



# **FLOTATION PROCESS FOR CARBONATE REMOVAL**

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## ABSTRACT

It is necessary to grind ROM phosphate rock to about 1.5% to 8% +35 mesh for reacting in the dihydrate process. This same grinding also enhances the liberation of calcium and magnesium carbonates from the phosphate. The Florida Institute of Phosphate Research sponsored Jacobs Engineering to conduct a test program to evaluate the preliminary feasibility of treating ground reactor feed by froth flotation to remove liberated carbonate gangue minerals. Three flotation processes were examined and estimates of capital and operating costs for the most effective process were prepared. The flotation process consumes a minor quantity of pond water for pH control and reduces both sulfuric acid consumption and the phosphogypsum produced per ton of recovered  $P_2O_5$ .

## **ACKNOWLEDGMENT**

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The phosphate rock samples tested during the study were donated by the following companies: IMC-Agrico, Cargill Fertilizer, Mobil Mining and Minerals, and CF Industries, Inc.

## **SUMMARY**

### **Background**

Separation of calcite and/or dolomite from phosphate rock by flotation is becoming the practice in several phosphate mining areas where higher carbonate contamination is encountered. In almost all cases, the phosphate rock must be ground to liberate the calcite and/or dolomite so that it can be separated from the phosphate rock. Florida mines typically avoid the need to remove carbonate gangue from the phosphate rock by selectively mining their reserves. This approach avoids problems associated with grinding and handling the ground rock at the mine and minimizes fertilizer production costs; however, ore reserves are sacrificial.

The investigation of carbonate flotation of the phosphate rock feed to the phosphoric acid plant as a means of reducing the calcium and magnesium content of the rock used to produce phosphoric acid is of interest because the rock to be treated is already ground for use in phosphoric acid manufacture. Reduction of calcium would reduce the quantity of phosphogypsum produced per ton of phosphoric acid, and the reduction of magnesium associated with the dolomitic limestone would improve acid quality.

## Objectives

The goal of this study was to perform chemical analyses, laboratory and pilot plant flotation tests on low-grade phosphate rock leading to the development of technology that:

- Reduces the production of phosphogypsum per ton of phosphoric acid. (Use froth flotation to remove liberated calcium carbonates from phosphate rock after grinding, but before the reactor. Reducing the  $\text{CaO}:\text{P}_2\text{O}_5$  ratio will reduce phosphogypsum production.)
- Consume and/or neutralize pond water. (The use of pond water as a reagent for flotation will neutralize a small quantity of pond water.)

This study examined three froth flotation processes that remove calcium and magnesium carbonates from ground phosphate rock. The novel concept of the study is that the ground feed to the phosphoric acid reactor is treated by froth flotation.

## Results

Three flotation processes for removing calcium and magnesium carbonates from ground phosphate rock (reactor feed) were tested and the IMC anionic process was found to be superior to the other processes based on laboratory scale flotation tests.

Laboratory and pilot scale flotation tests with the IMC Anionic process demonstrated that liberated calcium and magnesium carbonate minerals can be removed from reactor feed at the expense of some  $\text{P}_2\text{O}_5$  losses

- The degree of calcium removal is dependent upon the quantity of nonapatitic calcium minerals (calcite and dolomite) present in the phosphate rock. Reducing the  $\text{CaO}:\text{P}_2\text{O}_5$  ratio of the reactor feed to about 1.5 with the attendant reduction in sulfur consumption and phosphogypsum production appears possible.
- The flotation process uses pond water as a reagent. About 216 pounds of pond water are consumed (112 in grinding and 104 in conditioning and flotation) per ton of phosphate rock.

- The flotation process also reduces the minor element ratio  $(I\&A + MgO)/P_2O_5$ . Consequently, phosphate rock unsuitable for DAP production can be treated by froth flotation and made acceptable for use in DAP production.
- The application of carbonate flotation at the chemical plant utilizes existing grinding capacity and avoids the problems associated with transporting finely ground rock.
- Carbonate flotation allows the recovery of more ore reserves, while maintaining the capability of producing high analyses fertilizers.

## SCOPE AND METHODOLOGY

An initial component of each of the two programs in this study was the acquisition and characterization of several samples of phosphate rock. With the cooperation of local phosphate producers, the following samples were obtained:

### Test Samples<sup>(1)</sup>

<u>Sample Identification</u>	<u>Quantity</u>	<u>Sample Source</u>
Flotation concentrate 1	500 lbs	IMC-Agrico – Noralyn <sup>(2)</sup>
Flotation concentrate 2	500 lbs	IMC-Agrico - Ft. Green <sup>(2)</sup>
Flotation concentrate 3	500 lbs	IMC-Agrico - Four Corners <sup>(2)</sup>
Flotation concentrate 4	500 lbs	IMC-Agrico - Four Corners <sup>(2)</sup>
Low grade pebble 1	1,000 lbs	Mobil - Big Four
Low grade pebble 2	1,000 lbs	IMC-Agrico - Ft. Green
Low grade pebble 3	1,000 lbs	IMC-Agrico - Four Corners
Low grade pebble 4	500 lbs	Cargill – Hookers Prairie
Low grade pebble 5	500 lbs	IMC-Agrico – Fort Green
Reject pebble 6	6,000 lbs	Cargill – South Fort Meade
Ground reactor feed 1	40 lbs	Cargill - Bartow
Ground reactor feed 2	40 lbs	IMC-Agrico - New Wales
Ground reactor feed 3	40 lbs	IMC-Agrico - South Pierce
Pond water 1	45 gal	Cargill - Bartow
Pond water 2	45 gal	IMC-Agrico - New Wales
Pond water 3	45 gal	IMC-Agrico - South Pierce
Pond water 4	45 gal	IMC-Agrico - South Pierce
Pond water 5	45 gal	CF Industries - Zephyrhills

(1) Sample numbers 1, 2, and 3 were collected in year 1, while sample numbers 4, 5, and 6 were collected in year 2.

(2) Quality of pebble and concentrate obtained for this study is not necessarily the quality of the run-of-mine products from the listed sample sources.

The samples of reactor feed and pond water were chemically analyzed to obtain background information. The samples of pebble and concentrate were selected to obtain phosphate rock with higher than average content of calcium and magnesium carbonates. These latter samples were ground in the laboratory and analyzed to

determine the chemical and mineral content by size fraction. The analytical methods utilized are listed below:

- pH: hydrogen ion electrode
- Redox: specific ion electrode
- P<sub>2</sub>O<sub>5</sub>: AFPC photometric method (page 11-10)
- Acid Insoluble: AFPC gravimetric method (page 9-8)
- CaO: AFPC EDTA volumetric method (page 9-29)
- MgO: AFPC atomic adsorption method (page 11-28)
- F: AFPC specific ion; electrode method (page 11-35)
- SO<sub>4</sub>: AFPC gravimetric method (page 11-39)
- Fe<sub>2</sub>O<sub>3</sub>: AFPC atomic adsorption method (page 9-12,13)
- Al<sub>2</sub>O<sub>3</sub>: AFPC atomic adsorption method (page 9-16,17)

Froth flotation is a process for separating fine particles of solids from each other based on the hydrophobicity of the particles surfaces. The particles are mixed with water in a flotation cell into which air is bubbled. The hydrophobic particles are collected by the rising air bubbles and then removed as a froth from the surface of the cell. The hydrophylic particles remain with the water mixture and are withdrawn from the cell underflow. The hydrophobic and hydrophylic properties of the fine particles are enhanced by chemical reagents. The three processes selected for testing in year 1 are described below:

### **BOM Process**

The Bureau of Mines Research Center at Albany, Oregon developed a flotation process for removing carbonate gangue from western phosphate rock. Rule (1977, 1982) described laboratory and pilot scale tests and test results.

In this process phosphate rock ranging from 212 to 20 microns is conditioned with a tall oil collector in the presence of a depressant (fluosilicic acid). During flotation the carbonate gangue minerals are removed with the froth while phosphate and silica are recovered as the cell underflow product. Bureau of Mines researchers reported that pond water could be successfully substituted for the fluosilicic acid, and that the presence of minus 10 micron particles had a detrimental effect on flotation performance.

### **BRGM Process**

It is Jacobs understanding that the BRGM process was developed in cooperation with the Gerlund Company. French patents 79.30868 and 80.19366 were issued to BRGM, HENCHIRI et al, in 1979 and 1980. Additional information was published by HENCHIRI (1981, 1993).

In this process the phosphate rock is conditioned with a reagent suite comprising a phosphoric ester collector and a depressant (sulfuric acid and/or fluosilicic acid). During flotation the carbonate gangue minerals are removed as a froth product while quartz and phosphate are recovered as the cell underflow product. For Tunisian phosphate, the process has been more effective in removing carbonate particles in the 74 to 20 micron size range.

### **IMC Anionic Process**

Snow (1982) invented a flotation process based on the use of a sulfonated oleic acid collector for carbonate minerals and a sodium tripolyphosphate (STPP) reagent for depressing the phosphate. In this process the phosphate rock slurry is adjusted to a pH of 5.5 to 6.0 and then conditioned with STPP and the carbonate collector. During flotation the carbonate minerals are removed with the froth and phosphate plus any quartz are recovered as the cell underflow product.

Following the characterization of samples in year 1, laboratory evaluation testing of the three froth flotation processes was performed. The three flotation processes utilize different chemical reagents; however, each removed carbonate minerals in the froth product and operated on a slurry having an acidic pH, somewhat similar to a flotation process described by Gruber (1986). After the laboratory evaluation tests were completed and analyzed, the IMC Anionic process was selected for laboratory optimization and confirmation testing. Statistically designed flotation tests were performed to examine variables in reagentization and flotation. Subsequently, locked cycle tests were performed to examine effects of recycling the water recovered from the tailings and concentrate from flotation.





Conceptual flowsheets and materials balances were prepared for flotation modules that could be added to a 1,000 ton  $P_2O_5$  per day phosphoric acid plant. Estimates of the constructed cost and direct operating cost of the flotation modules were prepared.

## STUDY RESULTS

### Sample Characterization

Analytical results from the samples of reactor feed and pond water collected at three phosphoric acid plants are shown on Tables 1 and 2. The  $\text{CaO}:\text{P}_2\text{O}_5$  ratios and the particle size distributions of the reactor feeds are of specific interest in this study. The  $\text{CaO}:\text{P}_2\text{O}_5$  ratios ranged from 1.462 to 1.513, indicating that nonapatitic calcium is not abundant in present day reactor feeds. Table 1 also shows the fine extremes of particle size distribution: -400 mesh (-38 microns). This fraction is usually problematic for flotation of phosphate rock due to increased reagent consumption and loss of selectivity. Analyses of pond water samples confirmed that pond water is very acidic and contains dissolved  $\text{P}_2\text{O}_5$  and fluorine (F). The pond water analyses also indicate that pond water may be an acceptable and economic substitute for reagents used in the three flotation processes to be studied.

Analytical results from the samples of flotation concentrate and washer pebble collected at phosphate rock beneficiation plants are presented on Tables 3 and 4. These samples were selected to obtain phosphate rock with higher than average contents of calcium and magnesium carbonates. As expected, the flotation concentrates contained less impurities than the washer pebble. In fact, it was necessary to obtain the lowest quality concentrate sample from a pilot plant because the concentrate from commercial plants did not contain the higher amounts of calcium and magnesium carbonate. The  $\text{CaO}:\text{P}_2\text{O}_5$  content of the pebble samples ranged from 1.471 to 1.648, indicating that washer pebble may contain nonapatitic calcium. Laboratory grinding in a batch rod mill resulted in 100 percent weight passing 35 mesh and more -400 mesh material than the plant ground samples of reactor feed for the year 1 sample. For year 2, the grind was coarsened.

**Table 1: Analyses of Ground Rock (phosphoric acid reactor feed)**

	dry basis					ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Plant 1	30.47	9.07	44.56	0.40	2.34	1.462	0.090
Plant 2	29.30	10.72	44.33	0.67	2.09	1.513	0.094
Plant 3	28.95	11.66	42.90	0.58	2.10	1.482	0.093
<b>average</b>	<b>29.57</b>	<b>10.48</b>	<b>43.93</b>	<b>0.55</b>	<b>2.18</b>	<b>1.486</b>	<b>0.092</b>
std. dev.	0.796	1.311	0.899	0.137	0.142	0.0255	0.0022

	-400 mesh distributions					-400 mesh ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Plant 1	25.8	16.7	25.8	28.1	28.8	1.462	0.100
Plant 2	20.7	11.4	21.3	37.9	25.6	1.558	0.130
Plant 3	30.9	14.5	30.8	48.8	35.2	1.478	0.114
<b>average</b>	<b>25.8</b>	<b>14.2</b>	<b>26.0</b>	<b>38.3</b>	<b>29.9</b>	<b>1.499</b>	<b>0.115</b>
std. dev.	5.10	2.66	4.75	10.35	4.89	0.0514	0.0150

**Table 2: Analyses of Plant Pond Water Samples**

	concentration (mg/liter)					pH Redox	
	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	F	SO <sub>4</sub>	pH	Redox
Plant 1	11,600	1,900	300	5,300	4,600	1.40	244
Plant 2	19,500	2,200	700	7,200	7,200	1.30	230
Plant 3	15,000	2,800	500	6,200	6,200	1.10	244
Plant 4	16,800	3,400	600	3,400	7,900	1.35	218
Plant 5	14,800	2,000	400	2,900	9,000	1.55	230
<b>average</b>	<b>15,540</b>	<b>2,460</b>	<b>500</b>	<b>5,000</b>	<b>6,980</b>	<b>1.34</b>	<b>233</b>
std. dev.	2,900	631	158	1,826	1,677	0.16	11

**Table 3: Analyses of Ground Flotation Concentrates**

	dry basis					ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Sample 1	30.66	5.13	46.08	0.90	2.70	1.503	0.117
Sample 2	32.25	4.21	46.97	0.43	2.36	1.456	0.087
Sample 3	31.14	5.89	46.24	0.61	2.17	1.485	0.089
Sample 4	30.97	6.45	45.79	0.45	2.75	1.479	0.103
<b>average</b>	<b>31.26</b>	<b>5.42</b>	<b>46.27</b>	<b>0.60</b>	<b>2.50</b>	<b>1.481</b>	<b>0.099</b>
std. dev.	0.692	0.971	0.502	0.217	0.277	0.0192	0.0142

	-400 mesh distributions (laboratory grinding)					-400 mesh ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Sample 1	30.0	19.5	30.9	58.3	38.4	1.547	0.170
Sample 2	31.7	19.8	31.5	35.4	37.6	1.447	0.102
Sample 3	29.4	18.2	29.7	47.6	38.6	1.499	0.123
Sample 4	na	na	na	na	na	na	na
<b>average</b>	<b>30.4</b>	<b>19.2</b>	<b>30.7</b>	<b>47.1</b>	<b>38.2</b>	<b>1.498</b>	<b>0.132</b>
std. dev.	1.19	0.85	0.92	11.46	0.53	0.0500	0.0348

**Table 4: Analyses of Low Grade Pebble**

	dry basis					ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Sample 1	29.84	11.24	43.88	0.59	1.89	1.471	0.083
Sample 2	28.60	8.93	44.71	1.11	2.41	1.563	0.123
Sample 3	25.56	12.17	42.12	2.28	2.18	1.648	0.174
Sample 4	22.85	27.55	35.81	0.62	1.94	1.567	0.112
Sample 5	23.71	19.61	38.32	1.47	1.71	1.616	0.134
Sample 6	26.71	12.98	42.25	1.30	2.25	1.582	0.133
<b>average</b>	<b>26.21</b>	<b>15.41</b>	<b>41.18</b>	<b>1.23</b>	<b>2.06</b>	<b>1.574</b>	<b>0.127</b>
std. dev.	2.724	6.940	3.429	0.626	0.260	0.0603	0.0300

	-400 mesh distributions (laboratory grinding)					-400 mesh ratios	
	P <sub>2</sub> O <sub>5</sub>	Insol	CaO	MgO	I&A	CaO:P <sub>2</sub> O <sub>5</sub>	MER
Sample 1	31.5	15.0	31.7	62.9	44.1	1.480	0.128
Sample 2	35.2	20.4	37.0	66.7	44.0	1.644	0.179
Sample 3	34.5	19.7	37.4	62.0	48.9	1.787	0.282
Sample 4	8.5	2.3	8.6	18.6	16.8	1.595	0.194
Sample 5	14.5	4.3	15.3	33.8	26.0	1.711	0.316
Sample 6	na	na	na	na	na	na	na
<b>average</b>	<b>24.8</b>	<b>12.3</b>	<b>26.0</b>	<b>48.8</b>	<b>36.0</b>	<b>1.643</b>	<b>0.220</b>
std. dev.	12.44	8.54	13.24	21.39	13.83	0.1164	0.0773

Mineralogical analyses performed by the Florida Institute of Phosphate Research determined the major mineral components of the phosphate rock samples to be francolite and quartz with varying amounts of dolomite and minor amounts of calcite. After grinding, the majority of the dolomite and calcite existed as liberated -400 mesh particles.

### **Flotation Process Evaluation**

The BOM, BRGM, and IMC Anionic processes were developed using phosphate from the western USA, Tunisia, and south Florida, respectively. The test data showed that the IMC Anionic process was superior to either the BOM or BRGM processes for the phosphate rocks tested in this study.

All of the liberated calcium and magnesium carbonates are concentrated in the -400 mesh fraction of the ground phosphate rock, unfortunately, all three processes evaluated were ineffective at treating only -400 mesh material. The +400 mesh component of the ground phosphate rock does not contain sufficient liberated carbonate minerals to warrant being processed separately, therefore, all of the ground rock must be treated to remove carbonate minerals by flotation.

### **Flotation Process Optimization**

The optimization test series performed on a blend of pebble sample 3 and flotation concentrate sample 1 resulted in improvements in flotation performance and a reduction in reagent consumption (cost). A comparison of the chemical analyses of the blend tested and concentrate produced by the IMC anionic process before and after optimization is presented on Table 5. The improvements resulted from:

- increasing the pulp density to 65% solids for conditioning with reagents
- increasing the collector conditioning time to 3 minutes
- substituting pond water for H<sub>2</sub>SO<sub>4</sub>, and using pond water to control the pH at 5.0 to 5.5 for grinding, conditioning, and flotation
- optimizing operating parameters for the laboratory flotation cell.

**Table 5: Summary of Optimization Test Results**  
(year 1 program)

	<b>Laboratory Flotation</b>		
	<b>ground</b>	<b>concentrate</b>	
	<b>flotation feed</b>	<b>before optimization</b>	<b>after optimization</b>
<b><u>rock quality</u></b>			
% P <sub>2</sub> O <sub>5</sub>	27.66	28.44	28.95
% CaO	43.88	44.48	43.46
% MgO	1.29	0.74	0.62
CaO:P <sub>2</sub> O <sub>5</sub>	1.586	1.564	1.501
<b><u>reagent consumption (lbs/ton feed)</u></b>			
collector (Westvaco CCS-502)		0.80	0.75
depressant (STPP)		1.13	0.75
pH modifier			
H <sub>2</sub> SO <sub>4</sub> (flotation only)		4.60	0.00
pond water (grinding & flotation)		0.00	161
<b>% P<sub>2</sub>O<sub>5</sub> recovery</b>	<b>100</b>	<b>91</b>	<b>93</b>



From the characterization study it was observed that most of the calcium and magnesium carbonates liberated by grinding were produced as -400 mesh particles. It was also noted that the plant ground rock contained more coarse particles than the laboratory ground rock. These observations indicate that plant ground rock containing free carbonates would respond to the flotation process as well as or better than the same rock ground in the laboratory. A block flow diagram for the conceptual flowsheet is presented on Figure 1.

### **Flotation Cell Comparison**

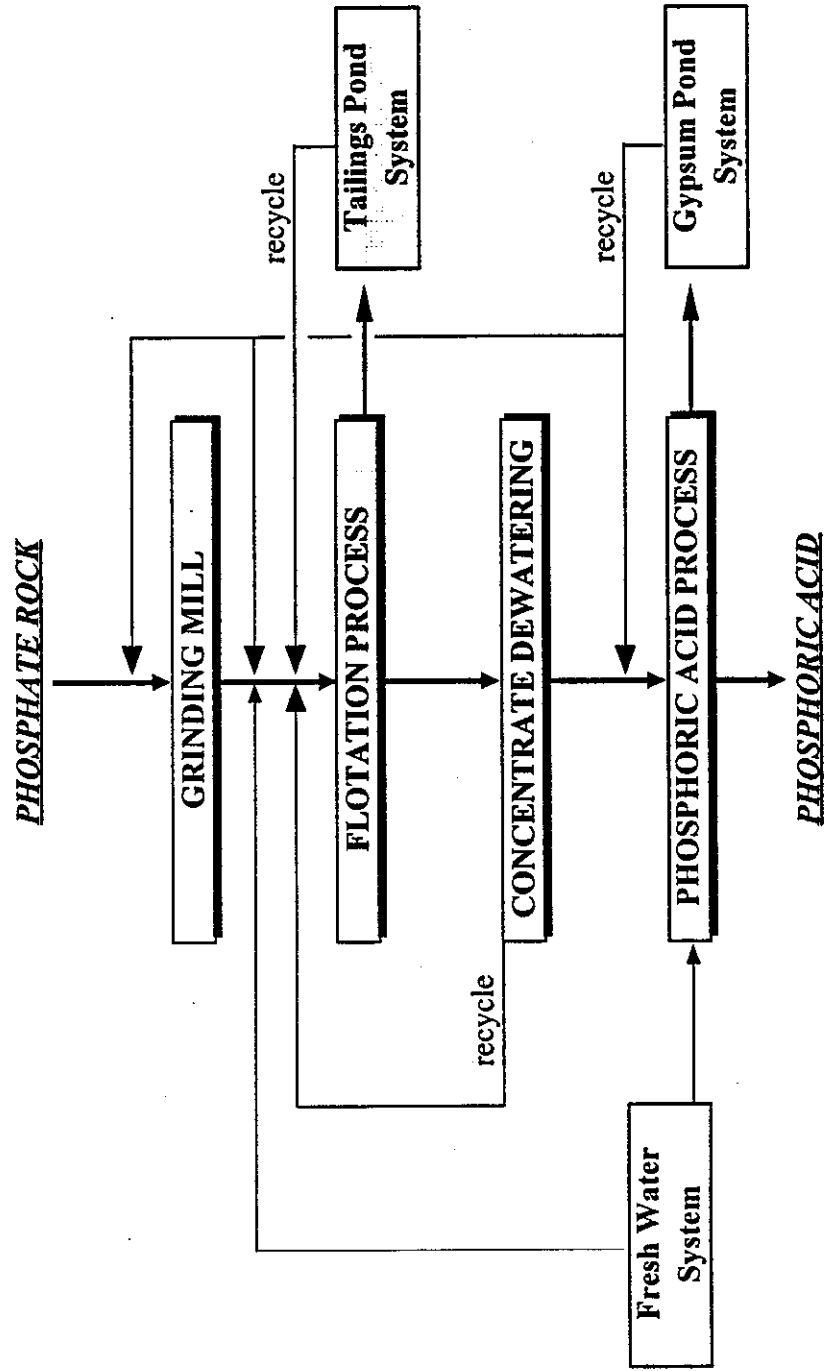
Comparative tests were performed to evaluate results obtained from a Denver laboratory cell and a 3-inch diameter column cell. The flotation tests for each cell were conducted on ground pebble and on ground pebble that had previously been scrubbed and deslimed at 200 mesh (pretreated). The data and analysis of variance for  $P_2O_5$  % recovery and concentrate of % MgO are given on Tables 6 and 7 respectively. No statistically significant differences were found with regard to cell type or to pebble pretreatment.

The higher MgO content of concentrates obtained from the column cell, although not determined as statistically significant from the limited number of laboratory tests, was confirmed in subsequent pilot plant testing.

### **Locked Cycle Flotation**

Locked cycle tests in years 1 and 2 confirmed that extensive recycle of water recovered from the flotation concentrate and tailings would be tolerated. With locked cycle testing, the water recovered from the concentrate and tailings produced in test "N" is used as make-up water for test "N+1". In this way laboratory tests can stimulate the use of recycle water.

Figure 1: Conceptual Process Block Flow Diagram



New

**Table 6: Flotation Recovery of P<sub>2</sub>O<sub>5</sub> to Concentrate**

Without Pretreatment		With Pretreatment	
Mechanical Cell	Column Cell	Mechanical Cell	Column Cell
90.4	89.8	91.3	91.2
92.8	92.2	92.8	93.9
<b>91.6</b>	<b>91.0</b>	<b>92.1</b>	<b>92.6</b>

<b>ANOVA</b>	<b>df</b>	<b>SSQ</b>	<b>MSSQ</b>	<b>F<sub>calc</sub></b>	<b>Significant</b>
<b>Between Treatments</b>	1	2.000	2.000	0.8981	no
<b>Between Cell Types</b>	1	0.005	0.005	0.0022	no
<b>Error</b>	5	11.135	2.227		
<b>Totals</b>	7	13.140			

**Table 7: % MgO Contained in Concentrate**

Without Pretreatment		With Pretreatment	
Mechanical Cell	Column Cell	Mechanical Cell	Column Cell
0.70	0.72	0.73	0.73
0.76	0.80	0.74	0.82
<b>0.73</b>	<b>0.76</b>	<b>0.74</b>	<b>0.78</b>

<b>ANOVA</b>	<b>df</b>	<b>SSQ</b>	<b>MSSQ</b>	<b>F<sub>calc</sub></b>	<b>Significant</b>
<b>Between Treatments</b>	1	0.0002	0.0002	0.1087	no
<b>Between Cell Types</b>	1	0.0024	0.0024	1.3043	no
<b>Error</b>	5	0.0092	0.0018		
<b>Totals</b>	7	0.0118			

Four series of 14 recycle tests each were performed in year 2. Two series were performed using South Pierce pond water for pH control. Two series were also performed using Zephyrhills pond water. The tests were statistically designed to also compare the flotation response of ground pebble to the flotation response of ground pretreated pebble.

The  $P_2O_5$  recovery data from the 56 tests are summarized on Table 8. Pretreatment increased the  $P_2O_5$  flotation recovery by an average of 1.27% absolute. The use of Zephyrhills pond water increased  $P_2O_5$  recovery by 0.28% over the use of South Pierce pond water. The last seven tests in the cycle averaged 0.61%  $P_2O_5$  recovery lower than the first seven tests. These recovery impacts, although not large, were statistically significant at  $\alpha = 0.05$ .

The MgO recovery data from the 56 tests are summarized on Table 9. Pretreatment increased the MgO flotation recovery by an average of 4.69%. The use of Zephyrhills pond water reduced the MgO recovery by an average of 4.25% relative to South Pierce pond water. The MgO recovery for the last seven tests. These impacts were also statistically significant at  $\alpha = 0.05$ .

### Pretreatment

The pretreatment mentioned above comprised scrubbing the 50% solids pebble slurry at pH 3.5 for five minutes, then desliming at 200 mesh to remove clays and fine carbonate material. The deslimed pebble was then stage ground to pass 28 mesh. The acidic scrubbing caused about 2% of the solids weight to dissolve and the desliming removed about 3% of the solids weight. When pretreatment losses plus flotation losses are considered, less materials are recovered to the concentrate than for flotation without pretreatment. As shown on Table 10, pretreatment penalizes overall  $P_2O_5$  recovery about 2%; however, the MgO and CaO contents of the concentrate are reduced (improved). For the 28 tests with pretreatment, the concentrate MgO averaged 0.78 vs 0.83 for the 28 tests without pretreatment.

**Table 8: Flotation Recovery of P<sub>2</sub>O<sub>5</sub> from Locked Cycle Tests**  
(four series of 14 tests)

Without Pretreatment			With Pretreatment		
South Pierce PW		Zephyrhills PW	South Pierce PW		Zephyrhills PW
first 7	last 7	first 7	last 7	first 7	last 7
92.06	91.54	93.44	92.54	94.25	93.11
		93.44	92.54	93.73	93.60

ANOVA		df	SSQ	MSSQ	F <sub>calc</sub>	Significant	impact
Between Treatments		1	22.70	22.70	145.1	yes	1.27
Between Pond Waters		2	12.68	6.34	40.5	yes	0.28
Between First 7 & Last 7		4	5.60	1.40	8.9	yes	-0.61
Error		48	7.51	0.16			
Totals		55					

**Table 9: Flotation Recovery of MgO<sub>5</sub> from Locked Cycle Tests**  
(four series of 14 tests)

Flotation Recovery of MgO			
Without Pretreatment		With Pretreatment	
South Pierce PW		Zephyrhills PW	
first 7	last 7	first 7	last 7
49.17	46.62	55.76	48.78
	46.99	55.73	50.38

ANOVA	df	SSQ	MSSQ	F <sub>calc</sub>	Significant	impact
Between Treatments	1	307.86	307.86	1968.6	yes	4.69
Between Pond Waters	2	304.23	152.11	972.7	yes	-4.25
Between First 7 & Last 7	4	9.41	2.35	15.0	yes	0.47
Error	48	33.79	0.70			
Totals	55					

**Table 10: Performance Comparison, With & Without Pretreatment**  
(averaged data from 28 tests each)

	Recovery of Materials			
	Weight	P <sub>2</sub> O <sub>5</sub>	MgO	CaO
<b>With Pretreatment</b>				
Pretreatment Losses	4.1	3.6	16.1	4.9
Flotation Tailings	8.3	6.1	39.7	8.1
<b>Flotation Concentrate</b>	<b>87.6</b>	<b>90.3</b>	<b>44.2</b>	<b>87.0</b>
<b>Without Pretreatment</b>				
Flotation Tailings	10.5	7.6	52.0	10.2
<b>Flotation Concentrate</b>	<b>89.5</b>	<b>92.4</b>	<b>48.0</b>	<b>89.8</b>

Pretreatment comprised scrubbing at 50 % solids for 5 minutes, using pond water to maintain a pH of 3.5.

Pretreatment losses include <200 mesh solids, and dissolved materials.

### **Pilot Plant Testing**

The pilot plant program examined five equipment arrangements and 23 test runs. The first three equipment arrangements were mechanically unreliable as a consequence of material/handling problems related to the combination of coarse particles and low flow rates. The fourth equipment arrangement was mechanically reliable, but the column flotation performance was not satisfactory at the test conditions. The results of the proof test conducted with the fifth equipment arrangement are shown on Figure 2.

The overall  $P_2O_5$ % recovery for the confirmation test was 86.6, with desliming and flotation recoveries of  $P_2O_5$  at 91.1% and 95.1% respectively. The MgO content of the reject pebble was reduced from 1.38 to 0.74%.

Pilot plant testing confirmed the flotation process, and also revealed that a defoamer (diesel oil) was required to control the excessive frothing caused by the collector.

### **Particle Size Influence**

Laboratory flotation test data from year 1 and pilot plant flotation test data from year 2 demonstrated that the carbonate flotation performance is dependent upon particle size. The data on Table 11 show that the recovery of material to the froth product increases as the particle size decreases. Fines float more readily than coarse particles.

### **Conceptual Flowsheets**

Two schemes for treating waste pebble at a 1000 tpd phosphoric acid plant were examined. Flowsheets and materials balances were prepared for each scheme, and process descriptions follow:

- Case 1: The waste pebble is blended with the regular rock. The blend is fed to existing ball mills, and ground to pass 28 mesh. The solids content of the grinding slurry is controlled at 67% by adding pond water and recycle water according to a ratio of 1 to 6. The ground slurry is pumped to reagent conditioners. Sodium tripolyphosphate (STPP) solution, collector and more pond



Figure 2: Process Configuration 5, Test 23 Mass Balance

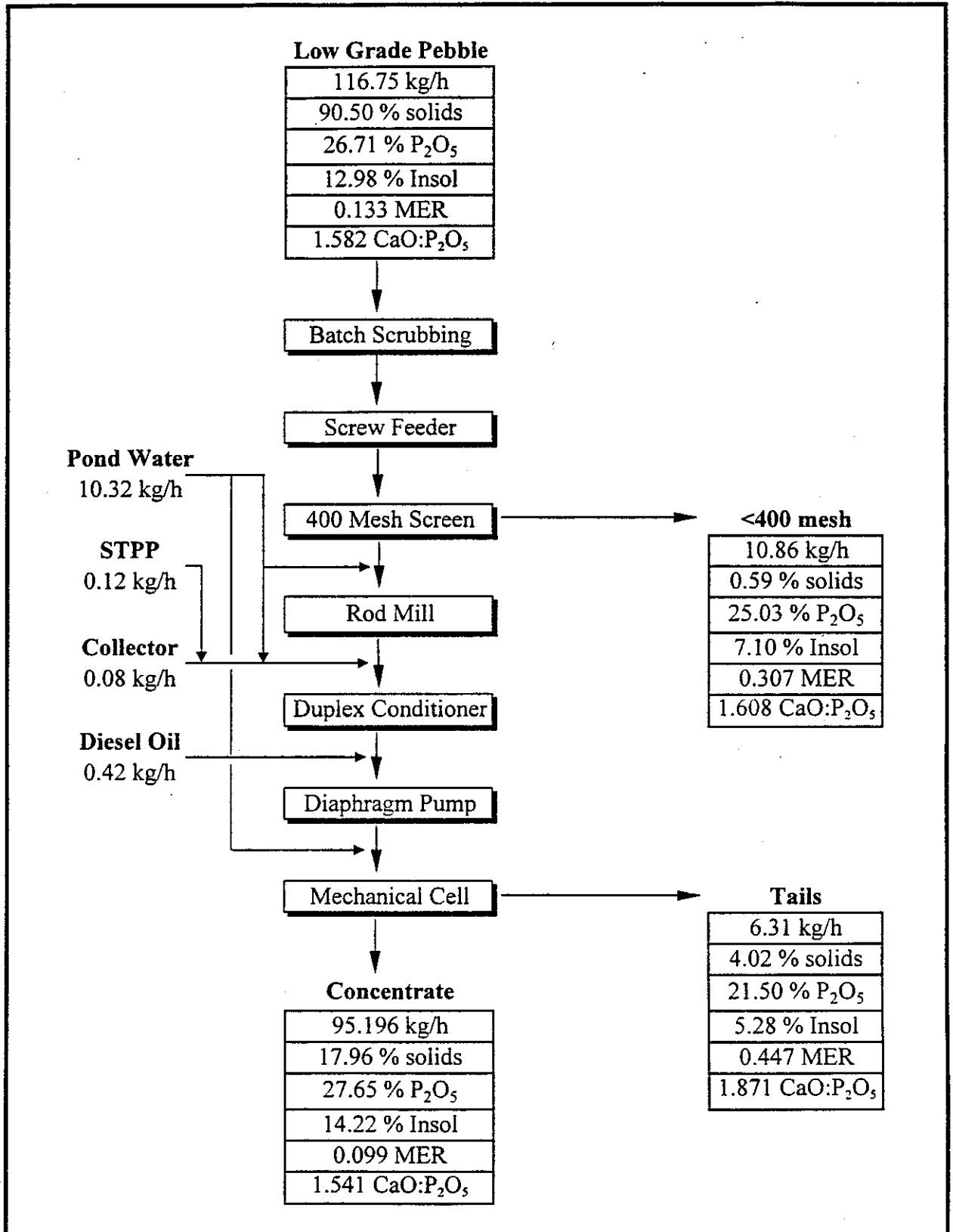


Table 11: Flotation Performance by Mesh Fraction

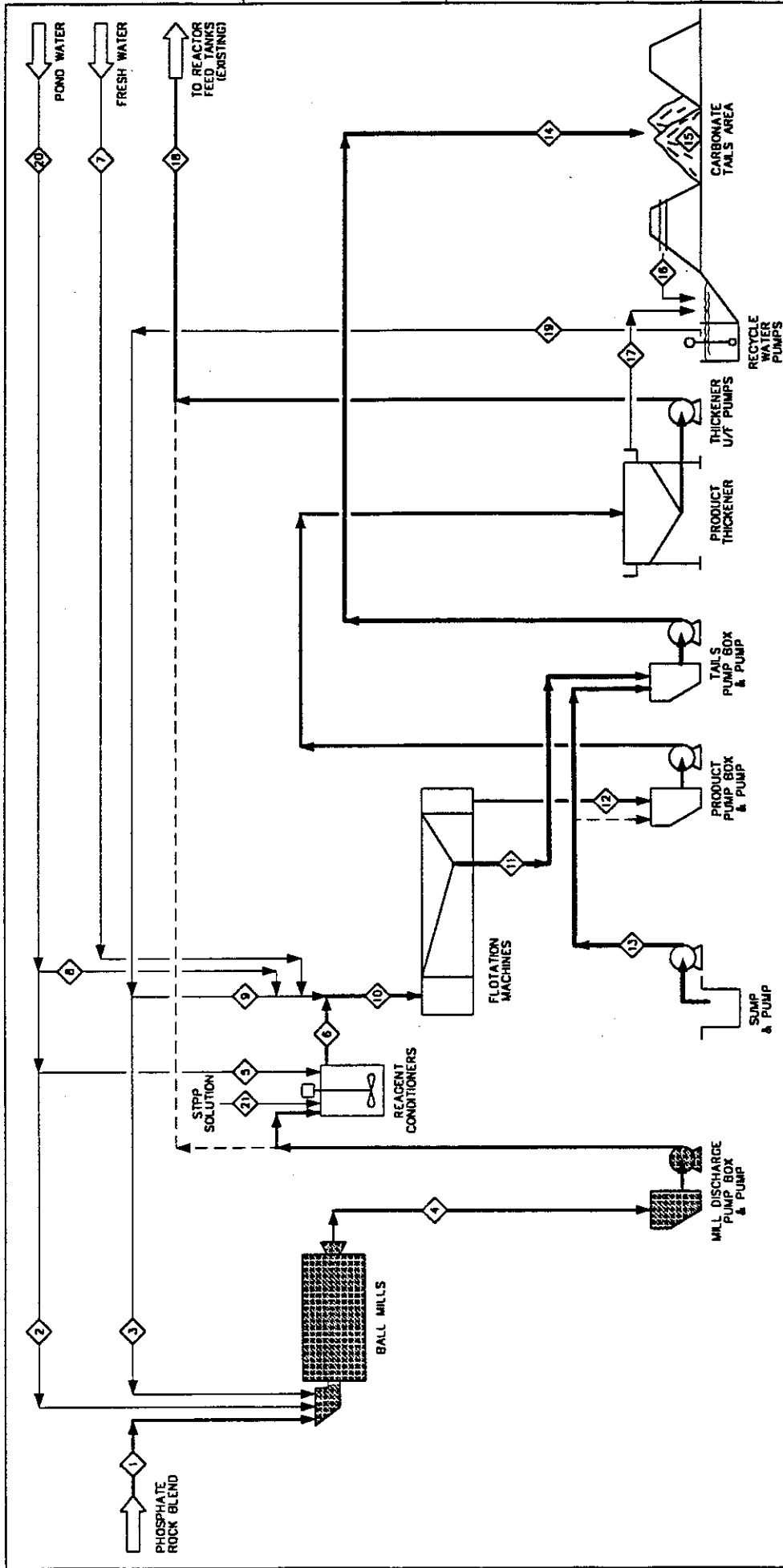
	Laboratory Flotation			Pilot Plant Flotation		
	% recovery to concentrate		separation coefficient	% recovery to concentrate		separation coefficient
	P <sub>2</sub> O <sub>5</sub>	MgO		P <sub>2</sub> O <sub>5</sub>	MgO	
35/48 mesh	100	100	0	100	100	0
48/65 mesh	100	97	3	100	100	0
65/150 mesh	99	86	13	99	84	15
150/200 mesh	97	63	34			
200/270 mesh	94	48	46			
270/400 mesh	89	34	55			
- 400 mesh	66	17	49			
				89	36	53

notes: The separation coefficient is computed as the difference between P<sub>2</sub>O<sub>5</sub> & MgO recoveries.

The pilot plant flotation used an antifoaming agent.

water are added to the conditioners. The slurry is conditioned at 65% solids. After conditioning, the slurry is transferred to flotation cells where it is diluted to about 16% solids for flotation of carbonates using a combination of fresh and recycle waters. The pH of the slurry is maintained at pH 5.5 by the addition of pond water. The carbonates are floated. Carbonate tailings, the froth product, are pumped to a carbonate tailings disposal area where they are dewatered to 40% solids. The concentrate, the cell product, is transported to a thickener using pumps. The overflow of the thickener is combined with the return water from the carbonate tailings disposal area, and used as recycle water in the process. The thickener underflow at 68% solids is fed to the reactor feed tanks of the phosphoric acid plant. Case 1 is illustrated on Figure 3.

- Case 2: Only the waste pebble is beneficiated. The waste pebble is conveyed to a pebble surge bin. It is fed via a belt scale to a log washer and diluted with recycle water. Most of the clays are rejected in the log washer. The log washer coarse product at 75% solids is discharged to a Vertimill. The pond water and recycle water are used to make a 67.8% solids slurry, which is ground to pass 28 mesh. The ground slurry is pumped to reagent conditioners. Sodium tripolyphosphate (STPP) solution, collector and more pond water are added to the conditioners. The slurry is conditioned at 65% solids. After conditioning, the slurry is introduced to flotation cells where it is diluted to 16% solids for flotation of carbonates using fresh and recycle waters. The pH of the slurry is maintained at pH 5.5 by the addition of pond water. The carbonates are floated. Carbonate tailings, the froth product, are pumped to a carbonate tailings disposal area where they are dewatered to 40% solids. The concentrate, the cell product, is pumped to a thickener. The overflow of the thickener is combined with the return water from the carbonate tailings disposal area, and used as recycle water in the process. The thickener underflow, the flotation concentrate, is combined with the regular rock. The blend is pumped to the reactor feed tanks of the phosphoric acid plant. The Case 2 is shown on Figure 4.

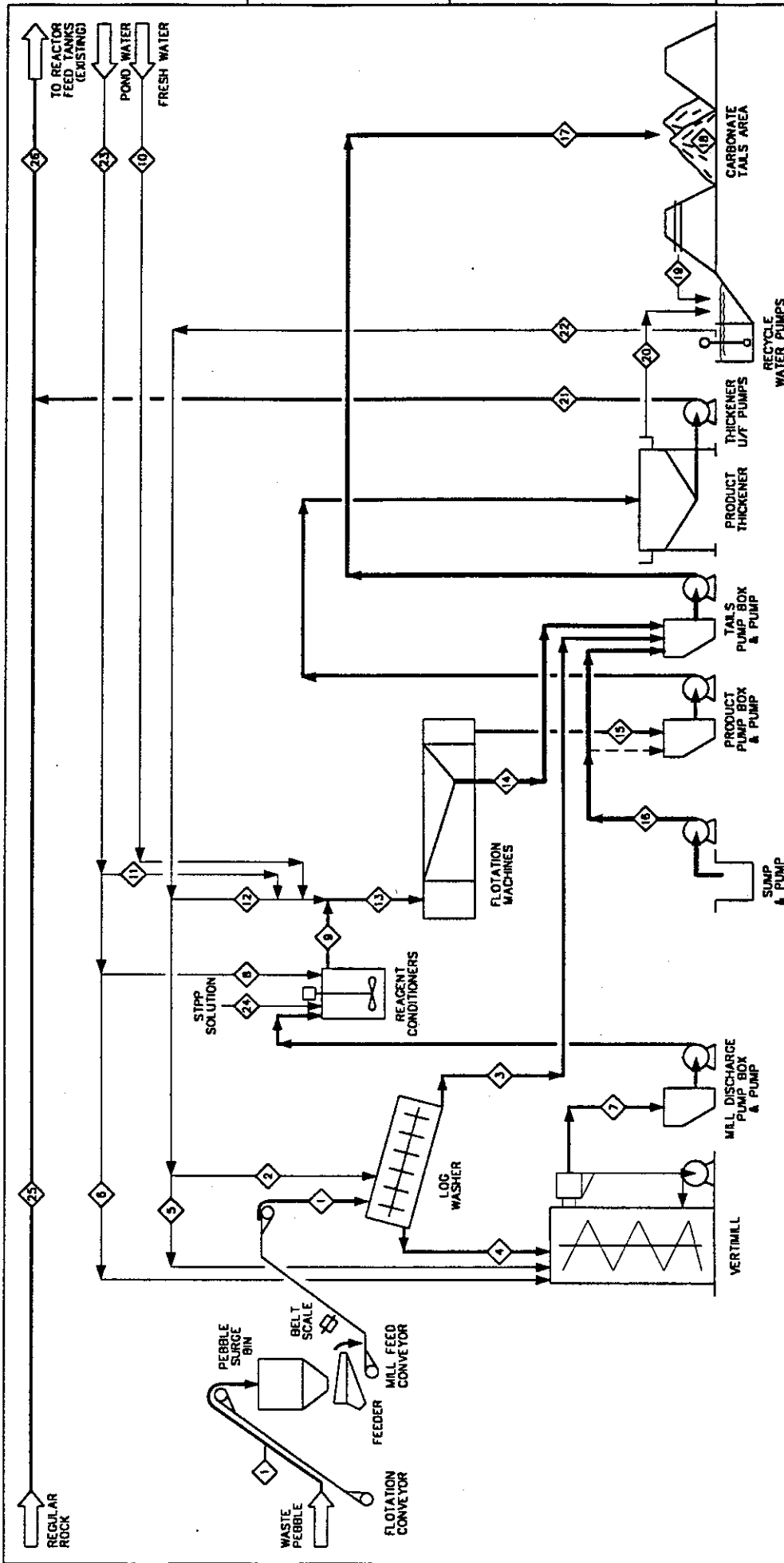


**JE** LANDLORD  
**JACOBS ENGINEERING GROUP INC.** FLORIDA

PHOSPHATE ROCK TREATMENT FOR WASTE REDUCTION  
 FIPR CONTRACT NO. 93-01-112R  
 CONCEPTUAL FLOTATION PROCESS PFD  
 CASE 1

PREPARED BY: MEX DRAWN BY: CWP  
 DATE: 11-23-98 CADD NO.: 923601C  
 SCALE: NONE FIGURE 2

DESCRIPTION	STREAM NUMBER																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
IPH (SOIDS)	168.48	0	0	168.48	0	168.48	0	0	168.48	12.00	156.49	0	0	156.49	0	0	0	0	0	0	0
% SOLIDS	88.0	0	0	87.0	0	65.5	0	0	16.0	4.5	20.0	0	0	40.0	0	0	68.0	0	0	0	0
GPM (WATER)	91.90	33.92	203.64	329.45	14.21	351.55	198.25	17.76	2945.30	3512.96	1009.06	2503.80	1009.06	71.46	937.60	2211.34	292.46	3148.94	65.88	7.89	7.89
GPM (PULP)	332.59	33.92	203.64	570.14	14.21	592.24	198.25	17.76	2945.30	3751.55	1026.19	2727.35	1026.19	88.60	937.60	2211.34	1.007	1.777	1.007	1.030	1.082
SP. GR. (PULP)	2.303	1.030	1.007	1.757	1.030	1.727	1.000	1.030	1.007	1.115	1.030	1.148	1.000	1.030	1.346	1.007	1.007	1.777	1.007	1.030	1.082
IPH - P <sub>2</sub> O <sub>5</sub> ROCK	47.26	0.00	0.00	47.26	0.00	47.26	0.00	0.00	0.00	47.26	2.46	44.80	0.00	2.46	2.46	0.00	0.00	44.80	0.00	0.00	0.00
IPH - P <sub>2</sub> O <sub>5</sub> SOLN	0.00	0.14	0.02	0.16	0.08	0.28	0.00	0.07	0.30	0.037	0.11	0.26	0.00	0.11	0.01	0.10	0.21	0.03	0.33	0.27	0.06
IPH - P <sub>2</sub> O <sub>5</sub> PPT	47.26	0.14	0.02	47.42	0.08	47.54	0.00	0.07	0.30	0.29	0.09	0.20	0.00	0.09	0.09	0.20	0.20	0.20	0.20	0.27	0.06
IPH - P <sub>2</sub> O <sub>5</sub> TOTAL	47.26	0.14	0.02	47.42	0.08	47.54	0.00	0.07	0.30	0.29	0.09	0.26	0.00	0.09	0.09	0.20	0.20	0.20	0.20	0.27	0.06
M <sub>3</sub> O IPH	1.50	0.01	0.00	1.51	0.00	1.51	0.00	0.00	0.03	1.54	0.48	1.06	0.00	0.48	0.47	0.01	0.02	1.04	0.03	0.01	0.00
C <sub>60</sub> IPH	71.51	0.02	0.01	71.54	0.01	71.55	0.00	0.01	0.15	71.72	4.61	67.08	0.00	4.61	4.56	0.05	0.11	66.96	0.16	0.04	0.00



MAJOR PROCESS STREAM  
 PROCESS STREAM  
 ALTERNATE FLOW

**JE** JACOBS ENGINEERING GROUP INC.  
 LANDLORD  
 FLORIDA

PHOSPHATE ROCK TREATMENT FOR  
 WASTE REDUCTION  
 CASE 2  
 FIPR CONTRACT No. 93-01-112R

CONCEPTUAL FLotation PROCESS PFD  
 PREPARED BY: MEX. ORLANDO  
 DATE: 11-23-98  
 SHEET: 20-9925-  
 NONE  
 SHEET NO. 3

DESCRIPTION	STREAM NUMBER																										
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	
IPH (SOLIDS)	41.08	0	3.20	37.87	0	0	37.87	0	37.87	0	0	37.87	3.18	34.70	0	6.38	6.38	0	0	34.70	0	0	0	0	0	123.23	157.92
% SOLIDS	88.00	0	6.90	75.00	0	0	67.80	0	66.28	0	0	16.00	5.02	20.00	0	5.82	40.00	0	0	68.00	0	0	0	0	0	68.00	68.00
CPM (WATER)	22.40	200.00	171.91	50.49	13.69	7.52	71.71	3.15	76.61	64.24	3.94	646.26	791.04	235.91	555.13	0	407.82	36.06	369.76	480.19	64.94	859.95	14.61	1.75	231.95	296.89	
CPM (PULP)	81.08	200.00	176.49	104.60	13.69	7.52	125.91	3.15	130.71	64.24	3.94	646.26	845.14	240.44	604.70	0	416.93	47.17	369.76	490.19	114.51	859.95	14.61	1.75	407.99	522.50	
SF. GR. (PULP)	2.303	1.006	1.053	1.931	1.006	1.030	1.776	1.030	1.749	1.000	1.030	1.006	1.120	1.052	1.148	1.000	1.052	1.352	1.006	1.006	1.006	1.006	1.030	1.082	1.777	1.778	
IPH - P <sub>2</sub> O <sub>5</sub> ROCK	10.97	0.00	0.73	10.24	0.00	0.00	10.24	0.00	10.24	0.00	0.00	0.00	0.00	0.00	0.55	9.68	0	1.28	1.28	0.00	0.00	0.00	0.00	0.00	0.00	35.12	44.80
IPH - P <sub>2</sub> O <sub>5</sub> SOLN	0.00	0.02	0.02	0.00	0.00	0.03	0.04	0.01	0.06	0.00	0.02	0.07	0.09	0.03	0.06	0	0.04	0.00	0.04	0.05	0.01	0.09	0.06	0.01	0.00	0.00	0.01
IPH - P <sub>2</sub> O <sub>5</sub> PPT	10.97	0.02	0.75	10.24	0.00	0.03	10.27	0.01	10.30	0.00	0.02	0.07	0.10	0.08	0.78	0	1.35	1.31	0.04	0.05	0.01	0.09	0.06	0.01	0.01	35.12	44.85
IPH - P <sub>2</sub> O <sub>5</sub> TOTAL	21.94	0.04	1.47	20.48	0.00	0.06	20.54	0.02	20.60	0.00	0.04	0.14	0.19	0.16	1.56	0	2.70	2.66	0.08	0.10	0.02	0.18	0.12	0.01	0.01	70.24	89.65
MgO IPH	0.00	0.00	0.09	0.45	0.00	0.00	0.46	0.00	0.46	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO IPH	0.01	1.30	1.30	15.76	0.00	0.00	15.76	0.00	15.76	0.00	0.00	0.03	15.80	1.03	14.00	0.00	2.34	2.32	0.02	0.03	14.74	0.05	0.01	0.00	52.69	67.42	

## Design Bases

In order to develop the materials balances for the above cases, it was necessary to adopt a basis of comparison. The assumed basis of comparison is a hypothetical phosphate mine and chemical plant. Phosphate ore reserves at the hypothetical mine underlay 1600 mineable acres which yield 12.45 million tons of acceptable quality phosphate rock and 4.15 million tons of low grade (discretionary) pebble. The discretionary tonnage can be excluded by selective mining of the upper horizon ore, or included by mining both upper and lower horizon ore. The phosphate rock produced is dedicated to a phosphoric acid plant producing 1000 tons per day (tpd) of  $P_2O_5$ . The phosphoric acid is converted to diammonium phosphate (DAP).

Characteristics of the hypothetical ore reserves are summarized on Table 12. The demands for standard or acceptable quality rock and low grade pebble for three production scenarios are presented on Table 13 along with the corresponding process losses and upgraded reactor feed.

In scenario one (base case), only the upper zone ore is mined and the standard phosphate rock is ground and fed directly to the reactor. In case 1, the upper and lower zone ore are mined and the combined product is ground in existing milling equipment, floated to remove carbonate gangue, thickened, and then fed to the reactor. In case 2, the upper and lower zones are mined but the standard rock and low grade pebble are segregated. The standard rock is ground in existing milling equipment, blended with thickened concentrate obtained from low grade pebble, and then fed to the reactor. Only the low grade pebble is beneficiated. The pebble treatment comprises scrubbing, desliming, grinding in a new mill, flotation to remove carbonates, and thickening. In each scenario the reactor feed contains nominally 1,075 tons per day of  $P_2O_5$ , and phosphoric acid containing 1,000 tpd of  $P_2O_5$  is produced.

The extended years of operation for cases 1 and 2 are possible because mining both the upper and lower zones increased product recovery from the existing reserves relative to the base case.

**Table 12: Hypothetical Ore Reserves (1600 acres)**

	<b>Base Case Product</b>	<b>Discretionary Pebble</b>	<b>Combined Product</b>
% P <sub>2</sub> O <sub>5</sub>	28.50	26.70	28.05
% Insol	10.00	13.00	10.75
% CaO	42.75	41.50	42.44
%MgO	0.75	1.32	0.89
% I&A	2.10	2.15	2.11
CaO:P <sub>2</sub> O <sub>5</sub>	1.500	1.554	1.513
MER	<b>0.100</b>	<b>0.130</b>	<b>0.107</b>
overburden yd <sup>3</sup> /t	4.00	n/a	3.00
ore yd <sup>3</sup> /t	4.30	n/a	4.03
product tons	<b>12,450,000</b>	<b>4,150,000</b>	<b>16,600,000</b>

**Table 13: Hypothetical Production Scenarios**

	<b>Base Case</b>	<b>Case 1</b>	<b>Case 2</b>
<b>Reserves Life - years</b>	<b>10.00</b>	<b>12.44</b>	<b>12.76</b>
Delivered Rock - mmtpy	1.245	1.335	1.301
Upgrading Losses - mmtpy	0.000	0.096	0.050
<b>Reactor Feed - mmtpy</b>	<b>1.245</b>	<b>1.239</b>	<b>1.251</b>
reactor feed analyses			
% P <sub>2</sub> O <sub>5</sub>	28.50	28.63	28.37
% Insol	10.00	11.28	10.73
% CaO	42.75	42.78	42.69
% MgO	0.75	0.66	0.74
% I&A	2.10	2.01	2.06
CaO:P <sub>2</sub> O <sub>5</sub>	1.500	1.494	1.505
<b>MER</b>	<b>0.100</b>	<b>0.093</b>	<b>0.099</b>



## Economic Evaluation

The internal rates of return on the capital investments for cases 1 and 2 were determined from the margins generated by selling DAP produced from phosphate rock recovered by the hypothetical production scenarios presented on Table 13. The margins were computed as the difference between DAP selling price and production costs, taking into account rock production costs, rock transportation costs, the costs of carbonate flotation, as well as the costs to convert reactor feed to phosphoric acid and DAP. The costs of urea to upgrade the DAP to 18:46:00 are included.

The FOB costs of rock production and DAP production were estimated by Jacobs cost models as of January 1, 1999. The costs of carbonate flotation were estimated on the basis of pilot plant test data and a preliminary engineering study. Table 14 presents the various components of the DAP production cost, as well as the sales price and margin per ton of DAP for each case. The base case has the lowest cost DAP. Case 2, which floated all of the reactor feed, had very nearly the same DAP production cost as the base case (\$144.66 vs. \$144.16 per short ton of DAP).

The preliminary cash flows over the life of the hypothetical phosphate reserve for the three cases are presented on Table 15. This table also presents incremental analyses of cases 1 and 2 relative to the base case. Capital recovery for either case 1 or case 2 requires more than 10 years; however, the internal rates of return without inflation or taxes are 17.0% and 10.7% respectively for cases 1 and 2.

The capital cost of adding a carbonate flotation module to an existing phosphoric acid plant (1000 tpd  $P_2O_5$ ) is 6.5 million dollars for case 1 and 7.1 million dollars for case 2 as of January 1, 1999. Case 1 has more flotation capacity but utilizes the existing grinding capacity. Case 2 requires less flotation capacity, but with new desliming and grinding equipment. The cost of the carbonate tailings dam is included in each case.

**Table 14: Dollars per ton DAP**

<b>cost elements</b>	<b>Base Case</b>	<b>Case 1</b>	<b>Case 2</b>
Mine Production	39.35	39.33	38.80
Freight	4.51	4.83	4.71
Carbonate Flotation	0.00	6.09	2.39
Reactor Feed Subtotal	43.86	50.25	45.90
MER Penalty (urea)	5.54	0.00	5.55
Sulfur	27.09	26.97	27.16
Ammonia	26.55	26.55	26.55
Processing Costs	27.15	26.98	27.24
Book Cost	13.97	13.91	14.00
<b>DAP Cost FOB</b>	<b>144.16</b>	<b>144.66</b>	<b>146.39</b>
<b>DAP Price FOB</b>	<b>175.00</b>	<b>175.00</b>	<b>175.00</b>
<b>DAP Margin \$/ton</b>	<b>30.84</b>	<b>30.34</b>	<b>28.61</b>

**Table 15: Preliminary Cash Flow Analysis**

Project Year	Investment & Margins (\$1,000,000)			Incremental Analyses	
	Base Case	Case 1	Case 2	Case 1	Case 2
-1	0	-6.515	-7.106	-6.515	-7.106
1	21.285	20.940	19.746	-0.345	-1.539
2	21.285	20.940	19.746	-0.345	-1.539
3	21.285	20.940	19.746	-0.345	-1.539
4	21.285	20.940	19.746	-0.345	-1.539
5	21.285	20.940	19.746	-0.345	-1.539
6	21.285	20.940	19.746	-0.345	-1.539
7	21.285	20.940	19.746	-0.345	-1.539
8	21.285	20.940	19.746	-0.345	-1.539
9	21.285	20.940	19.746	-0.345	-1.539
10	21.285	20.940	19.746	-0.345	-1.539
11	0.000	20.940	19.746	20.940	19.746
12	0.000	20.940	19.746	20.940	19.746
13	0.000	9.214	15.017	9.214	15.017
<b>Totals</b>	<b>212.853</b>	<b>253.982</b>	<b>244.865</b>	<b>41.128</b>	<b>32.012</b>

**Pay Back            +10 yrs            +11 yrs**

**IRR                    17.0%            10.7%**

1) Margins based on selling 690,186 tpy of DAP for each case.

## REFERENCES

Rule A.R., D.E. Kirby, and D.C. Dahlin. Recent Advances in Beneficiation of Western Phosphates. Paper presented at AIME Conference in St. Louis, 1977.

Rule, A.R., D.E. Larson, and C.B. Daellenback. Application of Carbonate-Silica Flotation Techniques to Western Phosphate Materials; Bureau of Mines RI 8728, 1982.

Henchiri, A., G. Barbery, and G. Baudet, 1979 French Patent 79.30868.

Henchiri, A., G. Baudet, P.C. Hergibo, 1980 French Patent 80.19366.

Henchiri, A., 1981, Ph.D Thesis, Orleans.

Henchiri, A. A Contribution to Carbonates - Phosphate Separation by Flotation Technique; Beneficiation of Phosphate: Theory and Practice, SME, 1993.

Snow, Robert E. United States Patent 4364824, Flotation of Phosphate Ores Containing Dolomite.

Gruber, G.A., J.D. Raulerson, R.P. Farias. Adapting Technology to Beneficiate a Low Grade Phosphate Ore. Paper presented at AIME Conference in New Orleans, 1986.