

BENEFICIATION OF PHOSPHATE ORES CONTAINING SILICEOUS  
AND CALCIUM CARBONATE GANGUE - FINAL REPORT

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by

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ABSTRACT

Beneficiation tests were carried out on a high-grade phosphate matrix sample containing siliceous and calcium carbonate gangue. The objective was to find a practical method for separating silica and calcium carbonate from phosphate. Initial tests showed that, by use of the standard Crago process for beneficiating phosphate, a high-grade concentrate with good phosphate recovery could be obtained, but the  $\text{CaO}/\text{P}_2\text{O}_5$  ratio was abnormally high. Results of further beneficiation tests showed that, by use of various flowsheets, a high-grade concentrate could be obtained, with relatively high phosphate recovery and a low  $\text{CaO}/\text{P}_2\text{O}_5$  ratio.

INTRODUCTION

Overlying the main ore zone of the North Carolina phosphate deposit is four to six feet of high-grade matrix (approximately 19%  $\text{P}_2\text{O}_5$ ) containing siliceous and calcium carbonate gangue (shell and coquina). Samples 3441 and 3756 were obtained from this zone. It is understood that the material is mined on an erratic basis by Texas Gulf, Inc. It is assumed it is not mined all the time due to the calcite present and the difficulties involved in removing calcite from phosphate.

The open-pit mining method used by Texas Gulf, Inc. makes it possible to selectively discard this high-grade, high-calcium-carbonate material with the overburden, as desired. Several companies had planned to mine the North Carolina phosphate by slurry mining methods, which would be much less selective than the open pit method. The development of a practical process for economically recovering phosphate from calcite-contaminated ore, such as this upper high-grade zone, should enable these operations to overcome their beneficiation problems. Also, if a practical process is developed, it could make possible the processing of the upper fifteen feet and lower eight feet of low-grade ore, which contains siliceous and calcium carbonate gangue.

#### OBJECTIVE

The initial objective of this project was to develop a practical method for beneficiating low-grade phosphate ores containing calcium carbonate and siliceous gangue. However, two attempts to obtain a sample of the low-grade, high-calcium-carbonate material that lies over the high-grade zone proved unsuccessful. Instead, samples were shipped to the Laboratory from the high-grade, calcite-contaminated zone that lies immediately over the 40-foot main ore zone. These samples were used for laboratory tests; therefore, the project was redirected toward finding a practical method for beneficiating high-grade phosphate ores containing siliceous and calcium carbonate gangue.

#### DESCRIPTION OF SAMPLES

Laboratory Samples Nos. 3441 and 3756 were obtained by Texas Gulf, Inc. from the high-grade, calcite-contaminated zone immediately over their 40-foot main ore zone. These samples consisted principally

of quartz, phosphorite and calcium carbonate. The weight percents shown in Table I were obtained for the different screen fractions of the matrix for both samples 3441 and 3756.

TABLE I  
WEIGHT PERCENT OF FRACTIONS OBTAINED FROM SCRUB TESTS,  
MATRIX SAMPLES 3441 AND 3756

Size	Sample 3441		Sample 3756	
	% Wt	Cum. % Wt	% Wt	Cum. % Wt
+1"	0.3	0.3	2.7	2.7
-1"+4" Mesh	7.4	7.7	3.3	6.0
-4+14 Mesh	9.4	17.1	7.0	13.0
-14+200 Mesh	64.0	81.1	71.6	84.6
-200 Mesh	<u>18.9</u>	100.0	<u>15.4</u>	100.0
Total	100.0		100.0	

The following procedure was used in preparing these matrix samples for flotation tests. This laboratory procedure was set up to duplicate, as much as possible, the preparation of flotation feed in an operating plant.

- 1) Representative 50-pound (wet) samples were cut out and scrubbed for 10 minutes at approximately 33% solids in a laboratory scrubber at 500 rpm.
- 2) The scrubbed sample was wet screened on one-inch, four mesh and 14 mesh.
- 3) The minus 14 mesh material was deslimed at 200 mesh. The minus 200 mesh slimes were allowed to settle, and clear water was decanted. The total dry weight of slimes was determined by drying and weighing a representative aliquot.

- 4) The minus 14 plus 200 mesh fraction was dewatered, and coned and quartered. Representative samples were cut out for screen analyses, moisture determination and flotation. The wet samples for flotation, each weighing 625 grams, were put in plastic bags.

The analysis of the minus 14 plus 200 mesh fraction of each ore sample is shown in Table II.

TABLE II

Sample No.	Assay %			CaO/P <sub>2</sub> O <sub>5</sub>
	P <sub>2</sub> O <sub>5</sub>	Insol.	CaO	
3441	18.4	34.4	32.5	1.77
3756	19.2	35.0	33.6	1.74

STANDARD CRAGO FLOAT

A standard Crago double float was carried out on both samples 3441 and 3756 in order to obtain a basis of comparison for subsequent calcite removal studies. Feed for these tests was prepared, as in all subsequent tests, by scrubbing a 625-gram sample of deslimed minus 14 mesh ore for five minutes at 75% solids and then desliming at 200 mesh. The scrubbed feed was conditioned with saponified fatty acid and fuel oil for five minutes at 65% solids. The reagentized pulp was put in a flotation cell, and a phosphate rougher concentrate was removed as the froth product. In order to remove reagents from the froth product, it was scrubbed for five minutes at 50% solids with sulphuric acid and was then washed. The dereagentized rougher concentrate was treated in an amine float to remove most of the remaining silica.

Results of the above tests, based on visual observation, are as follows:

- 1) In the initial anionic phosphate float, the greater percent of the silica, along with minor amounts of coarse carbonate and phosphate, constituted the machine discharge. The froth product contained the phosphate, a minor amount of fine silica, and most of the calcium carbonate.
- 2) The amine phosphate concentrate contained between 2 and 3% silica, and the majority of the calcium carbonate from the initial feed.
- 3) The amine tails consisted principally of fine silica along with minor amounts of fine shell and phosphate.

Data on tests using the Crago double float procedure for samples 3441 and 3756 are shown in Table III.

TABLE III

Sample 3441

<u>Product</u>	<u>% Wt</u>	<u>Assay %</u>			<u>Distribution %</u>			<u>CaO/P<sub>2</sub>O<sub>5</sub></u>
		<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Insol.</u>	<u>CaO</u>	<u>P<sub>2</sub>O<sub>5</sub></u>	<u>Insol.</u>	<u>CaO</u>	
Conc.	62.7	29.2	1.7	50.5	97.4	3.2	94.1	1.72
Amine Tails	4.4	5.0	79.9	10.1	1.0	10.2	1.2	
Ro. Conc.	67.1	27.5	6.8	47.7	98.4	13.4	95.3	1.74
Ro. Tails	32.4	1.1	92.1	5.1	1.6	86.6	4.7	
Float Feed	99.5	18.8	34.4	33.7	100.0	100.0	100.0	1.79
-200 M. Slimes	0.5							
Total	100.0							

Sample 3756

Conc.	61.6	29.5	2.0	50.5	94.3	3.4	92.6	1.71
Amine Tails	11.1	9.2	67.5	16.3	5.2	21.4	5.4	
Ro. Conc.	72.7	26.4	12.0	45.2	99.5	24.8	98.0	1.71
Ro. Tails	27.3	0.5	96.4	2.7	0.5	75.2	2.0	
Float Feed	100.0	19.3	35.0	33.6	100.0	100.0	100.0	1.74

FLOTATION PROCEDURES FOR REMOVING CALCIUM  
CARBONATE AND SILICEOUS GANGUE

Numerous flotation tests were carried out using various flowsheets in attempts to concentrate the phosphate from the ores containing siliceous and calcium carbonate gangue. Of the various flowsheets attempted, the following showed the most promise.

- 1) Selective deoiling with either hydrated lime, hydrated lime and Peritan  $\text{NH}_4^*$ , or ferrous sulfate.
- 2) Anionic phosphate float with depression of the siliceous and calcium carbonate gangue.
- 3) Anionic silica float followed by an anionic phosphate float and depression of the calcium carbonate.
- 4) Amine silica float followed by an amine phosphate float with a calcite depressant ( $\text{FeSO}_4$ ).
- 5) Amine silica float followed by an amine phosphate float.

Descriptions of the above flowsheets are given in the following section, along with results of one of the better tests with each flowsheet.

1) Selective Deoiling

In this process, a normal phosphate float was carried out on the flotation feed, whereby most of the calcium carbonate gangue floated with the phosphate. The rougher phosphate concentrate was conditioned with a reagent, or combination of reagents, in hopes of selectively deoiling the calcium carbonate and the remaining silica gangue. The pulp was then subjected to one or more cleaner floats in which the gangue material was to be rejected in the machine discharge. This separation of phosphate from calcium carbonate is based on the theory that the calcium

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\* Lignosulfonate manufactured by Arthur C. Trask Corporation.

carbonate does not retain its anionic reagent coating as well as does the phosphate. In order to substantiate this theory, the following tests were carried out.

In the first test, a normal anionic phosphate float was followed by repeated cleaning of the froth product without removing water from the froth product between cleaning steps. This cleaning operation was carried out until, by visual observation, the phosphate concentrate was devoid of any free calcium carbonate. In this test, eleven cleaning steps were required. Observation of the machine discharge from each cleaning step showed a decrease in the amount of calcium carbonate rejected and an increase in the amount of phosphate rejected in each successive cleaning step. The particle size of the rejected material decreased as the number of cleanings increased. The following is the analysis of the final concentrate.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	52.6	29.7	3.3	47.9	82.5	5.3	73.9	1.61

The next test was similar to the above, except that the froth product was dewatered after each float. Five cleaning steps were run. Visual results were the same as for the previous test. As shown in the following tabulated results, the CaO to P<sub>2</sub>O<sub>5</sub> ratio in the concentrate is higher than in the previous test, even though very little calcite could be seen under the microscope.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	51.4	30.0	3.1	49.0	81.0	4.8	73.5	1.63

The third test was similar to the first two, except that the froth product was washed before each cleaner float by pulping with fresh water and decanting. The froth product was cleaned three times, after which it appeared to be devoid of calcite. The concentrate had the analysis shown in the following table.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	47.5	30.2	3.1	49.5	76.5	4.4	68.5	1.64

In hopes of simplifying and improving the process, an investigation was conducted on the use of reagents for selectively deoiling the calcium carbonate. This investigation involved the use of various amounts of hydrated lime alone or in conjunction with Peritan NH<sub>4</sub> lignosulfonate. Also tests were carried out using Horsehead quebracho (bi-sulfited, cold-water extract of the quebracho tree wood), Marasperse CB (sodium lignin sulphonate), and sodium silicate in conjunction with hydrated lime. Also, selective deoiling tests were carried out using ferrous sulphate. Descriptions of those tests in which the above reagents were used are given in the following sections.

#### Use of Hydrated Lime for Selective Deoiling

Hydrated lime by itself was used in several attempts to selectively deoil the calcium carbonate. This series of tests showed that 10 pounds per ton of lime under the following conditions produced the best results. The rougher concentrate was scrubbed with lime for one minute at 40% solids and at 450 rpm. A cleaner float was then carried out on the



rougher concentrate, whereby principally quartz and shell were dropped out. The froth product was subjected to another cleaner float in which the remaining shell along with a large amount of phosphate was dropped out. This constituted the second cleaner tails. The froth product, consisting of 38.3% of the flotation feed, constituted the final concentrate. The second cleaner tails was then subjected to a scavenger float where additional collector was added to the cell. The second cleaner tails was cleaned twice, thus producing a scavenger concentrate. The analysis of the combined concentrate and scavenger concentrate is shown below.

Sample No.	Conc % Wt	Assay			Distribution			
		% <u>P<sub>2</sub>O<sub>5</sub></u>	% <u>Insol.</u>	% <u>CaO</u>	% <u>P<sub>2</sub>O<sub>5</sub></u>	% <u>Insol.</u>	% <u>CaO</u>	<u>CaO/P<sub>2</sub>O<sub>5</sub></u>
3441	54.8	29.2	4.2	47.1	84.6	7.1	76.8	1.61

Use of Hydrated Lime and Peritan NH<sub>4</sub>\*

Numerous flotation tests were carried out using the combination of hydrated lime and Peritan NH<sub>4</sub> under various conditions. These tests showed that a high-grade concentrate, with relatively good phosphate recovery and good rejection of the calcium carbonate, could be obtained by the following procedure. The rougher concentrate was scrubbed for two minutes at approximately 40% solids, at 450 rpm, with 15 pounds per ton of hydrated lime and 0.5 pound per ton of Peritan NH<sub>4</sub>. The pulp was washed three times and was then subjected to three or four cleaner floats, whereby the calcium carbonate was dropped out in the machine discharge. Before each cleaner float, the water was decanted off the froth product. This procedure was carried out on both ore samples,

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\* Lignosulfonate

and it gave relatively good results on both, as shown below.

Sample No.	Test No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
			% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	A-12	53.1	29.5	3.8	47.6	91.0	6.7	79.7	1.61
3756	A-57	59.9	29.4	4.6	47.1	92.1	7.8	87.8	1.60

Hydrated lime was also used in conjunction with Horsehead quebracho, Marasperse CB, Goulac and sodium silicate in attempts to selectively deoil the calcium carbonate. Observation of these tests and microscopic examination of the products showed that these tests were not successful.

#### Use of Ferrous Sulfate

Numerous tests were carried out using ferrous sulphate in attempts to selectively deoil the calcium carbonate. This procedure called for conditioning the phosphate rougher concentrate with ferrous sulphate (4.0 pounds per ton) for one minute at 40% solids. The conditioned pulp was then subjected to three cleaner floats to reject the calcium carbonate. The results of one of the better tests are tabulated below.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	53.6	29.3	4.3	48.9	84.9	6.8	77.3	1.67

#### 2) Anionic Phosphate Float with Depression of the Siliceous and Calcium Carbonate Gangue

Several attempts were made to depress both the siliceous and calcium carbonate gangue in one operation. The best results were obtained by conditioning with Horsehead quebracho (1.0 pound per ton), followed

by conditioning with saponified fatty acid (0.6 pound per ton) and fuel oil (0.5 pound per ton). This was followed by one cleaner float to drop out the remaining calcium carbonate. The results are tabulated below.

Sample No.	Conc % Wt	Assay			Distribution			
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	CaO/P <sub>2</sub> O <sub>5</sub>
3756	57.9	29.4	4.7	47.6	89.9	7.4	85.7	1.62

3) Anionic Silica Float Followed by an Anionic Phosphate Float and Depression of the Calcium Carbonate

A number of tests were conducted using this procedure, which involved first an anionic silica float, whereby the greater portion of the silica was rejected in the froth product. This was followed by washing of the machine discharge to eliminate reagents. The wash was followed by attempts to selectively float the phosphate with anionic reagents while depressing the calcium carbonate. This last operation usually required several cleaning steps.

Variations in the anionic silica float were minor. The float consisted of depressing the phosphate and calcium carbonate with Goulac\* at a pH of approximately 11.0 (NaOH used as pH regulator). The silica was floated with a tall oil - kerosene mixture. The machine discharge, which consisted of phosphate, calcium carbonate and coarse silica, was washed three times. Numerous reagents were then used in attempts to selectively float the phosphate and reject the calcium carbonate. The best results in this series of tests were obtained when using 1.0 pound per ton of Goulac, 0.2 pounds per ton caustic soda, and 1.2 pounds per ton tall oil-kerosene mix (ratio 2 : 1) at a pH of 10.5. The collector

\* Goulac = calcium ligninsulphonate

was stage added, and the initial float was followed by three cleaners. The results of this test are shown below.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	52.7	29.7	1.8	48.2	85.2	2.7	76.7	1.62

4) Amine Silica Float Followed by an Amine Phosphate Float with a Calcite Depressant (FeSO<sub>4</sub>)

This flowsheet called for an amine silica float at a high pH (11.0) followed by dewatering of the machine discharge. The machine discharge was then subjected to an amine phosphate float in the presence of a calcite depressant (FeSO<sub>4</sub>). In one of the better tests, the delimed flotation feed was subjected to 15 seconds conditioning with 0.7 pound per ton NaOH at 1200 rpm in the flotation cell, then 30 seconds conditioning with 0.5 pound per ton Armac T-fuel oil emulsion\* whereby a silica froth was removed. After the silica float, the machine discharge was dewatered, washed, and conditioned 15 seconds in the flotation cell with 1.0 pound per ton FeSO<sub>4</sub>. This was followed by 20 seconds conditioning with 0.3 pound per ton Armac T - fuel oil emulsion.\*\* The phosphate float product was cleaned two times. The results of this test are shown in the following table.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3441	59.6	28.2	5.8	45.4	91.8	10.3	83.9	1.61

\* One part Armac T (amine acetate) to two parts fuel oil.

\*\* One part Armac T to six parts fuel oil.

5) Amine Silica Float Followed by an Amine Phosphate Float

A number of tests were carried out using the following procedure. The flotation feed was subjected to a cationic float at a high pH (10.5-11.5). The machine discharge was decanted, scrubbed at a high pH (10.5) with Marasperse CB, and then washed several times. The pulp was then subjected to a cationic phosphate float followed by a cleaner float to drop out the fine calcium carbonate. In one of the better tests using this procedure, the flotation feed was subjected to an amine silica float at pH 10.5. The machine discharge was decanted and conditioned at 450 rpm with 0.3 pound per ton of caustic soda (pH = 10.3) and Marasperse CB (1.0 pound per ton) for five minutes at 50% solids, after which it was deslimed three times. The pulp was then conditioned in the cell with 0.3 pound per ton of an amine-fuel oil mixture\* for 15 seconds at 40% solids and 1200 rpm, after which a phosphate concentrate was floated. The concentrate was cleaned one time to eliminate the fine shell. Results of this test are shown below.

Sample No.	Conc % Wt	Assay			Distribution			CaO/P <sub>2</sub> O <sub>5</sub>
		% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	% P <sub>2</sub> O <sub>5</sub>	% Insol.	% CaO	
3756	55.7	29.7	4.2	48.5	86.9	6.6	82.1	1.63

6) Additional Studies

Additional studies were carried out in attempts to reject the siliceous and calcium carbonate gangue. These flowsheets are described below along with a brief statement concerning the results obtained.

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\* One part Armac T to two parts of fuel oil.

(a) Crago Flowsheet Followed by a Secondary Anionic Phosphate Float and Rejection of the Calcium Carbonate - Only a few tests were carried out using this complex flowsheet, which produced a high-grade phosphate concentrate with only moderate phosphate recovery.

(b) Anionic Silica Float Followed by an Amine Silica Float and an Amine Phosphate Float - This complex flowsheet gave only mediocre results.

(c) Two-Stage Amine Silica Float Followed by an Amine Phosphate Float - In order to produce a high-grade product by this procedure, it was necessary to sacrifice phosphate recovery.

(d) An Amine Silica Float Followed by an Anionic Phosphate Float in the Presence of a Calcite Depressant ( $\text{FeSO}_4$ ) - The amine silica float was satisfactory but the anionic phosphate float was not.

#### DISCUSSION

Preliminary test results revealed that simple cleaning of the phosphate rougher concentrate (11 times) results in selective rejection of the calcium carbonate and produces a high-grade phosphate concentrate with fair phosphate recovery and a good  $\text{CaO}/\text{P}_2\text{O}_5$  ratio. This indicated that the calcium carbonate is slightly less susceptible to flotation by the anionic phosphate float than is the phosphate.

Attempts were made to take advantage of the above results by conditioning with hydrated lime by itself and in conjunction with other chemicals, particularly Peritan  $\text{NH}_4$ . Tests using hydrated lime by itself showed the following:

1. Amount of hydrated lime used is critical. Too much (15 to 20 pounds per ton) depresses everything. Too little (5 to 2.5 pounds per ton) causes erratic results and increases complexity of flowsheet.

2. A conditioner speed of about 450 rpm gives best selectivity.

Tests using hydrated lime in conjunction with Peritan  $\text{NH}_4$  showed the following:

1. Washing the pulp after selective deoiling reduces complexity of float and produces better results.

2. As conditioning time is increased from 2 to 8 minutes, phosphate recovery decreases.

3. The quantity of lime does not appear to be as critical when used with Peritan  $\text{NH}_4$  as when used by itself.

4. With 15 pounds per ton of hydrated lime, the quantity of Peritan  $\text{NH}_4$  needed does not appear to be critical.

Tests using ferrous sulphate for selective deoiling of the calcium carbonate showed the following:

1. Ferrous sulfate does not reject silica.

2. Decanting prior to deoiling improves  $\text{P}_2\text{O}_5$  recovery.

3. Conditioning time does not seem to be critical.

4. Better results were obtained with 4.0 pounds per ton of  $\text{FeSO}_4$  than with 6.0 pounds per ton.

5. Optimum pulp density for selective deoiling seemed to be about 30 to 40% solids.

6. When using  $\text{FeSO}_4$ , it was not possible to lower the  $\text{CaO}/\text{P}_2\text{O}_5$  ratio below 1.65.

Attempts were made to float the phosphate with anionic reagents while depressing the siliceous and calcium carbonate gangue in the same operation. These tests showed the following:

1. When conditioning with Calgon prior to conditioning with saponified fatty acid and fuel oil, no float was obtained.
2. When conditioning with Goulac prior to conditioning with caustic soda and a tall oil-kerosene mix, considerable shell and some coarse phosphate and quartz were rejected.
3. Conditioning with sodium silicate by itself or in combination with sodium carbonate, Peritan  $\text{NH}_4$  or Goulac, prior to conditioning with anionic reagents, proved unsuccessful.
4. The best results were obtained by conditioning with Horsehead quebracho. Approximately 1.0 pound per ton seemed to be the optimum amount.

In the procedure involving anionic flotation of silica, followed by anionic phosphate flotation and simultaneous depression of calcite, the following observations were made:

1. In order to float coarse quartz with anionic reagents, it is necessary to float some fine phosphate.
2. Use of the following reagents in the anionic phosphate float resulted in only partial rejection of calcite: sodium silicate and caustic, quebracho and sodium carbonate, and Marasperse CB with caustic.

Attempts were made to float the silica with amine reagents followed by amine flotation of the phosphate with a calcite depressant ( $\text{FeSO}_4$ ). These tests showed the following:

1. The  $\text{FeSO}_4$  appeared to activate the phosphate and quartz, and to depress the shell.



2. If the amine phosphate float is not carried out at a low pH (6.5<sup>+</sup>-), a size separation occurs.

3. A minor amount of fine phosphate which floats in the amine silica float can be dropped out in a scavenger float.

4. Results indicate that the CaO/P<sub>2</sub>O<sub>5</sub> ratio can be lowered from about 1.64 to 1.61 by washing for two minutes prior to the amine phosphate float.

Attempts were made to float the silica present with amine reagents followed by a rejection of the shell by amine flotation of the phosphate. These tests showed the following:

1. The amine phosphate float, carried out after scrubbing with Marasperse CB alone, did not reject sufficient shell or quartz.

2. The amine phosphate float, carried out after scrubbing with caustic soda, rejected most of the shell but also rejected quite a bit of phosphate.

3. The amine phosphate float, carried out after scrubbing with caustic soda and Marasperse CB, rejected a relatively clean shell tails, but the concentrate still contained some shell.

4. The lowest CaO/P<sub>2</sub>O<sub>5</sub> ratio obtained in this test series was 1.63.

5. The amine phosphate float carried out at a pH of 9.0 to 9.7 rejected quite a bit of phosphate along with the coarse quartz.

#### CONCLUSIONS

The Crago process, when applied to the high-calcite matrix, produced high-grade concentrate (29.5% P<sub>2</sub>O<sub>5</sub>) with good phosphate recovery (97.4%), but the CaO/P<sub>2</sub>O<sub>5</sub> ratio was abnormally high (1.71).

A preliminary test, based on selective deoiling of the calcium carbonate, showed that a high-grade concentrate (29.7%  $P_2O_5$ ) and fair phosphate recovery (82.5%), with good rejection of the calcium carbonate ( $CaO/P_2O_5$  ratio = 1.61), could be obtained by multiple cleaning of the phosphate rougher concentrate. In an attempt to simplify the above process of selective deoiling, the rougher concentrate was subjected to a scrub with hydrated lime followed by two cleaner floats and a scavenger float. In this test, the  $P_2O_5$  recovery was slightly increased (84.6) and the calcium carbonate rejection remained high ( $CaO/P_2O_5$  ratio = 1.61). Further testing revealed that with the addition of Peritan  $NH_4$  to the scrub, followed by washing of the scrubbed rougher concentrate and three cleaner floats, the  $P_2O_5$  grade remained high (29.5),  $P_2O_5$  recovery increased (92.1) and calcium carbonate rejection remained high ( $CaO/P_2O_5$  ratio = 1.60).

When ferrous sulphate was used for selectively deoiling the calcium carbonate, a high-grade concentrate was obtained (29.3%  $P_2O_5$ ), with only fair phosphate recovery (84.9%), and the  $CaO/P_2O_5$  ratio was not lowered sufficiently.

Attempts were made to reject the calcium carbonate along with the silica in the rougher phosphate float. By addition of Horsehead quebracho in the initial conditioning step, a high-grade concentrate could be obtained (29.4) with a phosphate recovery of 89.9 and a  $CaO/P_2O_5$  ratio of 1.62.

An anionic silica float, followed by an anionic phosphate float with Goulac used as a depressant for the calcium carbonate, produced a high-grade concentrate (29.7), with only fair  $P_2O_5$  recovery (85.2), and a  $CaO/P_2O_5$  ratio of 1.62.

An amine silica float, followed by an amine phosphate float with  $\text{FeSO}_4$  used as a depressant for calcium carbonate, produced only a fair grade product (28.2), with relatively good phosphate recovery (91.8) and a low  $\text{CaO}/\text{P}_2\text{O}_5$  ratio of 1.61. When this flowsheet is used without the  $\text{FeSO}_4$  in the amine phosphate float, a high-grade concentrate is obtained (29.7) with fair  $\text{P}_2\text{O}_5$  recovery (86.9), but with a  $\text{CaO}/\text{P}_2\text{O}_5$  ratio of 1.63.

#### RECOMMENDATIONS

It is recommended that any future work on high-calcite phosphate matrix be carried out on the 15-foot section of low-grade material (6.0%  $\text{P}_2\text{O}_5$ ) overlying the high-grade ore body. This section contains approximately 12% of the  $\text{P}_2\text{O}_5$  values of the total phosphate ore body. If a practical method were developed for processing this material, it could be mined and processed with the main zone, thereby increasing the recoverable reserves by about 12%.