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RECOVERY OF PHOSPHATE FROM FLORIDA PHOSPHATIC CLAY WASTES

by

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ABSTRACT

As part of its goal of maximizing minerals and metals recovery from domestic resources, the Bureau of Mines, U.S. Department of the Interior, is investigating the recovery of phosphate from Florida phosphatic waste clays. Phosphate equivalent to about one-eight of the world consumption is discarded annually in these clay wastes from phosphate beneficiation plants. Concentration of phosphate in exploratory flotation tests on the plus 5-μm fraction of a waste clay sample showed promise. Therefore, a classification-flotation technique is being investigated as a possible means of recovering part of the lost phosphate. Onsite classification tests at six phosphate washing plants were conducted with a two-stage hydrocyclone system designed to recover the plus 5-μm material. The cyclone underflows contained 8.3 to 19.1 percent P_2O_5 and 81 to 95 percent of the plus 5-μm P_2O_5. Overall phosphate recovery from the total slimes ranged from 38 to 47 percent. Batch flotation studies currently are being conducted.

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INTRODUCTION

As part of its goal of maximizing minerals and metals recovery from domestic resources, the Bureau of Mines, U.S. Department of the Interior, is conducting mineral beneficiation research for recovering phosphate from the Florida phosphate slimes. Recovery of this wasted phosphate would significantly increase recovery from this important domestic phosphate resource. The most important source of phosphate in the United States is the Bone Valley Formation in central Florida. Seventy-eight percent of our domestic production, roughly 34 million tonnes per year of phosphate rock, comes from mining and beneficiating this Flordia phosphate rock ore, which is known as matrix (1). A typical matrix contains about one-third phosphate rock, one-third silica sand, and one-third clay. The bone phosphate of lime (BPL) content of the matrix ranges from 15 to 40 percent, which is equivalent to 7 to 18 percent P_2O_5 (2). During beneficiation, the minus 105-μm size clay wastes are removed from the matrix by hydrocyclones or hydroseparators. The phosphatic clay wastes, or slimes, are primarily a suspension of finely-divided particles in water. The solids concentration of the slimes discharged from a plant usually averages 2 to 6 percent. About 50 weight-percent of the particles are minus 1-μm in size. These phosphate slimes wastes contain 6 to 17 percent P_2O_5, which amounts to almost one-third of the phosphate in the matrix ore (3, 4). This is equivalent to about 17 million tonnes per year of phosphate rock, or nearly two-fifths of our domestic production.

Preliminary characterization studies of a sample of phosphate slimes indicated that theoretically it should be possible to produce a high-grade phosphate concentrate containing as much as 35 to 36 percent P_2O_5 if a beneficiation scheme could be established successfully. Beneficiation techniques such as selective dispersion, selective flocculation, spherical agglomeration, piggyback flotation, and froth flotation were employed without success on this particular sample of slimes. However, after the minus 5-μm slimes particles were removed, exploratory froth flotation tests showed that a high-grade phosphate concentrate containing 34 percent P_2O_5 could be recovered. The P_2O_5 recovery in this case was about 12 percent of the total P_2O_5 values, or about 58 percent of the P_2O_5 in the plus 5-μm fraction. Based on these encouraging results, by the Bureau of Mines, Tuscaloosa Metallurgy Research Center an investigation of a classification-flotation technique as a possible means for recovering part of the phosphate lost to the slimes was initiated. This report presents the progress of this investigation.

Classification Studies

Classification of the plus 5-μm slimes might be accomplished by two methods: a thickener-hydroseparator system, or a hydrocyclone system. With several stages, the underflow from a thickener-hydroseparator system would contain only minor amounts of minus 5-μm material. Complete dispersion would be necessary for a thickener-hydroseparator system to effectively classify the phosphate slimes at the 5-μm size. Previous work on characterization of Florida phosphate slimes indicated that the slurries were not dispersed (3) so dispersion studies were conducted on a sample of phosphate slimes. Several common dispersants and pH modifiers were used to completely disperse the slurry. None of these reagents were able to disperse the slurry with less than 4.5 kg dispersant per tonne of solids. Further attempts to classify the

phosphate slimes by a thickener-hydroseparator were discontinued.

A hydrocyclone system does not require complete dispersion of the phosphate slimes for effective classification. The high shear forces within the cyclone temporarily disperse the particles, and an effective classification can be made. Semicontinuous two-stage hydrocyclone studies were made on a sample of phosphate slime containing 30 weight-percent plus 5-μm material. Results showed that an underflow product containing 92 weight-percent plus 5-μm material could be recovered. The underflow product accounted for 93 weight-percent of the total plus 5-μm material.

Size analyses of slimes and test products were determined by sedimentation and decantation. Sedimentation times were calculated from Stokes' equation. A known quantity of slimes was dispersed and allowed to settle at constant temperature for a calculated time, and the minus 5-μm material was removed by siphon. The sedimentation process was repeated three times. Sizing by this method has been estimated to be accurate within 1 percent (5).

Based on these preliminary results, a simple two-stage hydrocyclone system was designed to size the phosphate slimes at 5-μm. A schematic diagram and a photograph of the two-stage cyclone unit are shown in Figures 1 and 2. A 210-μm screen was used to remove tramp material

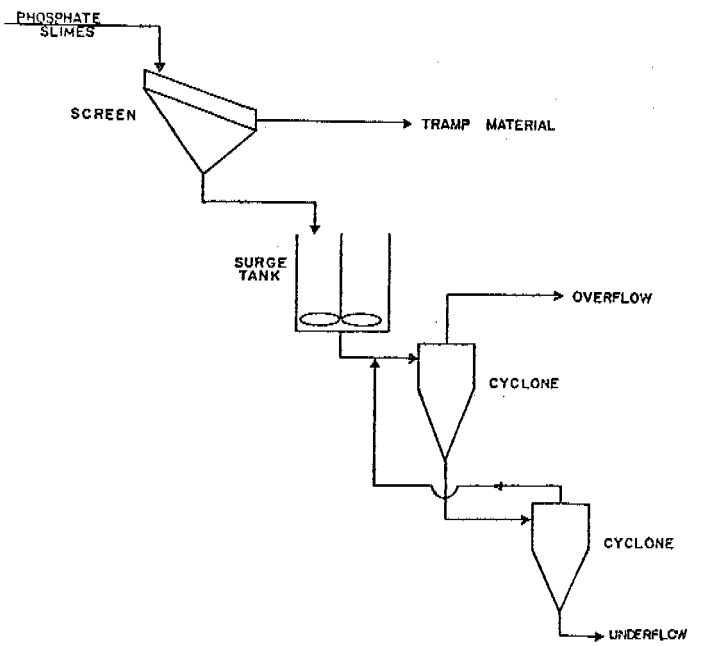

Figure 1. Schematic diagram of two-stage cyclone unit used for onsite testing at six operating phosphate washers.

that would otherwise plug the cyclones. Most of the phosphate producers deslime the matrix at 105-μm particle size. A 210-μm size classification of the phosphate slimes would not significantly alter their composition. After passing through the 210-μm screen, the slimes entered a surge tank prior to the cyclone circuit. The first stage of the cyclone system was four 25-mm-diameter cyclones arranged in a parallel circuit. Each cyclone had a 4.6-mm-diameter inlet, a 4.6-mm-diameter vortex finder, and a 3.5-mm-diameter apex. The cyclone length was 150 mm, and the included angle of the cyclone was 7 degrees. The inlet pressure to the four cyclones was 240 kPa (kilo Pascals), and the feed rate of the pulp to the four cyclones was 34 l/min. The four cyclone overflows contained most of the minus 5-μm material and were discarded. The combined four cyclone underflows were used to feed the second-stage cyclone.

The second stage of the cyclone system was a single 25-mm-diameter cyclone. This cyclone had a 4.6-mm-diameter inlet, a 3.0-mm-diameter vortex finder, and a 3.5-mm-diameter apex. The cyclone length was 150 mm, and the included angle of the cyclone was 7 degrees. The inlet pressure was about 240 kPa, and the feed rate of the pulp was about 8.4 l/min. The second-stage cyclone overflow had a significant amount of the plus 5-μm material and was recirculated to the first-stage cyclones. With the recirculating load taken into account, the slimes feed rate to the entire two-stage cyclone system was 31 l/min. This feed rate varied depending upon the percent solids of the feed pulp and the particle size distribution of the slimes. The second-stage cyclone underflow contained most of the plus 5-μm material and was stored for flotation studies.

The two-stage cyclone unit and a diesel electrical generator were mounted on a truck for onsite testing in Florida. Onsite testing at six operating phosphate washers was conducted to determine the efficiency of the sizing operation on phosphate slimes and to provide sufficient plus 5-μm material for bench-scale flotation.

About 200 liters of the cyclone underflow product from each phosphate washer would be adequate for the bench-scale flotation studies. Only 1 hour of onsite testing was required to obtain that amount. Five samples of each phosphate slime fed were obtained during the testing period. Periodically, samples of the cyclone overflow were collected as shown in Figure 3. These samples were weighed and combined in a 110-liter drum to be evaluated later in the laboratory. The cyclone underflow was pumped into a 210-liter drum for storage.

The phosphate slimes encountered during onsite testing were highly variable, as indicated in table 1. The percent solids of the pulp ranged from as low as 0.7 percent solids to as high as 3.4 percent solids. During the 1-hour sampling time at each phosphate washer, the percent solids of the slimes pulp varied greatly. The weight-percent of the plus 5-μm material also varied among the six phosphate washers, ranging from 18 to 39 percent. Also the amount of plus 5-μm material varied from washer to washer. In most cases, the weight-percent of the plus 5-μm material varied inversely to the percent solids of the slimes pulp. The phosphate content of the clay slimes was largely dependent upon the matrix being mined. During the sampling time at each phosphate washer the phosphate content showed minor variations. These minor variations appeared to have no correlation to either the percent solids of the pulp or the weight-percent of the plus 5-μm material.

TABLE 1. - Characteristics of phosphate slimes fed to the two-stage cyclone system at six operating phosphate washers

Phosphate washer number	Solids wt-pct		Plus 5-μm material wt-pct		Percent P_2O_5	
	Range	Mean	Range	Mean	Range	Mean
1	1.3 - 3.6	3.0	16 - 24	18	7.3 - 7.7	7.6
2	0.6 - 2.4	0.7	28 - 43	34	16.4 - 20.2	18.4
3	2.0 - 3.3	2.7	20 - 25	22	8.0 - 8.6	8.2
4	0.7 - 2.2	1.8	22 - 33	25	8.6 - 9.7	9.2
5	3.0 - 3.7	3.4	29 - 32	31	7.7 - 8.3	7.9
6	2.4 - 3.5	2.8	36 - 44	39	8.9 - 9.9	9.3

The results from the onsite two-stage cyclone tests are shown in table 2. In general the percent solids of the cyclone underflow was double that of the feed pulp, and the weight-percent of the plus 5-μm material was also about double that of the feed material. Between 73 and 84 percent of the slimes pulp weight was discarded in the cyclone overflow. The cyclone overflow percent solids of the pulp was slightly less than that of the feed slimes, and the weight-percent of the plus 5-μm material in the overflow ranged from 5.9 to 11.0. The cyclone underflow contained 8.3 to 19.1 percent P_2O_5, and the cyclone system recovered 81 to 95 percent of the plus 5-μm P_2O_5 values. In all except one case, the P_2O_5 content of the cyclone underflow was higher than that of the slimes fed to the cyclone system. The cyclone underflow still had significant amounts of the minus 5-μm material.

After returning to the laboratory, dispersion studies were initated on the cyclone underflows to further concentrate the plus 5-μm material with a thickener-hydroseparator system. The reagent requirement to attain a dispersed pulp was still too high to be practical. Modifications were made on the two-stage cyclone system to obtain a higher concentration of the plus 5-μm material in the cyclone underflow. The diameter of the apex opening of the first-stage cyclones was decreased to 2.9 mm. The second-stage cyclone apex diameter was decreased to 1.5 mm, and the diameter of the vortex finder was increased to 4.6 mm. To compensate for the smaller apex diameter of the first-stage cyclones, the operating pressure was increased to 280 kPa. The second-stage cyclone was operated at 170 kPa. At these pressures the slimes pulp feed rate to the cyclone system was 38 l/min. Samples of the phosphate slimes from the six phosphate washers tested in Florida also were tested with the modified cyclone system. The results are shown in table 3. More than 96 weight-percent of the slimes pulp was discarded with the cyclone overflow. The cyclone overflow percent solids of these pulps also was slightly less than that of the feed slimes, and the weight-percent of the plus 5-μm material in the overflow ranged from 2.7 to 7.5. The cyclone underflow solids were thickened to about 13 to 33 percent solids. The solids of the cyclone underflow analyzed 85 to 95 weight-percent of plus 5-μm material, and the cyclone system recovered 81 to 92 percent of the plus 5-μm P_2O_5 values. In most cases the P_2O_5 content of the cyclone underflow was higher than that of the phosphate slimes fed to the cyclone system.

Flotation Studies

Froth flotation studies were initiated on the cyclone underflows from the classification testing. As of the preprinting date of this report, only a few preliminary flotation tests had been completed. These include some trial tests on samples of 100 percent plus 5-μm

TABLE 2. - Results from onsite testing with the two-stage cyclone unit at six operating phosphate washers

Phosphate washer number	Phosphatic Clay Wastes			Cyclone Underflow				
	Weight-percent solids	Weight-percent PFM[1]	Percent P_2O_5	Weight-percent of pulp	Weight-percent solids	Weight-percent PFM	Percent P_2O_5	Percent recovery of PFM (P_2O_5)
1	3.0	18	7.6	17	5.5	45	9.3	89
2	0.7	34	18.4	16	2.0	71	19.1	95
3	2.7	22	8.2	16	5.0	53	10.6	89
4	1.8	25	9.2	20	3.6	48	10.6	81
5	3.4	31	7.9	22	6.4	58	8.8	83
6	2.8	39	9.3	27	5.1	69	8.3	84

[1] PFM - plus 5-μm material.

TABLE 3. - Results of modified two-stage cyclone tests on samples of phosphate slimes from six phosphate washers

Phosphate washer number	Phosphatic Clay Wastes			Cyclone Underflow				
	Weight-percent solids	Weight-percent PFM[1]	Percent P_2O_5	Weight-percent of pulp	Weight-percent solids	Weight-percent PFM	Percent P_2O_5	Percent recovery of PFM (P_2O_5)
1	3.0	18	7.6	2.0	23	85	12.2	87
2	0.7	34	18.4	1.8	13	93	17.7	92
3	2.7	22	8.2	2.2	25	86	13.8	81
4	1.8	25	9.2	2.8	17	86	14.3	87
5	3.4	31	7.9	2.6	33	92	10.3	82
6	2.8	39	9.3	3.2	33	95	6.1	92

[1] PFM - plus 5-μm material.

material and on samples of cyclone underflows from the modified cyclone system. A sample of each of the six phosphate washer slimes was dispersed, which required large amounts of dispersant. The pulp was diluted and allowed to stand until the plus 5-μm material had settled; then the minus 5-μm material was decanted by siphon. After several decantations virtually all of the minus 5-μm material was removed. Heavy liquid separations were made on samples of this plus 5-μm material, and the results are shown in table 4. Physical separation of the plus 5-μm material could yield a phosphate concentrate containing 29 to 33 percent P_2O_5 if a flotation scheme could be developed successfully. Froth flotation tests were conducted on these plus 5-μm samples with a fatty acid collector scheme. The amount of fatty acid used was 1.0 kg/tonne. The pH was varied between 9.5 and 10.5, and various proportions of fuel oil were used to aid the flotation. The results are shown in figures 4 and 5. Only a rougher float was made for these tests, and the concentrate grades were low. Phosphate recovery ranged from 55 to 80 percent at both alkalinities tested; the addition of fuel oil lowered or did not change the concentration ratios. More selective flotation of phosphate occurred at pH 9.5, but phosphate recovery was higher at pH 10.5. These results represent preliminary data from current test work. The best rougher flotation phosphate concentrate obtained to date from the plus 5-μm material contained 25 percent P_2O_5. The recovery of P_2O_5 from the plus 5-μm material was 56 percent, and the recovery of P_2O_5 from the total slimes was 18 percent. Several different reagent schemes are being investigated to improve phosphate grade and recovery.

TABLE 4. - Heavy liquid separation of plus 5-μm phosphate slimes

Phosphate washer number	Specific gravity separations		
	Float 2.70, percent P_2O_5	Sink 2.70 and float 2.94, percent P_2O_5	Sink 2.94, percent P_2O_5
1	7.3	23.2	32.5
2	10.8	25.4	32.8
3	5.6	19.3	28.8
4	9.7	16.0	28.4
5	3.5	16.6	29.1
6	1.5	16.9	29.1

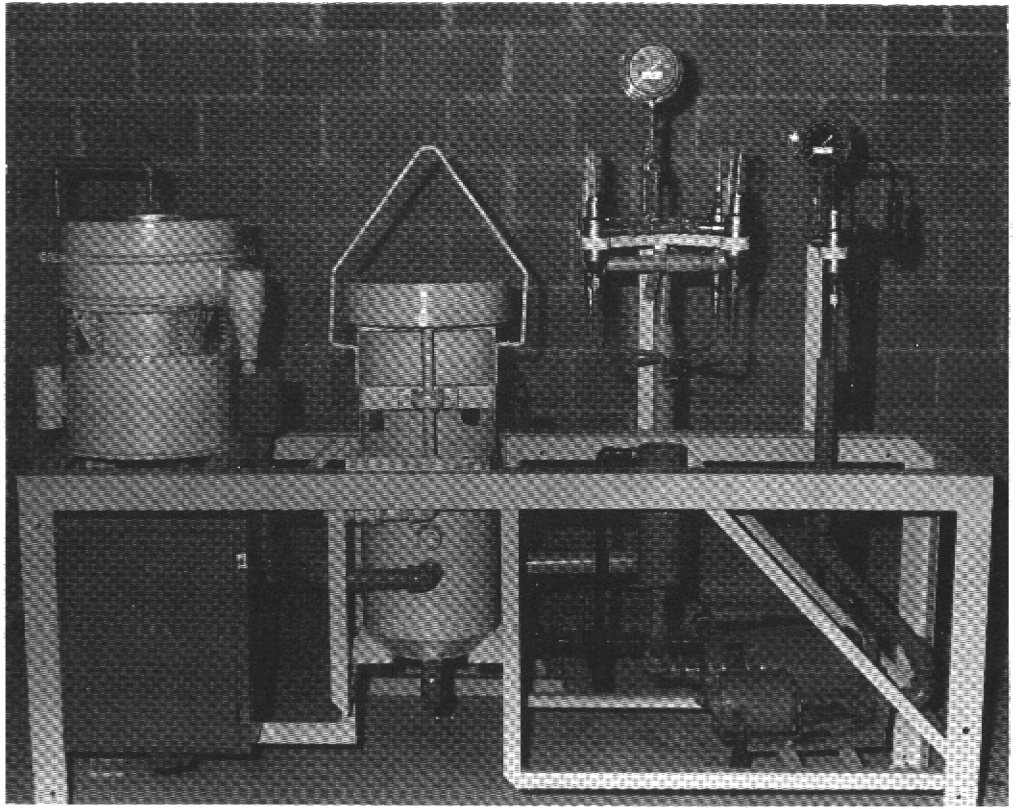

Figure 2. Two-stage cyclone unit used for onsite classification of phosphate slimes at six operating phosphate washers.

Figure 3. Two-stage cyclone unit for onsite classification of phosphate slimes at six operating phosphate washers.

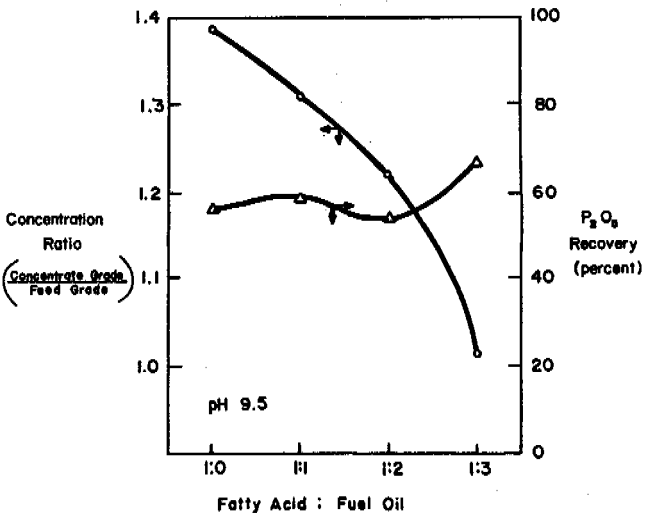

Figure 4. - Flotation results from tests using various proportions of fatty acid and fuel oil at 9.5 pH.

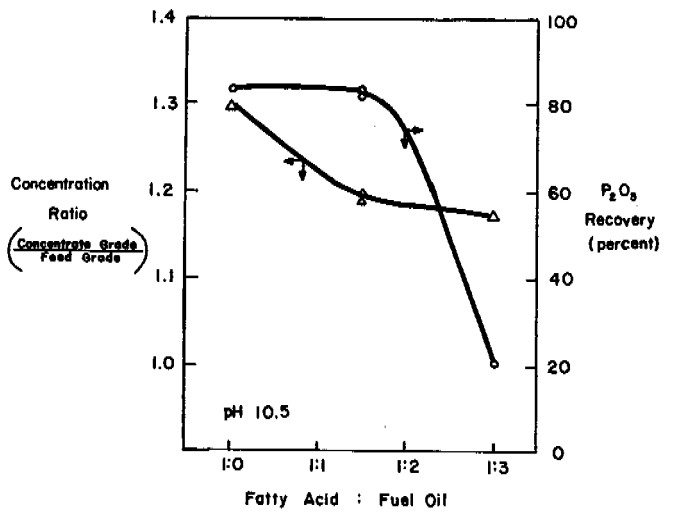

Figure 5. - Flotation results from tests using various proportions of fatty acid and fuel oil at 10.5 pH.

Conclusions and Recommendations

The Bureau of Mines is investigating a classification-flotation technique to recover phosphate from waste phosphate slimes. A two-stage cyclone system was used to concentrate the plus 5-μm phosphate slimes in the cyclone underflow. The concentration of plus 5-μm material was better than 85 weight-percent solids in the cyclone underflows from six phosphate washers tested. The recovery of plus 5-μm phosphate in these cyclone underflows was better than 81 percent. Flotation studies conducted on the six phosphate washer slimes showed promise for the recovery of plus 5-μm phosphate. Flotation studies are continuing to improve the phosphate grade and recovery and to limit the reagent consumption.

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