that exhibit a preference attraction to the gangue minerals, and a strong hydrophilicity by virtue of either the same or other functional groups in its molecular structure. At the same time, the depressant molecules should not have functional groups that compete effectively with the collector for the surface of the minerals to be floated.

The following major factors should be considered in selecting a depressant: charge density, molecular weight, and dosage. High-charge density polymers are not desirable depressants, because most collectors are either positively or negatively charged. Hydroxyl-bearing water-soluble polymers such as starch and guar have been used as depressants. The hydroxyl groups on these polymer molecules impart strong hydrophilicity as well as a fairly good affinity to gangue minerals. However, they are not nearly as surface active as most charged collector functionalities and therefore compete less effectively for the active sites on the surface of the minerals to be floated.

A basic rule for depressant selection is to consider what would be a good collector for the particular mineral that needs to be depressed, then select a depressant that includes the same functionality as the collector but in which the hydrophobe is replaced with a hydrophile. For example, fatty acids, which contain carboxylate functionality, are effective collectors for calcite, calcite, dolomite, apatite, and hematite. Therefore, a carboxylated depressant, such as carboxymethyl cellulose (CMC) would be an effective depressant for these minerals. Siliceous minerals such as silica and kaolinite clay are floated by cationic amine collectors. Therefore, depressants based on cationically modified polysaccharides are effective depressants for siliceous minerals. But, because of their relatively high cost, cationic polymeric depressants are not popular on industrial scale. Instead, underivatized polysaccharides such as starch and guar gum are commonly used to depress silica or “blind" slime. Polyglycols of high molecular weight are effective in depressing siliceous materials but could cause excessive foaming. Polyacrylamides and dextrines are also effective but costly.

Selection of molecular weight also depends on the mechanism of depression. If depression is through flocculation, higher molecular weight is desirable, while low molecular weight polymers work better if dispersion is the mechanism.

The optimal dosage varies with the type of ore, the particle size and size distribution, the type of depressant, the molecular weight of the depressant, and the influence of other species, particularly those in the water. As a general rule, higher dosages are needed for lower molecular weight polymers.

It should be noted that the effectiveness of a depressant is highly dependent on the mineral system. For example, polyphosphates are effective in depressing siliceous gangue in base metal flotation, but is not an ideal depressant in floating phosphate from silica.

Polymer Application in Phosphate Flotation

Figure 56 (Lin and Burdick 1988) indicates that a small amount of CMC (carboxymethyl cellulose) as phosphate depressant increased recovery by about 10 percentage points in floating silica from phosphate.

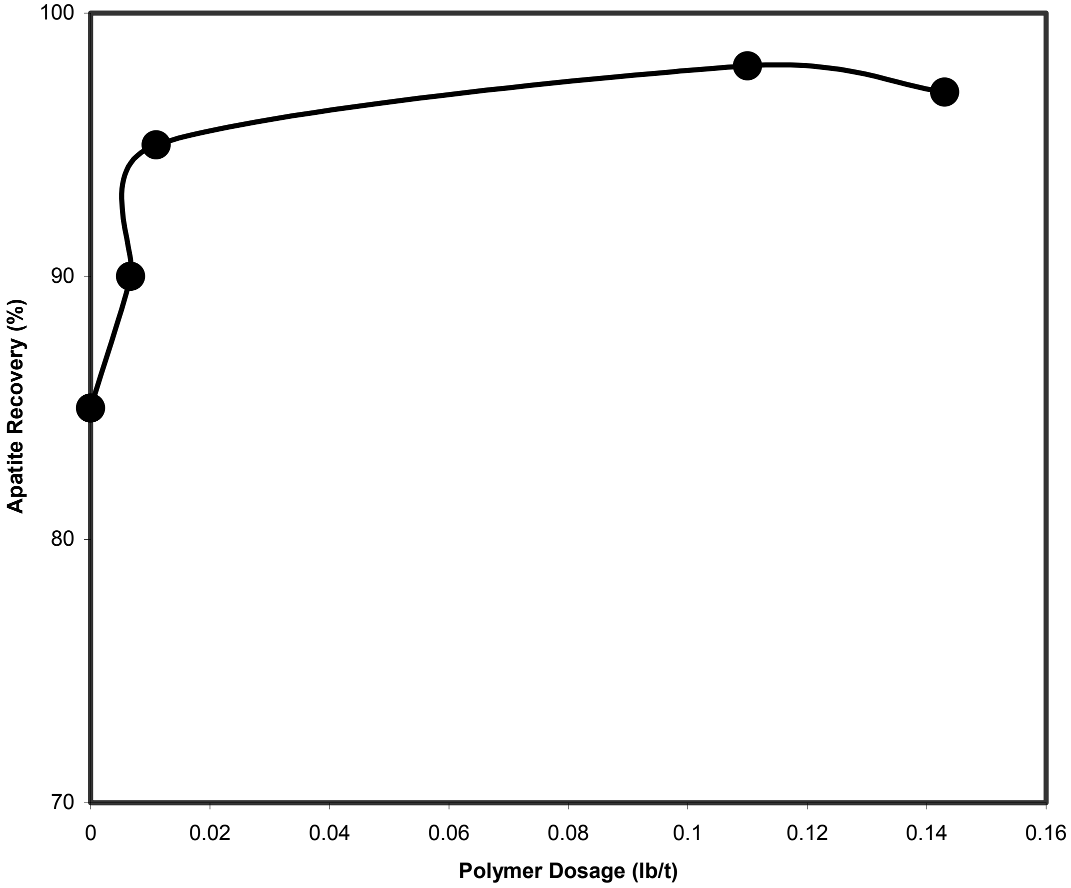


Figure 56. Reverse Flotation of Silica from Apatite with CMC as Phosphate Depressant at 0.22 Lb/Ton of Amine.

Polymeric depressants may increase recovery of coarse particles. This is particularly true for a slimy feed. Without the proper use of a polymeric depressant, the high surface area of the gangue can prevent the coarse particles from getting an adequate share of the collector to gain floatability. If one simply adds more collector in an attempt to float these coarse particles, an intolerable amount of gangue will also be floated thus rendering a poor-grade concentrate. A recent study by Jan Miller and others (2001) showed significant benefit of adding non-ionic polymer to fatty acid. It was found that non-ionic PEOs having a molecular weight between 1000 to 8000 are particularly effective. Outside this molecular weight range, the effect of PEO is insignificant. For example, in the case of a coarse feed (16x35 mesh), in order to achieve 85% recovery, 1200 g/t of the fatty acid/fuel oil blend is required, but only 500 g/t is required when PEO is used. At about the same collector addition, phosphate recovery can be improved by more than 10% with PEO addition.

In order to achieve one-step anionic flotation of phosphate, Nagaraj and others (1988) developed siliceous depressants of copolymers or terpolymers derived from 85-95% acrylamide and about 10% N-acrylamidoglycolic acid.

Polyacrylamide (I) containing both OH and COOH functional groups, obtained by reaction with aldehydes and ketones, and several related (I)-based copolymers, proved to be selective phosphate depressants in the amine flotation of silica (Nagaraj and others 1987). The addition of this modifier at even very low dosages (5-20 g/ton) resulted in a large increase in phosphate recovery (by 10% at 20 g/t polymer).

Flotation of phosphate was significantly improved by adding polymeric surfactants such as partial polyacrylic acid ester or polyphosphates (Smith and others 1982). Figure 57 (Lin and Burdick 1988) shows an example of polymer being used as silica depressant in floating phosphate. The recovery was improved by ten percentage points by adding less than one tenth of a pound of polymer. The use of sodium silicate to depress silica has been investigated by many researchers, and is practiced at some phosphate mines (Shaw 1983; Qi and others 1993; Snow 1990). Starch graft polymer was also proposed as a silica depressant (Jones and Jordan 1975).

In recent years, the Florida phosphate industry started using polymeric flocculants to treat return water from clay settling pond with significant recovery and grade benefits.

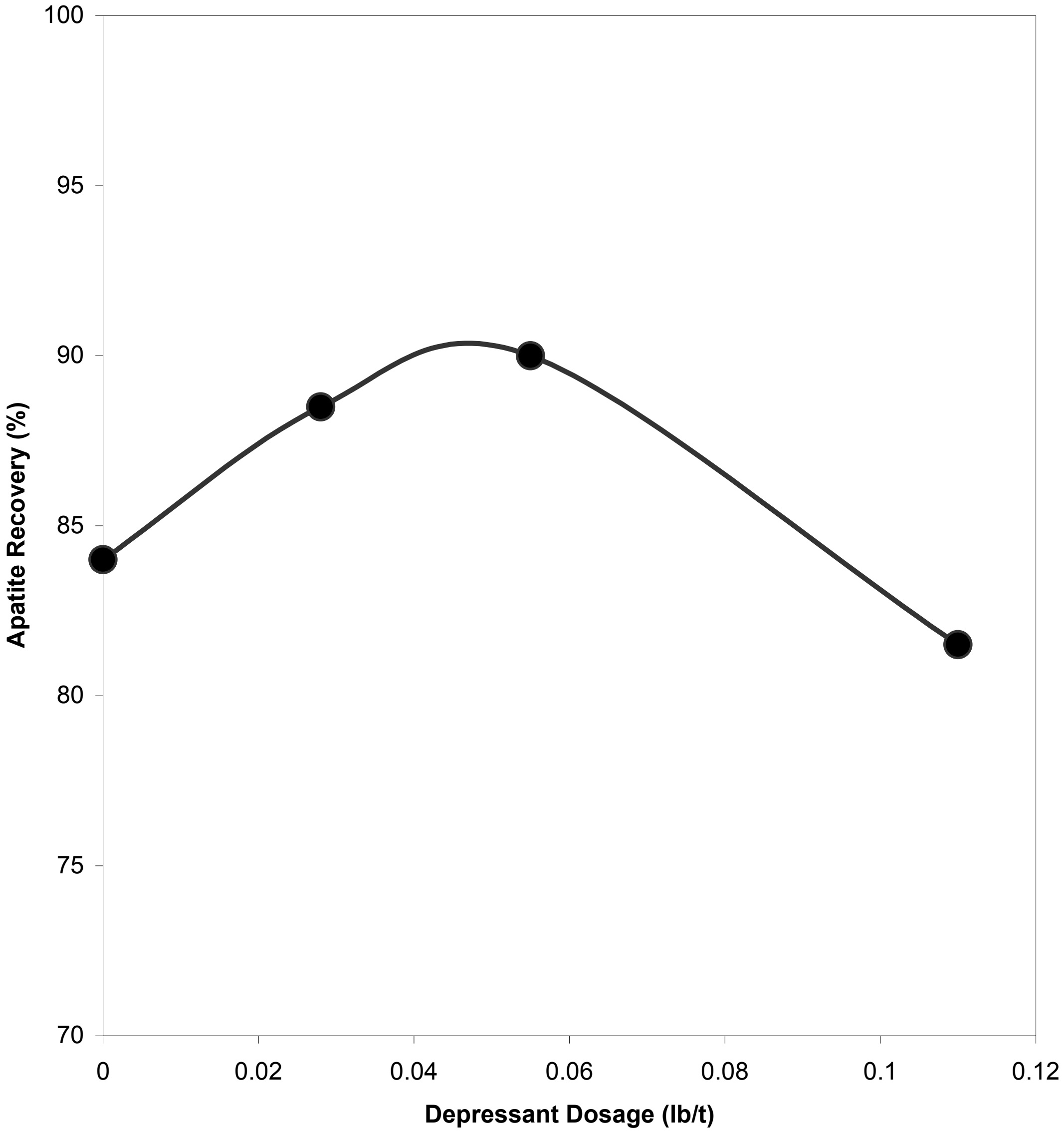


Figure 57. Flotation of Apatite from Silica with Cationic Guar as Silica Depressant at 1.1 Lb./Ton of Fatty Acid.

Polymer Uses as Flocculants

Table 50 (Santhana and others 1988) shows different types of polymeric flocculants. Polymers are used to selectively flocculate one component from a mixture of minerals. One such commercial operation is in iron ore. Polymers are widely used as slime blinder in potash flotation.

Table 50. List of Common Polymeric Flocculants.

Natural Flocculants	Synthetic Flocculants
Starch	anionic polymers – salts of polyacrylic acid, acrylamides
Galactomannans	cationic polymers – amino, imino or quaternary amino
Cellulose derivatives	nonionic polymers – polyacrylamide and polyethylene oxide
Alginates	
Chitin	

There are two main mechanisms of flocculation with polymeric flocculants: 1) adsorption of flocculant on the particles and 2) bridging the gap between adjoining particles. There are four kinds of physical forces for flocculant adsorption on particles: electrostatic forces, London-Van der Waals attraction, dipole attraction, and hydrophobic association. Chemical bonding, coordination bonding, and hydrogen bonding are the chemical forces.

EXPERIMENTAL

Lab Testing

Flotation Feeds

All the flotation feeds tested are unsized, and were collected from the secondary hydrocyclone underflows. Samples, all siliceous, from both the central and northern phosphate districts were tested. These feeds analyze 6-15% P_2O_5 and 60-80% insol. Most of the flotation experiments were conducted on the as-received feeds. In a few occasions, slight desliming (rinsing with tap water) was practiced for comparison.

Flotation Reagents

The quartz collector used is an amine condensate designated as Custamine 738 and provided by Westvaco. A blend of fatty acid and fuel oil was used as phosphate collector. These are all commercially available reagents. Soda ash and sulfuric acid were used as pH modifiers. Bartow tap water was utilized in the initial tests, and plant water was used for studying the slime effect.

Polymers

Fifteen commercial polyacrylamide polymer samples from Allied Colliods, ArrMaz Products, and Nalco Chemicals were obtained. These products included anionic, cationic, and nonionic polymers of varying molecular weights and percent charge. The majority are water-in-oil emulsions that require dilution, with water, to the recommended 0.1% level. Table 51 shows the polymers used.

Table 51. Brief Description of Test Polymers.

Brand Name	Type	Brand Name	Type
AMP 1050L	Anionic coagulant	AMP 890E	Non-ionic
AMP 575E	Anionic with Sulfonate group	Nalco 8871	Nonionic, high MLW
AMP 770E	Cationic	Nalco 9768	Anionic with sulfonate group
AMP 812E	Med. Anionic	Nalco 9806	High MLW, med. anionic, with carboxylic group
AMP 840E	Low anionic	Nalco 9818	Ultra-high MLW, med. anionic, carboxylic group
AMP 844E	Low ML-anionic	Percol 90L	Anionic, emulsion
AMP 869E	Med. Anionic	Percol 455	Anionic, power
AMP 863E	Medium anionic		

Polymer Screening Procedure

Initial screening was performed by adding varying amounts of the test polymer to a phosphatic clay sample (a slurry of approximately 2.7% solids) and observing settling characteristics at varying time periods. Criteria were fastest settlement at lowest usage. The slurry of 92-98 ml was placed in a 100-ml graduated cylinder. Upon addition of 1-8 ml of polymer solution into the graduated cylinder, the cylinder was capped and shaken for 30 seconds before recording the settling rates.

Flotation Testing Procedure

All the flotation tests were conducted in a standard one-liter Denver cell with a charge of about 500 g dry feed. Polymers selected from initial screening were evaluated in flotation tests at varied levels with amine reagent. An initial polymer performance criterion was the reduction in amine level that could be achieved while maintaining a similar silica flotation. Further testing examined concentrate acid insol and phosphate recovery that could be attributed to polymer use and/or changes in polymer level relative to amine level.

Pilot Testing

A pilot plant with a capacity of about 500 pounds per hour of feed was designed to evaluate flotation of silica with polymer as a modifier. Because of a mechanical difficulty, the feed to the pilot plant was collected from the plant feed pipeline prior to the last stage of cycloning. This feed, therefore, has higher slime than the feed to the plant conditioners, and is deslimed using a screw feeder before it is subjected to the Reverse Crago process. The feed coming out from the screw feeder is diluted to about 30% solids. The diluted slurry is conditioned briefly with the polymer for about 30 seconds, and then amine for about 10 seconds. Amine flotation is conducted in a bank of four mechanical cells with additional amine added in the first and/or second cell. The prefloat concentrate is dewatered with a Sweco screen, conditioned with a fatty acid/fuel oil blend at about 70% solids, and floated in a bank of four mechanical cells. In some cases, the fatty acid concentrated is refloated to further reduce the insol in the final product. Each processing stream is sampled using automatic samplers, which kick in for seven seconds at five-minute intervals.

RESULTS AND DISCUSSION

Effectiveness of Polymers in Flocculating Phosphatic Clays

Definite differences in polymer settling or flocculation characteristics were seen in initial screening tests. Table 52 summarizes flocculation data for all test polymers, and Figure 58 shows a comparison of the five most effective polymers.

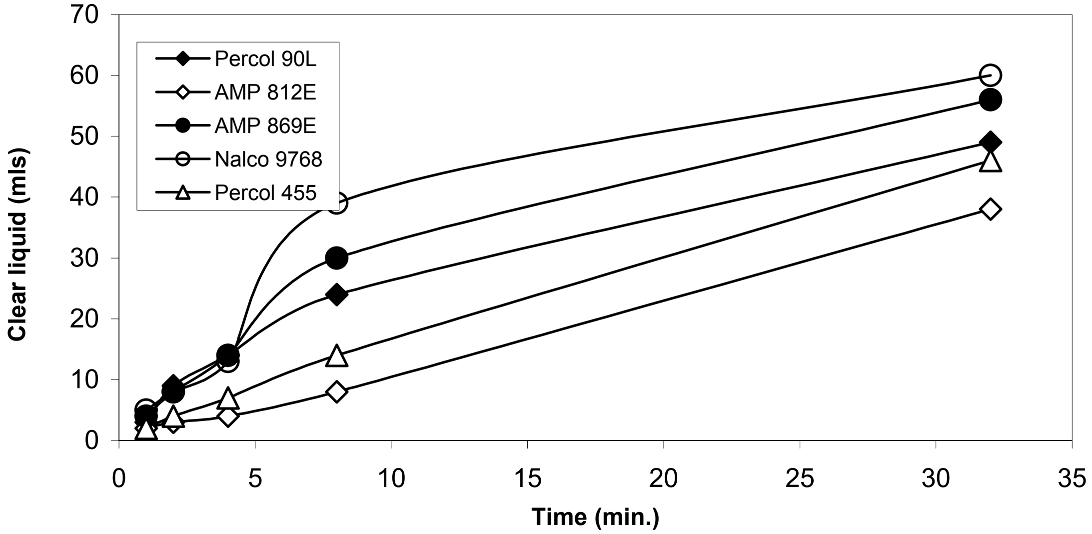


Figure 58. Comparison of Some Effective Flocculants for Phosphatic Clays.

Polymers of anionic type with medium- to high-molecular weights are generally more effective in flocculating phosphatic clays. The least effective polymers are AMP 770, a cationic type, and AMP 1050L, a coagulant type. Non-ionic polymers (AMP 890 and Nalco 8871) are also inefficient. Moderately anionic polymers are not as powerful as strongly anionic ones.

Table 52. Polymer Screening by Flocculation Tests.

		Clear liquid (ml)				
Polymer	Dosage (ml)	1 min	2 min	4 min	8 min	32 min
Percol 90L	4	3	9	14	24	49
AMP1050L	8	1	2	2	3	7
AMP 575E	4	2	3	4	6	38
AMP 575E	8	14	28	45	54	62
AMP 770E	8	1	2	3	5	36
AMP 812E	4	2	3	4	8	32
AMP 812E	8	33	42	49	53	57
AMP 840E	4	2	3	4	6	35
AMP 840E	8	12	25	41	53	63
AMP 844E	4	1	2	3	4	14
AMP 844E	8	6	13	26	45	59
AMP 869E	4	4	8	14	30	56
AMP 869E	8	35	42	47	53	59
AMP 890E	4	1	1	2	8	19
AMP 890E	8	4	6	12	27	53
Nalco 8871	4	1	2	2	3	25
Nalco 8871	8	2	4	10	22	53
Nalco 9768	4	5	8	13	39	60
Nalco 9768	8	44	54	59	64	69
Nalco 9806	4	2	3	6	8	33
Nalco 9806	8	29	42	52	56	63
Nalco 9818	4	1	3	3	4	14
Nalco 9818	8	7	14	34	53	63
Percol 455	4	2	4	7	14	46
Percol 455	8	32	39	45	48	53

Polymer Screening by Flotation

The amount of sand floated with the addition of a polymer is a good indication of the effectiveness of the polymer in blinding slime and reducing amine consumption. Therefore, the initial flotation tests were conducted at about the same amine dosage with varying amount of polymer. In other tests, both polymer and amine dosages were maintained at the same levels to compare the amount of sand floated. Table 53 summarizes some of the test results.

Table 53. Flotation Comparison of Different Polymers (at 0.02 Lb./Ton Feed).

% Slime	Lb Amine/ TOF	Amount of Sand (Wt.%) Floated				
		Percol 90L	AMP575E	AMP770E	AMP863E	Nalco9768
1.5	1.5	52.7	63.6	45.9	48.9	49.7
1.7	1.5	52.3	34.8	8.7	18.2	5.1
2.0	2.5	49.5	34.8	----	----	----
2.5	4.0	30.22	----	----	----	----

In these tests the flotation feed was scrubbed for ten minutes to produce secondary slime intentionally. Extra slime was also added in the flotation feeds for some tests.

The above simple table contains lots of information. First, it indicates that Percol 90L is the toughest in terms of slime tolerance. It also suggests that cationic polymers could work well on feed of lower slime, but is not powerful enough for high-slime feed. Increasing the dosage of the cationic polymer may achieve similar results as with Percol 90L, but would not be economically desirable because it is more expensive. When the slime level is more than 2%, the amount of sand floated is significantly reduced even with Percol 90L and at high amine dosage. Again, increasing Percol 90L dosage could probably reduce amine consumption, but it may compromise recovery dramatically.

The effects of polymer on amine consumption and the amount of sand floated are rather dramatic. Figure 59 shows the effect of polymer on the amount of sand floated and amine dosage. The amine usage had to be doubled without polymer for the same amount of sand floated. This test was done on a fine flotation feed with extremely cloudy water with only 0.03 lb/ton of polymer.

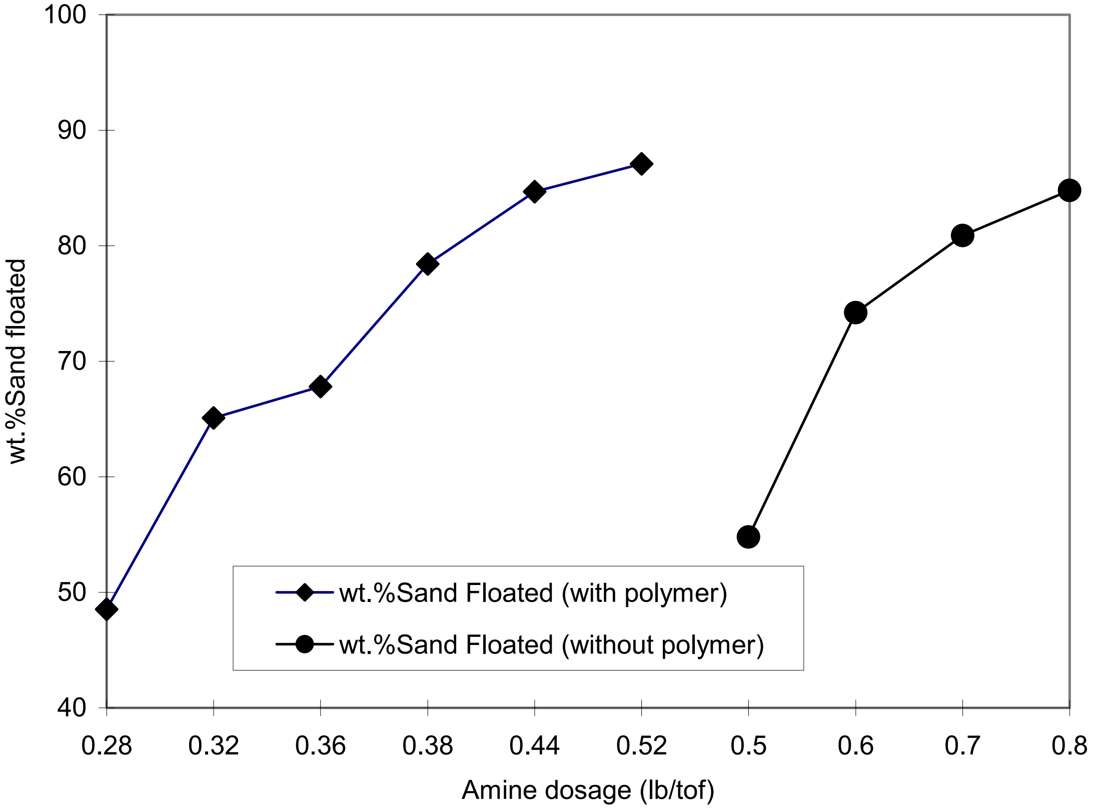


Figure 59. Effect of Percol 90L (at 0.03 Lb./Ton Feed) on Amine Flotation.

On the other hand, at the same amine level, increasing polymer dosage can significantly increase the amount of sand floated. Figure 60 shows the effect of AMP 863E dosage on the amount of sand floated for a feed of 1.7% slime at 1.5 lb/t of amine.

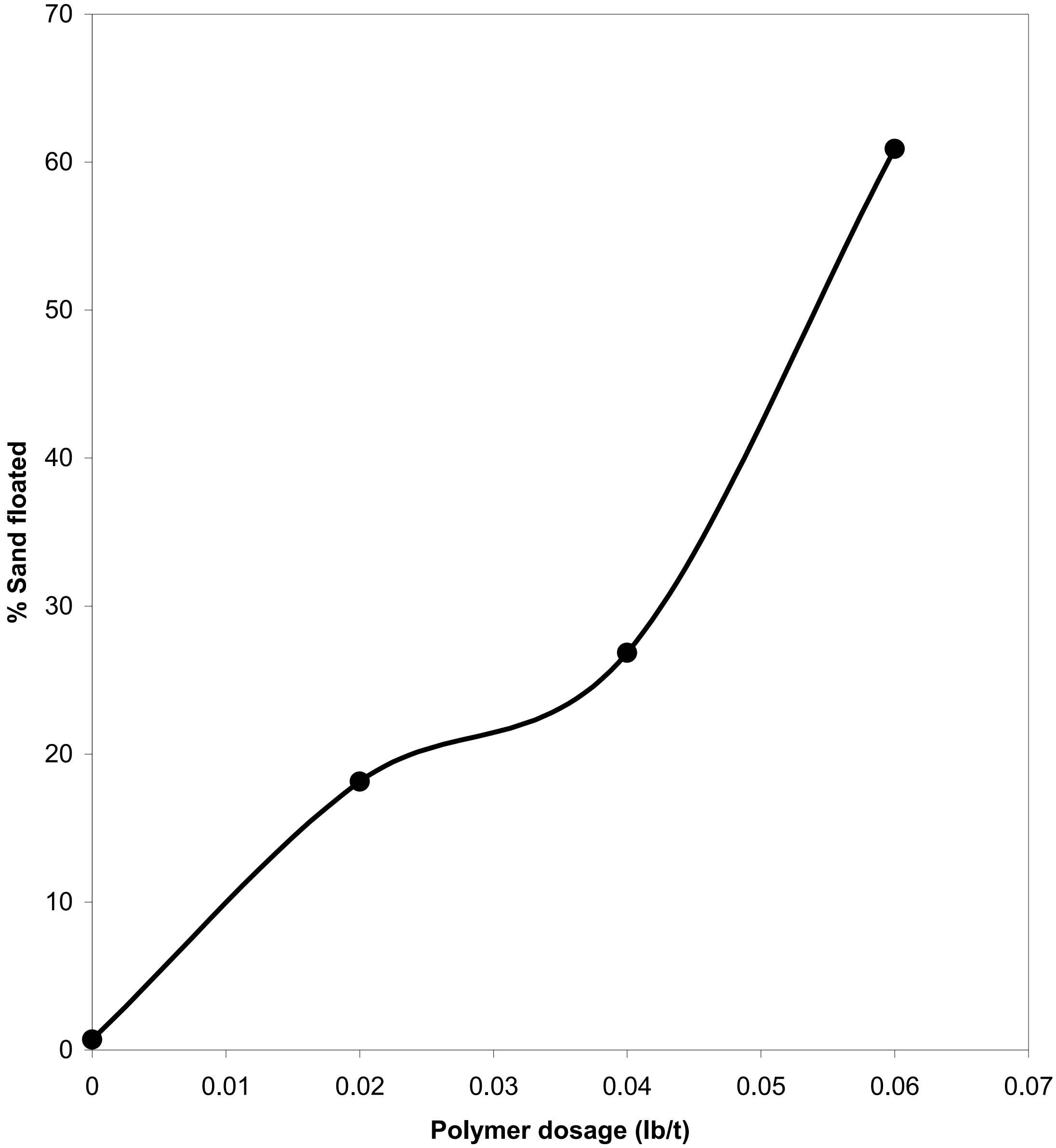


Figure 60. Effect of AMP 683E on Amine Flotation.

The effect of polymer on amine consumption is more remarkable for feeds with higher slime. Figure 61 shows that the amine consumption should be more than tripled to achieve the same amount of sand removal for a feed with 13.5% slime (-150 mesh).

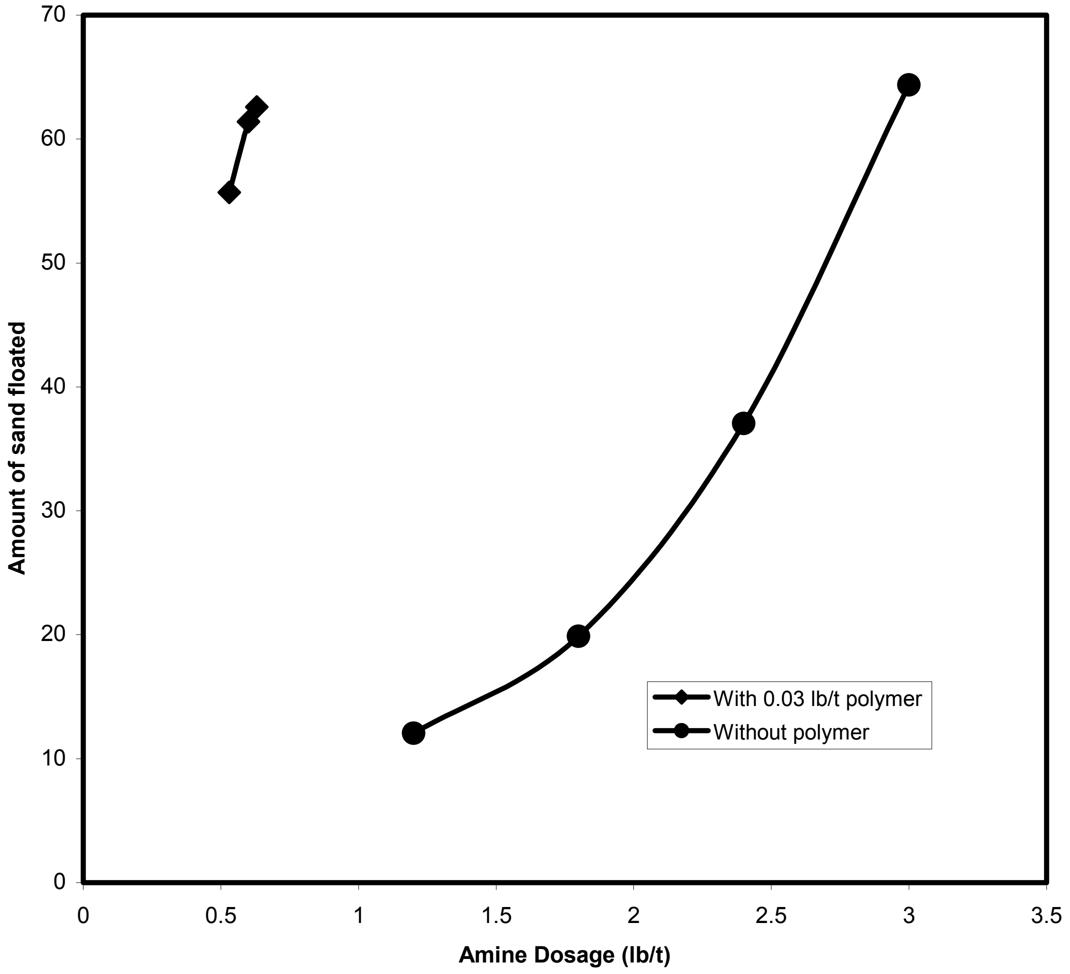


Figure 61. Effect of Percol 90L on Amine Dosage and the Amount of Sand Floated for a Extremely Slimy Feed (13.5%--150 Mesh).

The Polymer-Amine Synergy

The benefit of polymer is best realized when the polymer dosage is determined based the amount of slime. For high slime feed, the addition of polymer has a positive effect on flotation recovery at certain levels of amine collector. Figure 62 shows this trend for the high-slime feed.

As is indicated in Figure 63, however, polymer could have a detrimental effect on amine flotation beyond certain concentration. Overdose of polymer not only reduces phosphate recovery to an unacceptable level, but also reduces the total amount of sand floated, due to the effect of foaming.

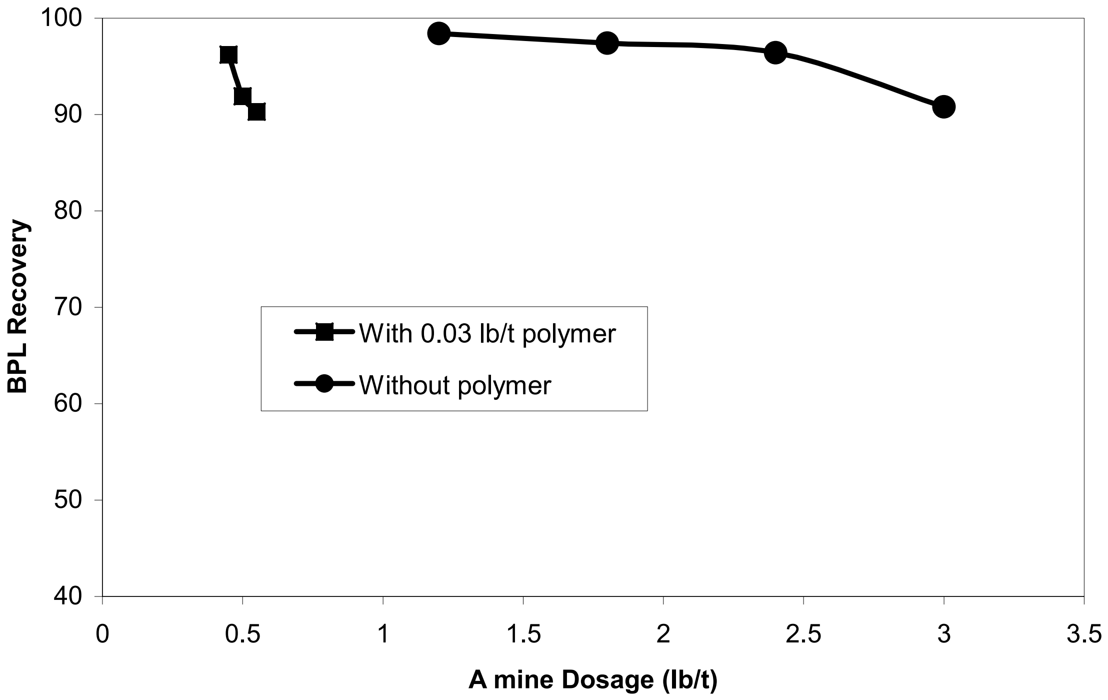


Figure 62. Effect of Polymer on Flotation Recovery.

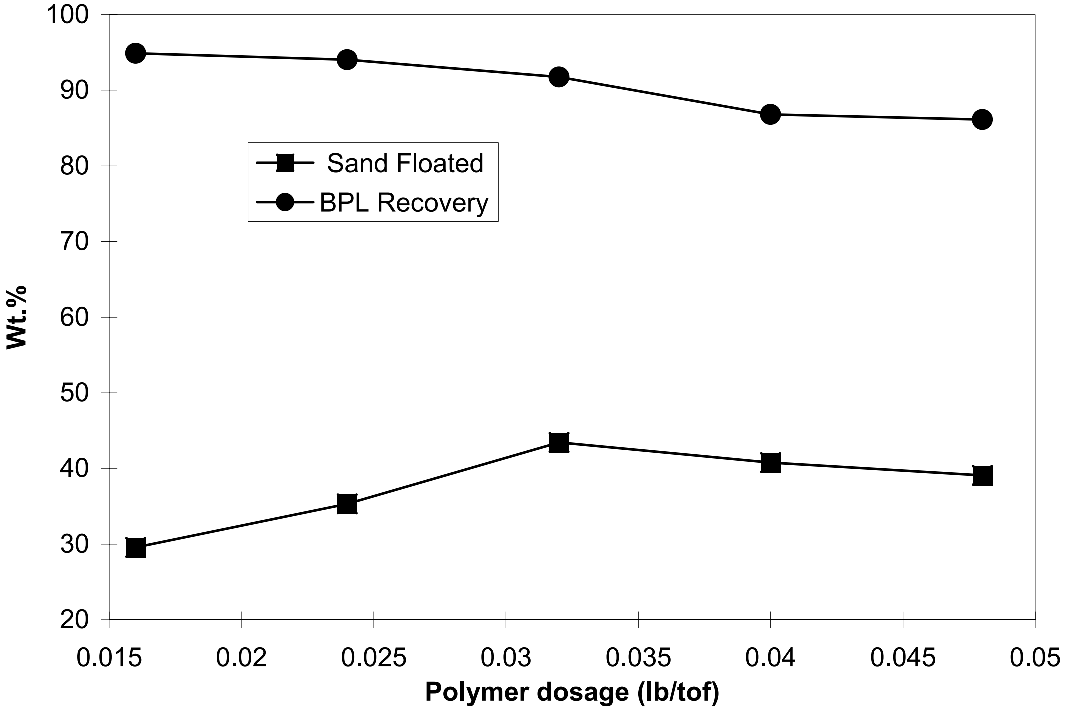


Figure 63. Effect of Polymer (Percol 90L) Dosage.

PILOT TESTING INDICATIONS

The pilot testing showed more distinct synergistic interaction between amine and polymer than the laboratory testing. In most of the lab tests, as long as the polymer dosage was below certain concentration, the amine level could be adjusted for the desired amount of sand floated with recoveries of more than 95%. On pilot scale adjusting the two was tricky. Excessive foaming occurred at both low and high polymer dosages, depending upon the amount of amine.

A cationic polymer was also tested on pilot scale, and showed better selectivity than Percol 90L but with significantly higher amine consumption.

However, a low molecular weight anionic polymer (AMP 844E) performed equally well, if not better, as the high molecular weight polymer (Percol 90L), as shown in Table 54.

Table 54. Comparison of Polymer Performance on Pilot Scale.

Test Conditions	Amine Dosage (lb/t)	% Sand Floated	Prefloat Recovery
Percol 90L, extra desliming	0.56	48	94.6
AMP 844E, extra desliming	0.57	44	95.6
Percol 90L, no extra desliming	0.61	27	98.3
AMP 844E, no extra desliming	0.70	32	97.9

Perhaps the most important indication of the pilot testing is that the FIPR Reverse Crago process has the potential to outperform the Crago process on industrial scale. Table 55 summarizes the final two rounds of parallel testing. These data clearly indicate that the Reverse Crago process is superior over the Crago process in terms of both recovery and reagent cost. The only drawback of the Reverse Crago process is the need for an additional step in order to produce low-insol products while maintaining high recovery.

Table 55. Parallel, Pilot-Scale Comparison of the Reverse Crago Process vs. the Crago Process.

Item	Parallel One		Parallel Two	
	Crago	Reverse Crago	Crago	Reverse Crago
Concentrate %P_2O_5	32.72	30.43	31.57	31.18
Concentrate % insol	3.20	9.34	6.91	7.46
%P_2O_5 Recovery	90.50	92.60	87.12	91.56
Reagent cost, \$/toc	2.43	1.16	2.62	1.02
Total reagent use, lbs/toc	41.80	13.10	48.00	12.50

CONCLUSIONS

It was found that the effectiveness of polymers in blinding phosphatic slimes for amine flotation of silica from phosphate decreases in the following order: cationic<non-inoic<media anionic<low molecular weight anionic< high molecular weight anionic.

The mechanism of depressing (blinding) slime by polymer is through flocculation. Therefore, in general, high molecular weight anionic polymer should be selected for this purpose. Low molecular weight anionic polymer may be better for feeds of low slime content.

Pilot scale testing indicated that the Reverse Crago process could achieve similar or better performance than the Crago process in terms of both recovery and operating costs, when flotation feeds were clean.

RECOMMENDATIONS FOR FUTURE WORK

Much work needs to be done to better understand the mechanism of the polymer effect, the synergistic reaction between polymer and amine, and the role of water chemistry.

There were indications that low molecular weight anionic polymer may be more suitable for reverse flotation of silica from phosphate. More research is needed to establish the minimum or the range of molecular weight for this purpose. Selection of polymer should also be correlated to slime level in the flotation feed.

More testing is needed to determine the slime tolerance level for the Reverse Crago process.

CITED REFERENCES

Gieseke EW, editor. 1985. Florida phosphate rock. In: Weiss NL, editor. SME mineral processing handbook. New York: Society of Mining Engineers. Section 21: Phosphate rock. p 21-2 to 21-5.

Gruber G, Moudgil BM, Somasundaran P. 1995. Understanding the basics of anionic conditioning in phosphate flotation. Bartow (FL): Florida Institute of Phosphate Research. FIPR Publication nr 02-090-121. p 31.

Hollingsworth CA, Sapp BL, inventors; Smith-Douglas Co., Inc., assignee. 1961 Dec 19. Beneficiation of phosphate rock. US patent 3,013,664.

Houot R. 1982. Beneficiation of phosphatic ores through flotation: review of industrial applications and potential developments. International Journal of Mineral Processing 9(4):353-84.

Hsieh SS, Lehr JR. 1985. Beneficiation of dolomitic Idaho phosphate rock by the TVA diphosphonic acid depressant process. Minerals and Metallurgical Processing 2(1):10-13.

Jones DA, Jordan WA, inventors; US Dept of Agriculture, assignee. 1975 Jan 21. Flotation beneficiation of phosphate ores. US patent 3,862,028.

Lawendy TAB, McClellan GH. 1993. Flotation of dolomitic and calcareous phosphate ores. In: El-Shall H, Moudgil B,Wiegel R, editors. Beneficiation of phosphates: theory and practice; 1993 Dec 5-10; Palm Coast, FL. Littleton (CO): Society for Mining, Metallurgy, and Exploration. p 231-43.

Leal Filho L and others. 1993. The influence of corn starch on the separation of apatite from gangue minerals via froth flotation. In: El-Shall H, Moudgil B, Wiegel R, editors. Beneficiation of phosphates: theory and practice; 1993 Dec 5-10; Palm Coast, FL. Littleton (CO): Society for Mining, Metallurgy, and Exploration. p 147-155.

Lehr JR, Hsieh SS, inventors; Tennessee Valley Authority, assignee. 1981 Sep 1. Beneficiation of high carbonate phosphate ores. US patent 4,287,053.

Lin KF, Burdick CL. 1988. Polymeric depressants. In: Somasundaran P, Moudgil B, editors. Reagents in mineral technology. New York: Marcel Dekker. p 471-83.

Miller J, Liu N, Lu Y. 2001. Improved phosphate flotation with nonionic polymers: final report. Bartow (FL): Florida Institute of Phosphate Research. FIPR Publication nr 02-113-150.

Somasundaran P, Moudgil B, editors. Reagents in mineral technology. New York: Marcel Dekker.

Nagaraj DR, Rothenberg AS, Lipp DW, Panzer HP. 1987. Low molecular weight polyacrylamide-based polymers as modifiers in phosphate beneficiation. International Journal of Mineral Processing 20(3/4):291-308.

Qi GW, Klauber C, Warren LJ. 1993. Mechanism of action of sodium-silicate in the flotation of apatite from hematite. Int. J. of Min. Proc. 39(3/4):251-73.

Rao KH, Antti BM, Forssberg E. 1989. Flotation of phosphatic material containing carbonatic gangue using sodium oleate as collector and sodium silicate as modifier. Int. J. of Mineral Processing 26(1/2):123-40.

Ratobylskaya LD and others. 1975. Preprints, 11th Congrès International de Valorisation de Minerais. Seminaire sur la valorisation de phosphates mineraux pauvres à gangue carbonetée. Cagliari, Italy. p 17-39.

Rule AR, Daellenbach CB. 1985. Beneficiation of complex phosphate ores containing carbonate and silica gangue. In: Proceedings, XVth International Mineral Processing Conference; 1985 Jun 2; Cannes, France. St. Etienne (France): Editions GEDIM. Volume 3. p 380-389.

Santhana V and others. 1988. Polymeric flocculants. In: Somasundaran P, Moudgil B, editors. Reagents in mineral technology. New York: Marcel Dekker. p 485-518.

Shaw DR, inventor; Resource Technology Associates, assignee. 1987 Sep 1. Selective flocculation process for the recovery of phosphate. US patent 4,690,752.

Smith EL Jr, Poulos AC, Ellwanger RE, inventors; American Cyanamid Co., assignee. 1982 Jan 5. Process of phosphate ore beneficiation in the presence of residual organic polymeric flocculants. US patent 4,309,282.

Smani MS, Blazy P, Cases JM. 1975. Beneficiation of sedimentary Moroccan phosphate ores: Part 3. Selective flotation and recovery. Trans. AIME 258:176-80.

Smani MS, Blazy P, Cases JM. 1975. Beneficiation of sedimentary Moroccan phosphate ores: Part 4. Depression of phosphate oolites and calcite flotation. Trans. AIME 258:181-2.

Snow RE, inventor; IMC Fertilizer, Inc., assignee. 1990 Feb 27. Sodium silicate as a phosphate flotation modifier. US patent 4,904,375.

Zhang P and others. 1997. Challenging the 'Crago' double float process. II. Amine-fatty acid flotation of siliceous phosphates. Minerals Engineering 10(9):983-94.

ADDITIONAL REFERENCES

Baumann AN, Snow RE. 1980. Processing techniques for separating MgO impurities from phosphate products. In: Proceedings, 2nd International Congr. Phosphorus Compounds; 1980 Apr 21-25; Boston, MA. Paris (France): Institut Mondial du Phosphate. p 269-80.

Borisov VM. 1956. Conditions for the beneficiation of the difficult-to-enrich phosphate ores of the Kara-Tau deposit. Khim. Prom. p 13-19.

Clerici C, Morandini AF, Mancini A, Mancini R. 1984. Flotation of a phosphate rock with carbonate-quartz gangue. In: Jones MJ, Oblatt R, editors. Reagents in the minerals industry. London: The Institute of Mining and Metallurgy. p 221-5.

Davis BE, Llewellyn TO, Smith CW. 1984. Continuous beneficiation of dolomitic phosphate rocks. Washington: U.S. Bureau of Mines. Report of Investigations nr 8903. p 10-13.

Fu E, Somasundaran P. 1986. Alizarin Red S as a flotation modifying agent in calcite-apatite systems. Int. J. of Mineral Processing 18(3/4):287-96.

Fuerstenau MC, Gutierrez G, Elgillani DA. 1968. The influence of sodium silicate in nonmetallic flotation systems. Trans AIME 241:319-23.

Good PC. 1976. Beneficiation of unweathered Indian calcareous phosphate rock by calcination and hydration. Washington: U.S. Bureau of Mines. Report of Investigations nr 8154. p 1-17.

Gruber GA, Raulerson JD, Farias RP. 1987. Adapting technology to beneficiate a low-grade phosphorite ore. Minerals and Metallurgical Processing 4(1):14-18.

Houot R, Polgaire JL. 1980. Inverse flotation beneficiation of phosphate ores. In: Proceedings, 2nd International Congress on Phosphorus Compounds; 1980 Apr 21-25; Boston, MA. Casablanca (Morocco): IMPHOS. p 231-46.

Lawver JE, Bernardi JP, McKereghan GF, Raulerson JD, Lynch D, Hearon RS. 1984. New techniques in beneficiation of the Florida phosphates of the future. Minerals and Metallurgical Processing 1(2):89-106.

Lawver JE, McClintock WO, Snow RE. 1978. Beneficiation of phosphate rock: a state of the art review. Minerals Sci. Engineering 10(4):278-294.

Lawver JE, Snow RE, McClintock WO, inventors; International Minerals & Chemical Corp., assignee. 1980 Feb 19. Method of beneficiating phosphate ores. US patent 4,189,103.

Lawver JE, Wiegel RL, Snow RE, Hwang, CL. 1982. Beneficiation of dolomitic Florida phosphate reserves. In: Proceedings, XIV International Mineral Processing Congress; 1982 Oct; Toronto, Ontario, Canada. p 380-389.

Leja J. 1982. Surface chemistry of froth flotation. New York: Plenum Press. 758 p.

Llewellyn TO, Davis BE, Sullivan GV, Hansen JP. 1982. Beneficiation of high-magnesium phosphate from southern Florida. Washington: U.S. Bureau of Mines. Report of Investigations nr 8609. 16 p.

Moudgil BM. 1986. Advances in phosphate beneficiation. In: Somasundaran P, editor. Advances in mineral processing. Littleton (CO): Society of Mining Engineers. p 426-41.

Moudgil BM. 1992. Flotation of Florida phosphate rocks using anionic collectors. Bartow (FL): Florida Institute of Phosphate Research. FIPR Progress Report nr 91-02-087.

Moudgil BM, Blanchard FN, Shah DO, Onoda GY, Whitney ED. 1987. Separation of dolomite from the South Florida phosphate rock: final report. Bartow (FL): Florida Institute of Phosphate Research. Volume 2. FIPR Publication nr 02-023-051.

Nagaraj DR, Rothenberg AS, Lambert AS, inventors; American Cyanamid Company, assignee. 1988 Jan 19. Flotation beneficiation process for nonsulfide minerals. US patent 4,720,339.

Rao DV, Narayanan MK, Nayak UB, Ananthapadmanabhan K, Somasundaran P. 1985. Flotation of calcareous Mussorie phosphate ore. Int. J. Mineral Processing 14:57-66.

Rule AR, Larson DE, Daellenbach CB. 1982. Application of carbonate-silica flotation techniques to western phosphate materials. Washington: U.S. Bureau of Mines. Report of Investigations nr 8728. 13 p.

Rule AR, Clark CW, Butler MO. 1974. Flotation of carbonate minerals from unaltered phosphate ores of the Phosphoria formation. Washington: U.S. Bureau of Mines. Report of Investigations nr 7864. 18 p.

Rule AR, Kirby DE, Dahlin DC. 1978. Recent advances in beneficiation of western phosphates. Mining Engineering 30(1):37-40.

Rule AR, Gruzensky WG, Stickney WA. 1970. Removal of magnesium impurities from phosphate rock concentrates. Washington: U.S. Bureau of Mines. Report of Investigations nr 7362. 12 p.

Smith R. 1988. Cationic and amphoteric collectors. In: Somasundaran P, Moudgil B, editors. Reagents in mineral technology. New York: Marcel Dekker. p 219-56.

Snow RE, inventor. 1979 Mar 20. Beneficiation of phosphate ore. US patent 4,144,969.

Snow RE, inventor; International Minerals & Chemical Corp., assignee. 1982 Dec 21. Flotation of phosphate ores containing dolomite; removal of alkali earth metal carbonates using a carbonate collector, phosphate depressant and pH regulator. US patent 4,364,824.

Tanaka Y and others. 1988. Reagents in phosphate flotation. In: Somasundaran P, Moudgil B, editors. Reagents in mineral technology. New York: Marcel Dekker. p 645-62.

Xiao L, Somasundaran P. 1989. Interactions between oleate collector and alizarin modifier in dolomite/francolite flotation system. Minerals and Metallurgical Processing 6(2):100-3.

Zellars-Williams Co. 1989. Anionic flotation of Florida phosphate. Bartow (FL): Florida Institute of Phosphate Research. FIPR Publication nr 02-063-071. 150 p.