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# DEVELOPMENT OF PICOBUBBLE FLOTATION FOR ENHANCED RECOVERY OF COARSE PHOSPHATE PARTICLES

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June 2006

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DEVELOPMENT OF PICOBUBBLE FLOTATION FOR ENHANCED  
RECOVERY OF COARSE PHOSPHATE PARTICLES

FINAL REPORT

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## PERSPECTIVE

The efficient capture of hydrophobic particles by air bubbles is the key to effective flotation. It is generally recognized that small bubbles enhance flotation of small and medium-sized particles, while some large air bubbles are required to lift coarse particles. However, the attachment of coarse particles to large bubbles is weak, resulting in detachment and eventually the loss of coarse particles in flotation. Air bubbles of less than one micron in size, i.e., picobubbles, have been found to be effective in preventing detachment. These tiny bubbles also make particles floatable with significantly less surfactant coverage, thus reducing reagent use for flotation. Picobubble-enhanced flotation is still largely in the development stage, but is gaining broad interest among researchers, equipment manufacturers and flotation practitioners.

The lab testing results have been phenomenal. Picobubbles improved phosphate recovery dramatically, particularly at lower collector dosages. For example, for an approximately 85%  $P_2O_5$  recovery, collector use was 0.4 lb/ton with picobubbles versus 0.9 lb/ton without picobubbles. The same trend was observed for frother dosage. Experiments also demonstrated that picobubbles are more tolerable to high-throughput flotation, enabling significant reduction in both energy consumption and capital costs.

It should be noted that FIPR organized an on-site evaluation of this laboratory development project. The project evaluation team, consisting of industry representatives from all Florida phosphate mining companies and FIPR staff, visited the research lab and observed picobubble-enhanced flotation. The amazing effect of picobubbles was visually observed by the color change of flotation tailings under the same collector dosage. This team concluded that a pilot testing program was justified by the encouraging lab results. The FIPR Board has indeed approved funding for a follow-on project for pilot-scale evaluation of this technology.

Patrick Zhang  
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## ABSTRACT

In a typical central Florida phosphate beneficiation plant, the phosphate ore is washed and classified into three major size fractions. The coarse +1.18 mm (+16 mesh) portion is primarily phosphate pebble with no further upgrading required, but the beneficiation of the -1.18mm (-16 mesh) fraction is needed. Froth flotation is the most widely used process for Florida phosphate beneficiation. However, flotation recovery of the coarse (16 + 35 mesh) phosphate is low (<80%), while the fine (-150 mesh or -106 microns) portion that contains virtually all of the clay minerals is discarded in the hydrocyclone overflow. The low flotation recovery of coarse particles is mainly due to the high probability of detachment of particles from the bubble surface.

The proposed project was aimed at developing practical and effective techniques for enhanced recovery of coarse phosphate particles. A specially designed flotation column that utilizes picobubbles (bubbles with a size under 1  $\mu\text{m}$  that are characterized by high collision probability, low detachment probability, low ascending rate, and high free surface energy) was developed to achieve the goal. Cavitation-generated picobubbles are characterized by an inherently high probability of collision, a high probability of attachment and a low probability of detachment, and therefore are very effective for enhancing flotation recovery of fine and coarse phosphate particles. Other major advantages of the developed technique include much lower collector dosage and air consumption since picobubbles are produced from air naturally dissolved in water and they act as the secondary collector.

The test results of two CF Industries phosphate samples and one Mosaic phosphate sample indicate that the  $\text{P}_2\text{O}_5$  recovery can be increased by up to ~23%-30%, depending on the characteristics of the phosphate samples. With picobubbles, collector dosage can be reduced by 1/3 or 1/2. The centrifugal force created by the specially designed column bottom further improves the separation performance.

## **ACKNOWLEDGMENTS**

This research program was funded by the Florida Institute of Phosphate Research (FIPR), contract number 02-02-154R. The project manager, Dr. Patrick Zhang, provided valuable advice and support, which is greatly appreciated. Special thanks are given to CF Industries and the Mosaic Company for supplying phosphate specimens and to ArrMaz Custom Chemicals Inc. for providing chemicals employed in this study.

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## **EXECUTIVE SUMMARY**

### **EXPERIMENTAL SETUP AND SAMPLES**

A flotation column that utilizes picobubbles was designed and manufactured. A modified Hallimond tube for microflotation experiments was used for fundamental studies of column flotation. Two Florida phosphate samples from CF Industries and one from the Mosaic Company were collected and characterized.

### **MICROFLOTATION EXPERIMENTS ON FLOTATION EFFICIENCY**

A modified Hallimond tube was refined for better performance. Microflotation experiments were to determine the particle collection efficiency by air bubbles for different particle and bubble sizes.

### **COLUMN FLOTATION WITH CF INDUSTRIES PHOSPHATE SAMPLE A**

To evaluate the effect of picobubbles on coarse phosphate flotation, a number of flotation experiments were performed at varying collector and frother dosages, superficial air velocities, and solid feed rates using several bubble generators. A four-factor, three-level Box-Behnken experimental design of flotation tests was conducted.

#### **Effect of Picobubbles**

The flotation recovery of more than 98% was achieved at a collector dosage of 0.9 kg/t in the presence of picobubbles, producing a concentrate of 28.53% P<sub>2</sub>O<sub>5</sub>. In the absence of picobubbles, the maximum flotation recovery was only 95%, which was achieved at a collector dosage of 2.1 kg/t.

A flotation recovery of more than 98% was achieved at a collector dosage of 0.9 kg/ton with a concentrate P<sub>2</sub>O<sub>5</sub> content of 28.51% in the presence of picobubbles. However, in the absence of picobubbles, the maximum flotation recovery was 88.72% achieved at a frother dosage of 10 ppm and collector dosage of 0.9 kg/t.

#### **Effect of Bubble Generators**

To evaluate the effect of various bubble generators on coarse phosphate separation, flotation experiments were performed at different superficial air velocities using sparger only, static mixer only, both static mixer and sparger, both static mixer and cavitation tube, and three bubble generators combined. The experimental results indicated that the use of both a cavitation tube and static mixer as bubble generators produced the highest

phosphate recovery. The sparger was almost useless in the presence of both a static mixer and cavitation tube. The use of picobubbles also significantly decreased the reagent and gas flow rate required.

### **Effect of Centrifugal Gravity Enhanced Flotation**

To evaluate the effect of a specially designed column bottom that takes advantages of centrifugal gravity separation on coarse phosphate separation, a number of flotation experiments were performed at several feed rates under different conditions: (1) without specially designed bottom or picobubbles, (2) with specially designed bottom but without picobubbles, (3) without specially designed bottom but with picobubbles, (4) with specially designed bottom and picobubbles. The collector and frother dosages were fixed at 0.9 kg/ton and 10 ppm, respectively. The specially designed column bottom increased the flotation recovery by up to 14% in the absence of picobubbles, although this increase was reduced to about 7% in the presence of picobubbles.

### **Statistically Designed Flotation Experiments**

To determine the optimum condition and evaluate the interactions of various parameters of the column flotation process, Design-Expert software was used for the Box-Behnken experimental design. Process parameters considered in the experimental design included gas flow rate, collector dosage, frother dosage and slurry flow rate ratio (flow rate in cavitation tube/flow rate in static mixer). The experimental results show that the collector dosage had much more significant effect on flotation recovery than air flow rate and frother dosage. The contours of  $P_2O_5$  recovery between collector dosage and slurry flow rate ratio revealed that, at a given  $P_2O_5$  recovery, increasing slurry flow rate ratio decreased the collector dosage. The contours of  $P_2O_5$  recovery between frother dosage and slurry flow rate ratio at the midpoint of air flow rate and collector dosage showed that, at a given  $P_2O_5$  recovery, the frother dosage can be reduced considerably by increasing the slurry flow rate ratio.

### **COLUMN FLOTATION WITH CF INDUSTRIES PHOSPHATE SAMPLE B**

The flotation test results of the CF Industries phosphate sample B (significantly different from sample A) indicate that flotation recovery was more sensitive to collector dosage in the absence of picobubbles than in the presence of picobubbles. The flotation recovery increased consistently as the collector dosage increased from 0.3 to 0.9 kg/t in the absence of picobubbles. The presence of picobubbles significantly increased flotation recovery, especially at lower collector dosages. At a given flotation recovery, the presence of picobubbles reduced the required dosage of collector. To achieve about 80%  $P_2O_5$  recovery, 0.9 kg/t collector was required in the absence of picobubbles, while in the presence of picobubbles, only 0.3 kg/t collector was needed.

## **COLUMN FLOTATION WITH MOSAIC PHOSPHATE SAMPLE**

The  $P_2O_5$  content and A.I. (aluminum and iron) content of the Mosaic phosphate sample were 12.22% and 63.35%, respectively. The presence of picobubbles increased flotation recovery by 14% at lower collector dosages. To achieve 90%  $P_2O_5$  recovery, 0.7 kg/t collector was required without picobubbles and 0.4 kg/t collector with picobubbles. In the absence of picobubbles, the  $P_2O_5$  recovery decreased from about 88% to 62% as the feed rate increased from 240 g/min to 600 g/min. In the presence of picobubbles, the  $P_2O_5$  recovery decreased slightly from about 98.4% to 97.9% as the feed rate increased from 240 g/min to 360 g/min. The use of picobubbles increased  $P_2O_5$  recovery as much as 23% at 90% A.I. rejection.

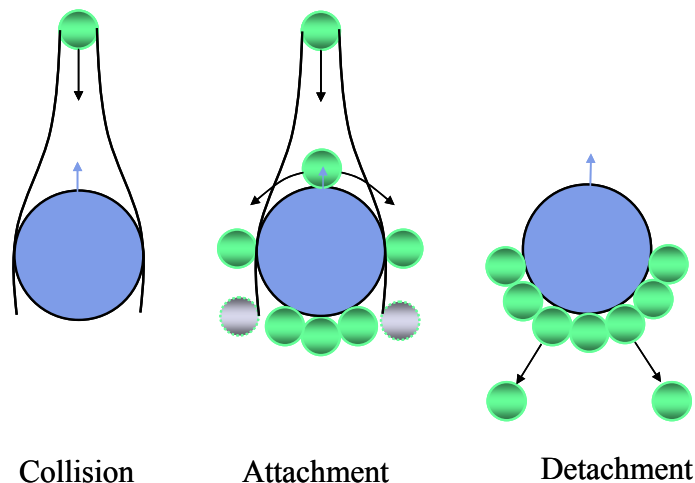
In summary, use of both a cavitation tube and static mixer as bubble generators for the flotation column to produce optimum bubble size distribution was very beneficial to coarse phosphate flotation, improving separation performance and decreasing collector and frother dosage. Picobubble column flotation, assisted by centrifugal gravity separation of phosphate particles, significantly improved separation performance.

## INTRODUCTION

About 30% of the world phosphate production in 1990 was produced by the United States (Bartels and Gurr 1994). This level of production has continued to the present. The Florida phosphate industry generates up to 85% of the United States phosphate rock.

A typical phosphate beneficiation process in central Florida includes washing, classification, fatty acid flotation, acid scrubbing, and amine flotation. The phosphate ore is washed and classified into three major size fractions. The coarse +1.18 mm (+16 mesh) portion is primarily phosphate pebble and no further upgrading is needed. The fine -106  $\mu\text{m}$  phosphate (-150 mesh) portion is discarded as the slimes. The intermediate -1 mm + 106  $\mu\text{m}$  (-16 +150 mesh) portion is a mixture of quartz and phosphate minerals. Beneficiation of this size fraction is often accomplished using the “Crago” two-stage froth flotation process. It is well known that the flotation recovery of coarse flotation feed (-16 + 35 mesh) is often below 80%. The combined loss of phosphate in flotation tailings and fine phosphate slimes usually amounts to about 40% of the original phosphate value (Patrick and Albarelli 1995).

The particle-bubble collision, attachment, and detachment are the most critical steps in the flotation process, as shown in Figure 1. The low flotation recovery of fine particles is mainly due to the low probability of bubble-particle collision, while the main reason for poor flotation recovery of coarse particles is the high probability of detachment of particles from the bubble surface. The efficient capture of hydrophobic particles by air bubbles is the key to effective flotation.



**Figure 1. Schematic of Particle-Bubble Collision, Attachment and Detachment.**

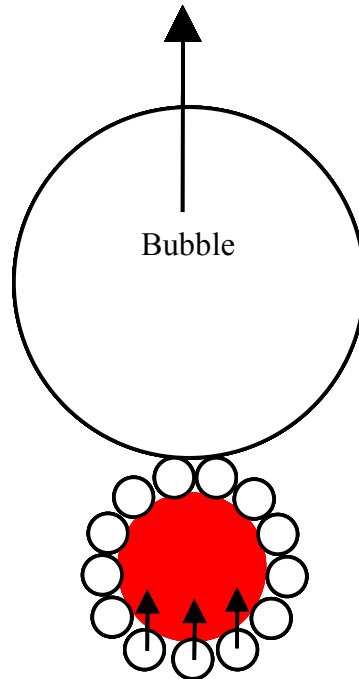
Collision: A particle is collided with a bubble as a result of a sufficiently close encounter, which is determined by the hydrodynamics of the flotation environment. The probability of collision ( $P_c$ ) can be calculated from stream functions for quiescent conditions. Some equations, derived by Yoon and Luttrell (1989, 2000), Schubert and Bischofberger (1979), Sutherland (1949), Gaudin (1957), Weber (1983) and Paddock (1983), show that  $P_c$  increases with increasing particle size and decreasing bubble size.

Attachment: Only those hydrophobic particles whose induction time is smaller than the sliding time can be attached to air bubbles. The attachment process is selective and the difference in attachment probability ( $P_a$ ) of different particles determines the selectivity of flotation. Yoon (2000) has shown that the probability of adhesion can be determined from the induction times or predicted using various surface chemistry parameters that determine the surface forces of particles and bubbles. Dai and others (1998) and Ralston and others (1999) studied the effect of particle size on attachment efficiency both experimentally and analytically. They found that  $P_a$  decreases with increasing particle size and increases with increasing particle hydrophobicity. Yoon and Luttrell (1989) showed that  $P_a$  increases with decreasing induction time and decreasing particle size;  $P_a$  also increases with decreasing bubble size until the bubble size becomes too small. Although the use of a higher dosage of collector improves particle hydrophobicity and thus increases  $P_a$ , it increases the operation cost. A better approach to increasing  $P_a$ , investigated in this program, is based on the use of picobubbles on the particle surface.

Detachment: Some of the particles attached to air bubbles detach from the bubble surfaces and drop back into the pulp phase. Particle detachment occurs when detachment forces exceed the maximum adhesive forces. One potential source of excessive forces is bubble oscillations caused by particle-bubble collisions. Kirchberg and Topfer (1965) showed that bubble collisions with large particles resulted in detachment of many particles from the bubble surface. Cheng and Holtham (1995) measured particle-bubble detachment forces by means of a vibration technique and found that the amplitude of oscillations imposed on the bubbles is the dominant factor in the detachment process.

Fundamental analysis indicated that the use of smaller bubbles is the most effective approach to increase the probability of collision and reduce the probability of detachment. The term “picobubbles” refers to bubbles with a size under  $1\ \mu\text{m}$  that are characterized by high collision probability, low detachment probability, low ascending rate, and high free surface energy. The picobubbles can be produced via Venturi cavitation tube; a specially designed column was developed to achieve this goal. Picobubbles are selectively attached onto the hydrophobic particles and act as the secondary collector on the particle surface, lowering collector dosage and reducing the effective density of the bubble particle aggregate, as shown in Figure 2.





**Figure 2. Coarse Particle Flotation Enhanced by Cavitation.**

The overall objective of the proposed research program was to develop a picobubble flotation process for enhanced recovery of coarse phosphate particles. A specially designed flotation column that utilizes cavitation-generated picobubbles has been investigated to achieve this goal. Specific objectives were:

- (1) To develop the most effective approach for bubble-particle collision and attachment, and to minimize the detachment probability of particles.
- (2) To design and construct an advanced flotation column that incorporates centrifugal gravity separation and picobubble flotation.
- (3) To perform separation experiments to evaluate the metallurgical performance of the specially designed column under different operating conditions.

## METHODS AND TECHNIQUES

### FLOTATION FEED SAMPLES

Two coarse phosphate samples from CF Industries and one phosphate sample from Mosaic company were collected after consultation with the FIPR Project Manager. The samples were collected from the plant conditioner feed streams and placed in sealed containers. The phosphate samples were thoroughly mixed and split into small lots for storage in the lab. Two representative samples were taken for size distribution analysis and chemical analysis.

### CHEMICAL ANALYSIS

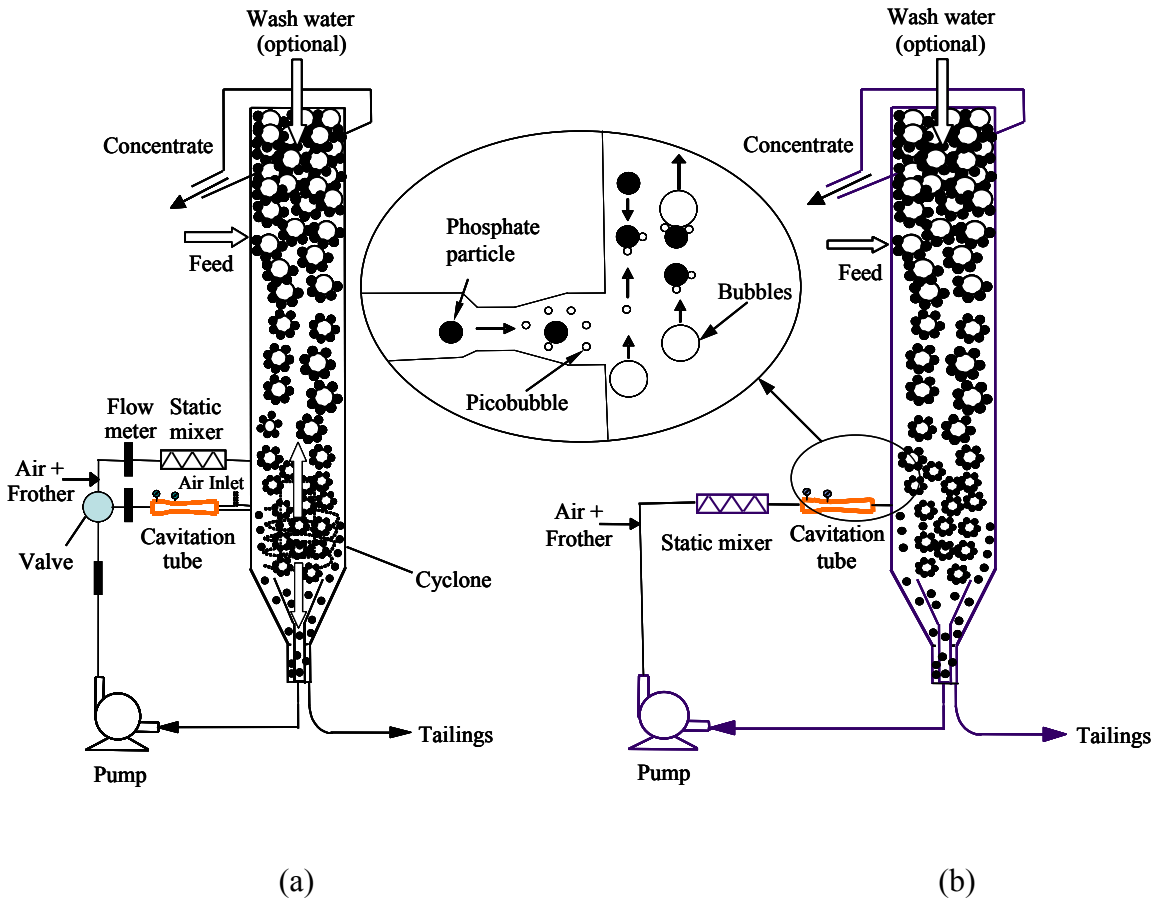
$P_2O_5$  content analysis: This was performed according to Section IX, No. 3, Method C as described in *Methods Used and Adopted by the Association of Fertilizer and Phosphate Chemists* (AFPC 2001). About 1 gm of the dried and ground representative sample was digested in 50 ml of boiling aqua regia on a hotplate until the reaction was complete. After cooling, this solution was filtered through a Whatman 42 filter paper into a 1000 ml volumetric flask. The filter paper and residue were then washed at least five times to remove all traces of dissolved salts and acid. The filtrate was diluted with distilled water and thoroughly mixed. The concentrations were analyzed using an Inductively Coupled Plasma (ICP) emission spectrometer.

Acid insoluble analysis: Acid soluble components and acid insoluble components were analyzed using the method described in Section IX, No. 4, Method A of the AFPC methods manual (2001). Acid-insoluble material was measured as an aqua-regia-insoluble material. Insoluble analysis was performed using the gravimetric method. Using a clean, tarred crucible, the filter paper and residue obtained from the digestion step was ignited at 900°C. After the crucible cooled, the acid insoluble in the sample was calculated.

### FLOTATION REAGENTS

The collector employed in the present study was a mixture of a fatty acid (FA-18G) and fuel oil at 1:1 ratio by weight. FA-18G is the reagent used by CF Industries. A glycol frother (F-507) was used. Both the frother and collector were obtained from ArrMaz Custom Chemicals Inc. Soda ash was used as the pH modifier for the three feed samples. Sodium silicate was used for some tests as a depressant.

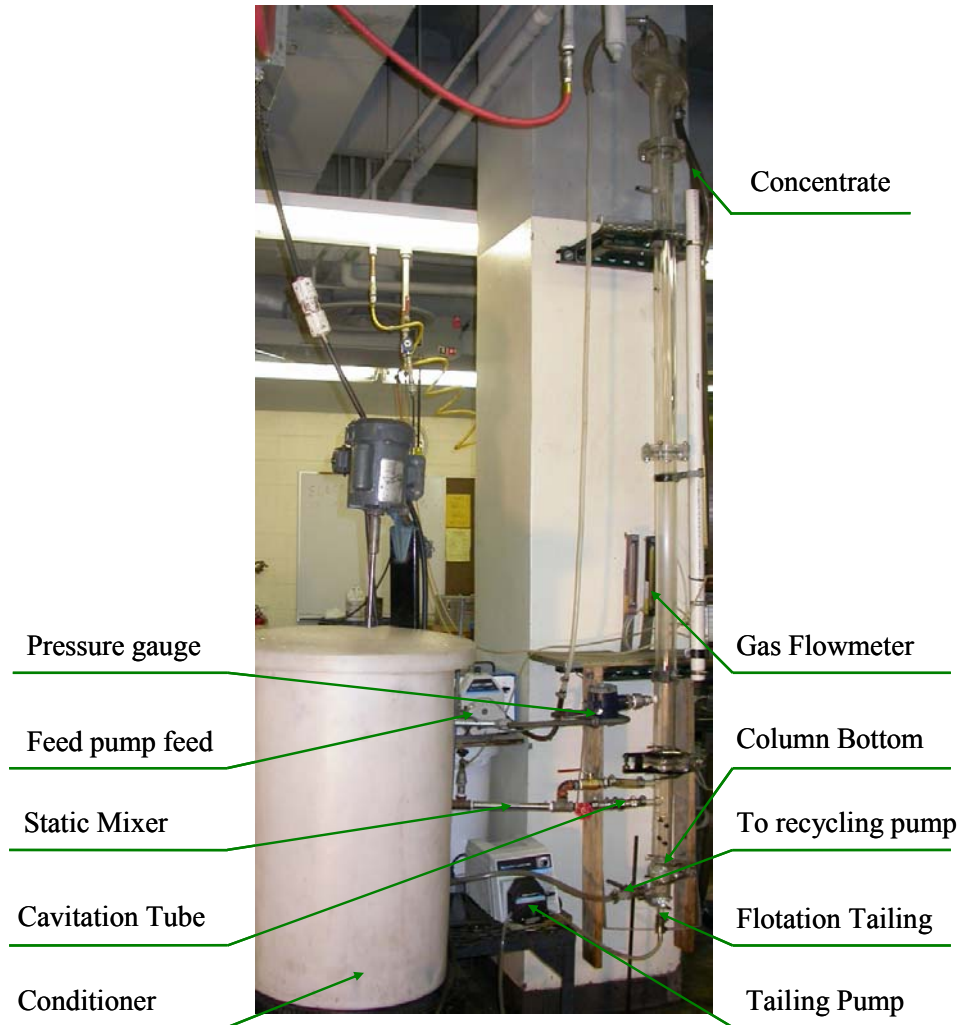
## PHOSPHATE FLOTATION WITH SPECIALLY DESIGNED COLUMN



**Figure 3. Schematic of Column Flotation System.**

Figure 3 shows schematic diagrams of two column flotation systems: (a) cavitation tube and static mixer installed in parallel; (b) cavitation tube and static mixer installed in series. A photograph of the fabricated flotation column is shown in Figure 4. The column was made of Plexiglas of 2 inches in diameter and up to 6 feet in height. In order to investigate the effect of column height on flotation performance, the column was composed of several removable segments so that the total height can be adjusted from 2 feet to 6 feet. The cavitation tube and the static mixer, both of which are compact and have no moving parts, were used to generate picobubbles and microbubbles, respectively. Due to the rapid drop of static pressure, the picobubbles are formed on the surface of phosphate particles and independently in the liquid and thus act as a secondary collector, enhancing the particle attachment probability to the larger bubbles and reducing the detachment probability in the flotation cell. The picobubbles were generated from air naturally dissolved in water by pumping flotation slurry already conditioned with reagents through the cavitation tube. Since the cavitation tube was used as the primary bubble generator and the static mixer as the secondary bubble generator, only a small

amount of air was needed for the static mixer to produce microbubbles to provide sufficient levitation for bubble/particle aggregates, further cutting the cost of beneficiation.



**Figure 4. Specially Designed Flotation Column.**

Since tailings are discharged from the bottom, a well-designed column bottom is one of the key components necessary for minimizing loss of valuable minerals and enhancing the overall performance of column flotation. The flotation column used in the present study integrates the centrifugal hydrocyclone separation by feeding the recycling slurry tangentially to the column under pressure and the slurry rotates inside the column at a high speed. The coarser and higher-density particles move outwards toward the column wall. The finer and lower-density particles or bubble-particle aggregate move inward toward the center and go up in the column or go to the recycling pump.

The flotation procedure is described as follows:

(1) Fatty acid (FA-18G) and fuel oil were mixed thoroughly at 1:1 ratio by weight as the flotation collector. The collector was used at varying dosages of 0.3, 0.6, 0.9, 1.2, and 1.5 kg/t.

(2) Phosphate samples were employed to make flotation feed slurry. Sodium hydroxide was used to adjust the pH between 9.1 and 9.5.

(3) The flotation feed was conditioned for three minutes at a predetermined solids concentration (75% solids for coarse phosphate) using a mechanical agitator.

(4) The conditioned phosphate sample was diluted to 25% solids content by weight and fed tangentially into the flotation column through a peristaltic pump. The tailing flow rate was controlled by another peristaltic pump.

(5) A glycol frother (F-507) was used at varying concentration of 5, 10 and 15 ppm for the coarse phosphate flotation tests.

(6) The total recycling flow rate for picobubble and microbubble generation was maintained at 8.0 l/min, which split through a three-way connector into the cavitation tube and the static mixer. As a result, the flow rate ratios (flow rate in the cavitation tube/flow rate in the static mixer) could be adjusted.

## **MICROFLOTATION EXPERIMENTS ON FLOTATION EFFICIENCY**

The microflotation setup is illustrated in Figure 5. The suspension was kept in the cone flask and stirred with a magnetic stirrer to keep the slurry homogeneous. The compressed air went into the flask and pushed the homogeneous suspension to the Hallimond tube. A three way tap was used to divide the Hallimond tube into upper and lower parts. The lower part was full of the suspension while the upper part was filled with the clear water. Flotation air bubbles were injected through the opening at the bottom of the tube. A container was utilized to collect the slurry overflow.



**Figure 5. Microflotation Experimental Setup.**

Microflotation experiments were performed to determine the particle collection efficiency of bubbles during flotation. The flotation collection efficiency is related to bubble size, particle size and contact angle of particles. To make accurate measurements, the suspension in the Hallimond tube should be kept at a constant solids concentration. However, when slurry was pushed into the Hallimond tube, all the particles began to settle down and the solids concentration decreased. To maintain the concentration in a certain range, the testing time should be maintained within a certain limit. In our experiments, approximately 60 bubbles were generated in 30 seconds for each test. If the particles had a relatively large size and settled quickly, the experiments were performed in two batches, each with 30 bubbles in 15 seconds. Because coal particles have low density and low settling velocity, they are ideal subjects for investigation of flotation fundamentals. The number of particles floated by each bubble was calculated by dividing the total floated particles by the number of bubbles. Division of the value by the number of particles in the suspension column (not including the particles already settled down) yielded the collection efficiency. The flotation efficiency was defined as the product of the collection efficiency multiplied by the number of bubbles. Bubbles of different sizes were produced using syringes or microsyringes of different specifications.

The experimental procedure was as follows:

- (1) Diluted water suspensions (about 0.1% by mass) of particles were stirred in a conditioning cell for 5 minutes with a magnetic stirrer.
- (2) The three-way tap was closed and the section of the flotation column below the tap was open to air through the overflow weir.

(3) Clean water was added into the column from the top to the desired level.

(4) At the end of the conditioning period, compressed air was introduced to force the suspension into the column. This upward flow prevented particle settling prior to flotation.

(5) When the suspension was about to overflow from the overflow weir which was at the same height as the three-way tap, the suspension flow was stopped and the three-way tap was turned so that the suspension came into contact with the clear water above. This caused little turbulence and no particles were entrained into the clear water.

Immediately after Step 5, single bubbles were generated and timed flotation started. Flotation lasted 30 seconds with a total of 60 bubbles.

The number of particles floated by each bubble was calculated by dividing the total floated particles by the number of bubbles.

Division of this value by the number of particles in the suspension column yielded the collection efficiency.

## RESULTS AND DISCUSSION

### MICROFLOTATION EXPERIMENTS ON FLOTATION EFFICIENCY

Microflotation experiments were conducted to provide a better understanding of bubble size and particle size on flotation efficiency and thus foster development of the innovative process to enhance coarse phosphate recovery. The microflotation setup is illustrated in Figure 5. Microflotation experiments were performed to determine the particle collection efficiency of bubbles during flotation. The flotation collection efficiency is related to bubble size and particle size. The collection efficiency in the absence of surfactant is listed in Table 1 for different bubble and particle sizes.

**Table 1. Collection Efficiency of Glass Beads.**

Bubble Size (mm)	Particle Size ( $\mu\text{m}$ )		
	35	85	203
2	4.50E-09	6.54E-08	2.16E-08
1.5	3.40E-09	4.34E-08	1.08E-08
0.8	1.20E-09	2.82E-08	8.00E-09

Table 1 shows that the flotation efficiency by a single bubble decreased with reducing the bubble size due to reduced surface area. It is obvious from Table 1 that the collection efficiency is higher for small bubbles for a given gas flow rate since the number of bubbles is inversely proportional to the third power of bubble diameter. In other words, if the bubble diameter decreased from 1.5 mm to 0.5 mm, the number of bubbles increased  $3^3$  or 27 times. Therefore the flotation efficiency, defined as the product of the collection efficiency multiplied by the number of bubbles, was greater for smaller bubbles, as shown in Figures 6 and 7.

For a given bubble size, coarser particles generally showed higher collection efficiency. Since the solids concentration was maintained constant at 0.1% for all particle sizes, there were fewer coarser particles in the Hallimond tube. The detachment did not play a very important role in the collection efficiency when the particle size was still relatively small compared to bubble size.



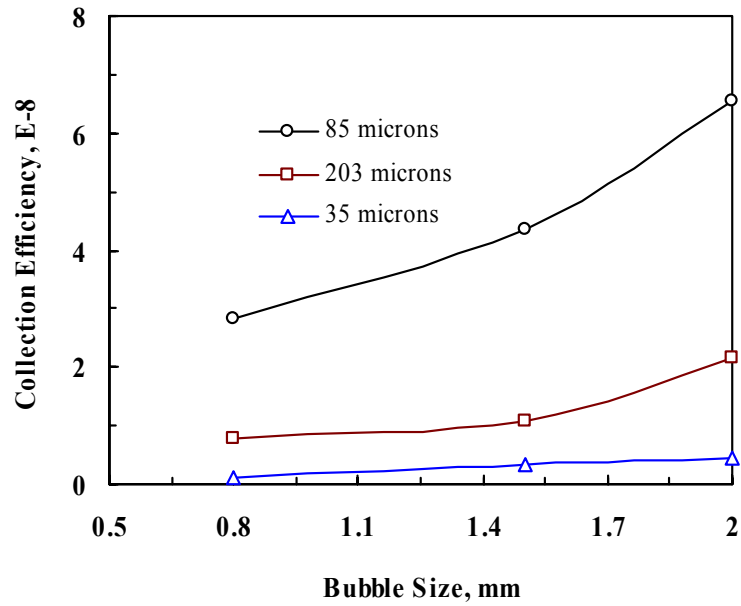


Figure 6. Collection Efficiency Versus Bubble Size with Single Bubble (Glass Beads).

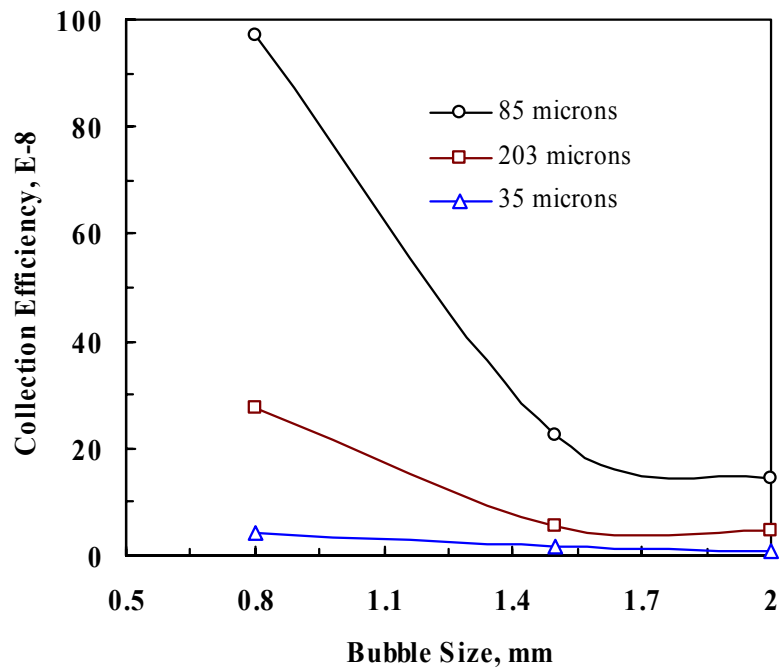
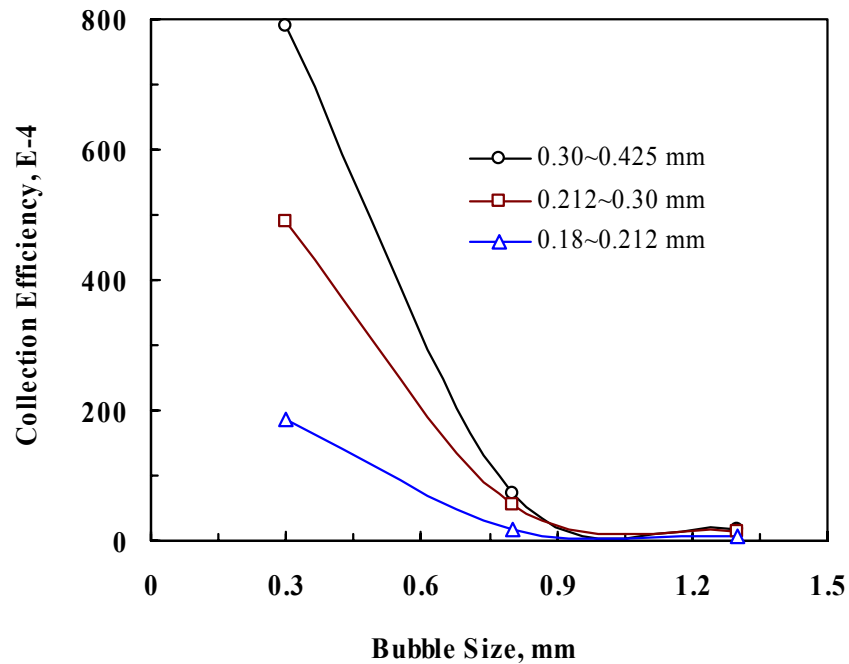


Figure 7. Collection Efficiency Versus Bubble Size at Same Air Flow Rate (Glass Beads).

Figure 8 shows the collection efficiency of different size coal particles with varying bubble size at the same air flow rate. The addition of surfactant reduced bubble size and the collection/flotation efficiency increased as the bubble size decreased. During the experiment, it was also observed that the collection efficiency increased partly because the surfactant induced some particle coagulation. This effect was more significant with smaller particles.



**Figure 8. Collection Efficiency Versus Bubble Size at Same Air Flow Rate.**

Based on the relationship between collection efficiency and bubble size and particle size, it can be concluded:

(1) For a given air flow rate, the bubble size should be reduced to improve flotation rate.

(2) Within a certain range of particle size, the collection efficiency can be increased by increasing the particle size. However, when the particle size exceeded a certain limit, the collection efficiency decreased when particle size increased due to high detachment rate.

(3) For fine particles, the use of surfactant reduced bubble size and induced particle coagulation, enhancing collection efficiency and flotation efficiency.

## COLUMN FLOTATION FEED SAMPLES

Two phosphate samples from CF Industries and one from Mosaic Company were collected. Sieve and chemical analyses of these feed samples are shown in the following tables and figures.

### CF Phosphate Sample A

Phosphate flotation feed sample A was acquired from CF Industries. The phosphate sample contained 10.41% moisture. It was wet screened into 12 size fractions. The size distribution data is shown in Table 2 and the cumulative screen undersize percentage is plotted against particle size in Figure 9. Most particles, i.e., 61.99%, are coarser than 50 mesh or 0.3 mm. Fewer than 3% particles are smaller than 140 mesh or 0.106 mm and few particles are larger than 16 mesh or 1.18 mm. Our research efforts were focused on the 0.425 ~1.18 mm portion, which accounted for 38.71%.

**Table 2. Phosphate Size Distribution Data.**

Mesh Number	Size (mm)	Mean (mm)	Wt (%)	Cumulative Overscreen	Cumulative Underscreen
+16	+1.18	1.67	0.07	0.07	100.00
16×20	1.18~0.85	1.02	1.44	1.51	99.93
20×30	0.85~0.6	0.73	11.49	13.00	98.49
30×40	0.6~0.425	0.51	25.78	38.78	87.00
40×50	0.425~0.3	0.36	23.21	61.99	61.22
50×60	0.3~0.25	0.28	11.80	73.79	38.01
60×80	0.25~0.18	0.22	15.49	89.28	26.21
80×100	0.18~0.15	0.17	4.14	93.43	10.72
100×120	0.15~0.125	0.14	2.44	95.87	6.57
120×140	0.125~0.106	0.12	1.91	97.78	4.13
140×200	0.106~0.075	0.09	1.42	99.20	2.22
-200	-0.075	0.05	0.80	100.00	0.8
Total			100.00		

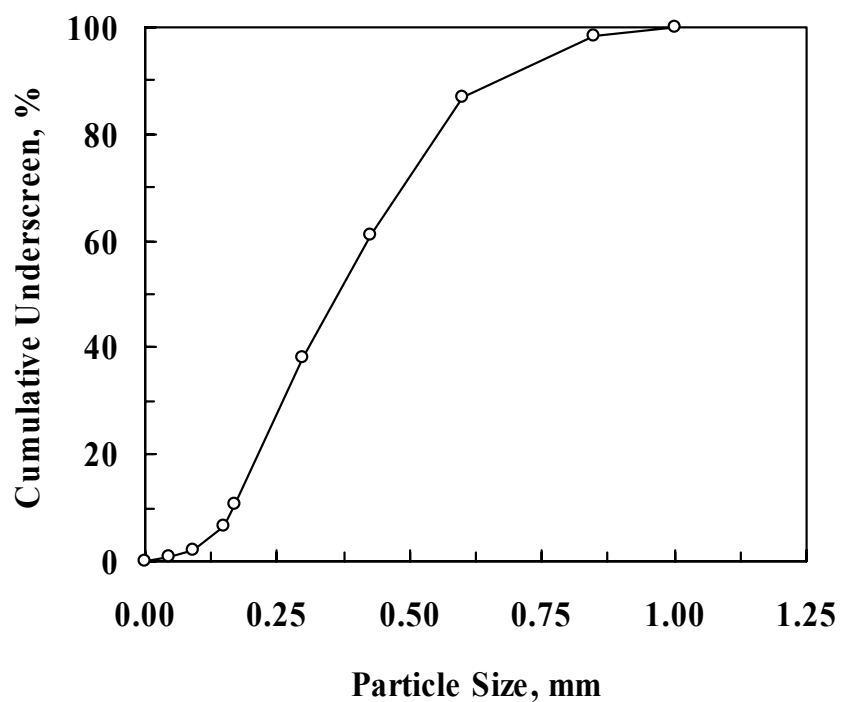


Figure 9. Cumulative Undersize Curve of Phosphate.

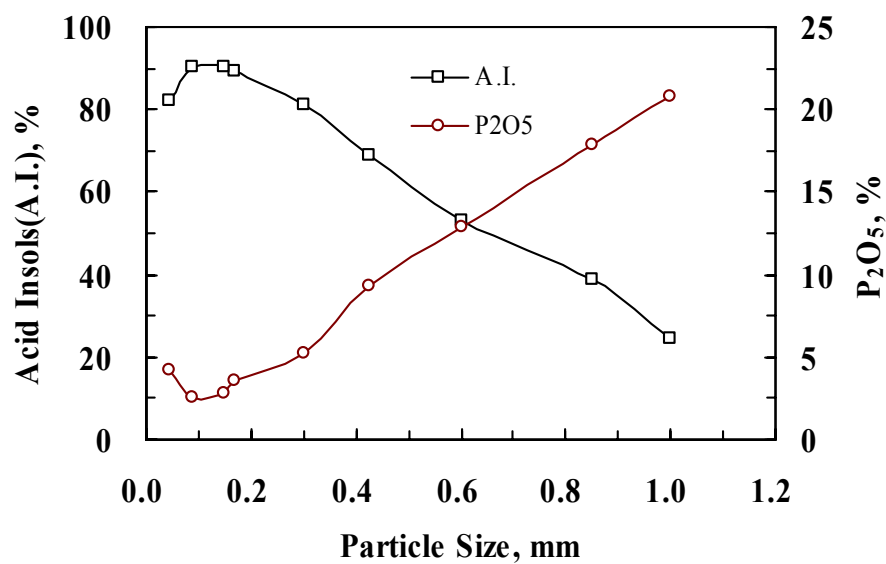


Figure 10. P<sub>2</sub>O<sub>5</sub> and Acid Insols (A.I.) Contents as a Function of Particle Size.

Figure 10 shows the  $P_2O_5$  content increased with increasing particle size while the A.I. content increased with decreasing particle size, except for the -200 mesh size fraction. Figure 11 shows the cumulative  $P_2O_5$  content and cumulative A.I. content as a function of particle size. The difference in  $P_2O_5$  content is reflected in the color and appearance of each size fraction, as shown in Figures 12 to 17.

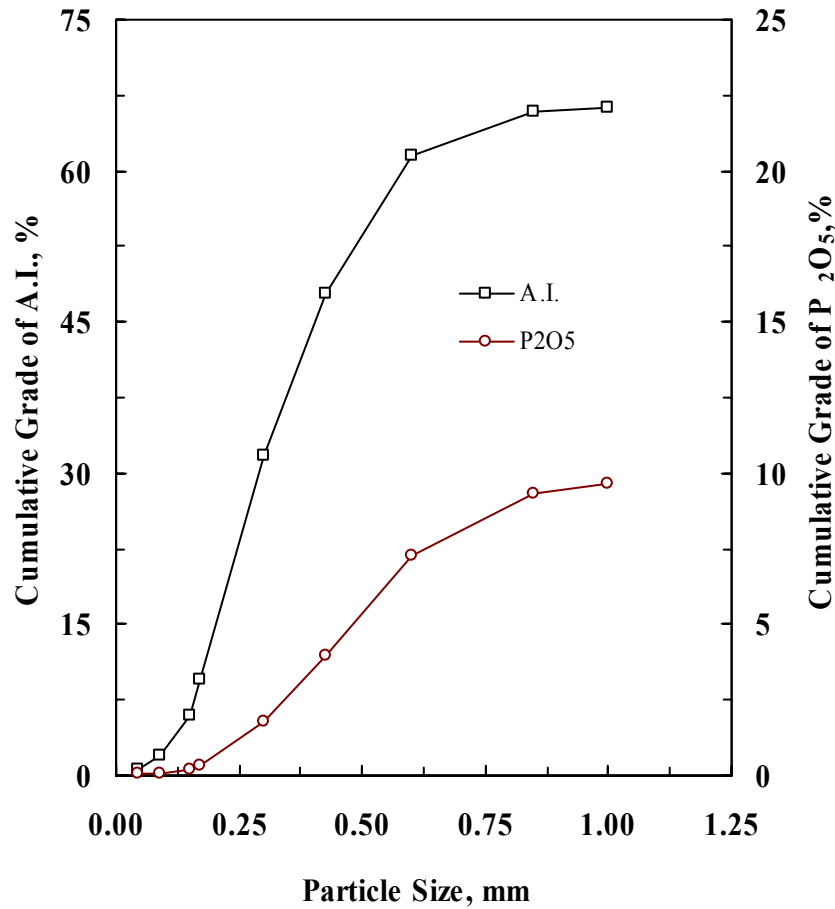
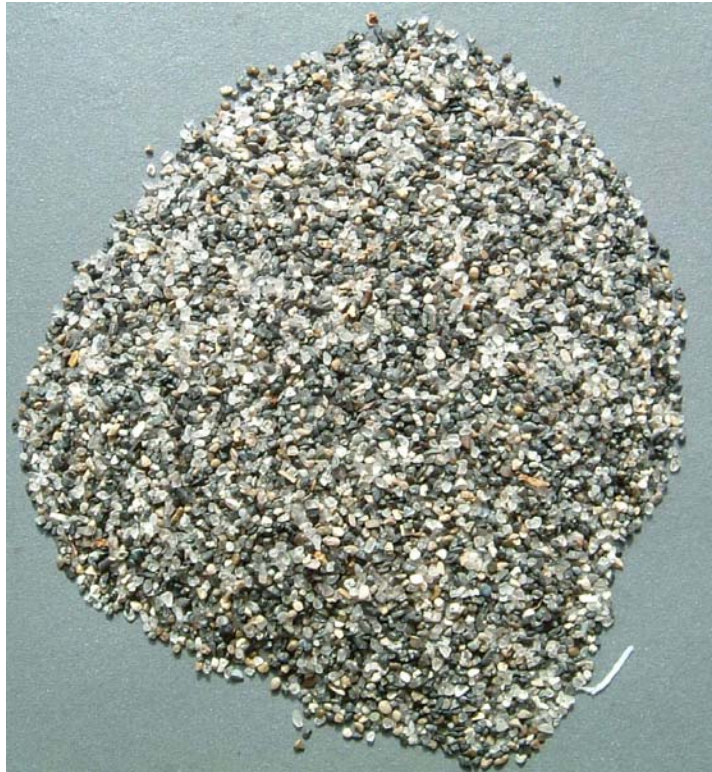


Figure 11. Cumulative Grades of  $P_2O_5$  and A.I. as a Function of Particle Size.



(a)



(b)

**Figure 12. Particle Size Fractions of CF Industries Phosphate Sample A: (a) +20 Mesh; (b) 20×30 Mesh.**





(a)



(b)

**Figure 13. Particle Size Fractions of CF Industries Phosphate Sample A: (a) 30×40 Mesh; (b) 40×50 Mesh.**





(a)



(b)

**Figure 14. Particle Size Fractions of CF Industries Phosphate Sample A: (a) 50×60 Mesh; (b) 60×80 Mesh.**





(a)



(b)

**Figure 15. Particle Size Fractions of CF Industries Phosphate Sample A: (a) 80×100 Mesh; (b) 100×120 Mesh.**



(a)



(b)

**Figure 16. Particle Size Fractions of CF Industries Phosphate Sample A: (a) 120×140 Mesh; (b) 140×200 Mesh.**



**Figure 17. Particle Size Fractions of CF Industries Phosphate Sample A: -200 Mesh.**

### **CF Phosphate Sample B**

Phosphate sample B collected from CF Industries is significantly different from sample A. Figures 18, 19 and 20 show the differences of the two phosphate samples in particle size distribution, A.I. contents of different particle size fractions, color and appearance. Sample A was mainly composed of black phosphate particles, while sample B is composed of brown phosphate particles.

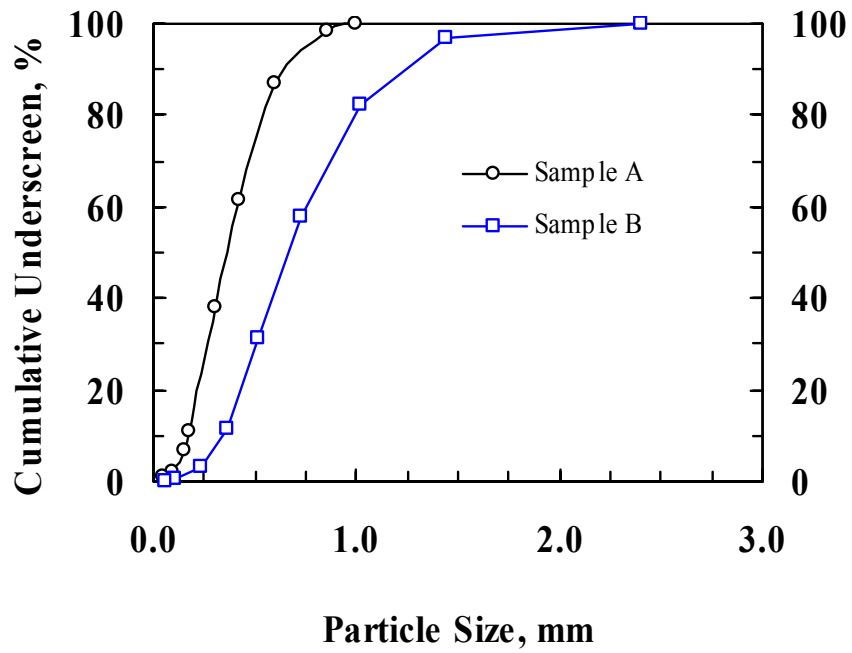


Figure 18. Particle Size Distribution of Two Phosphate Samples.

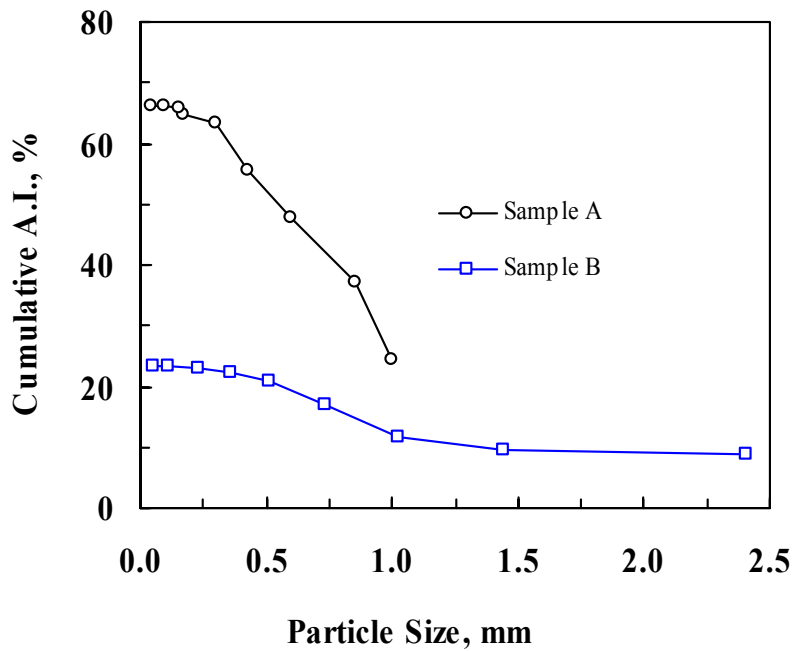
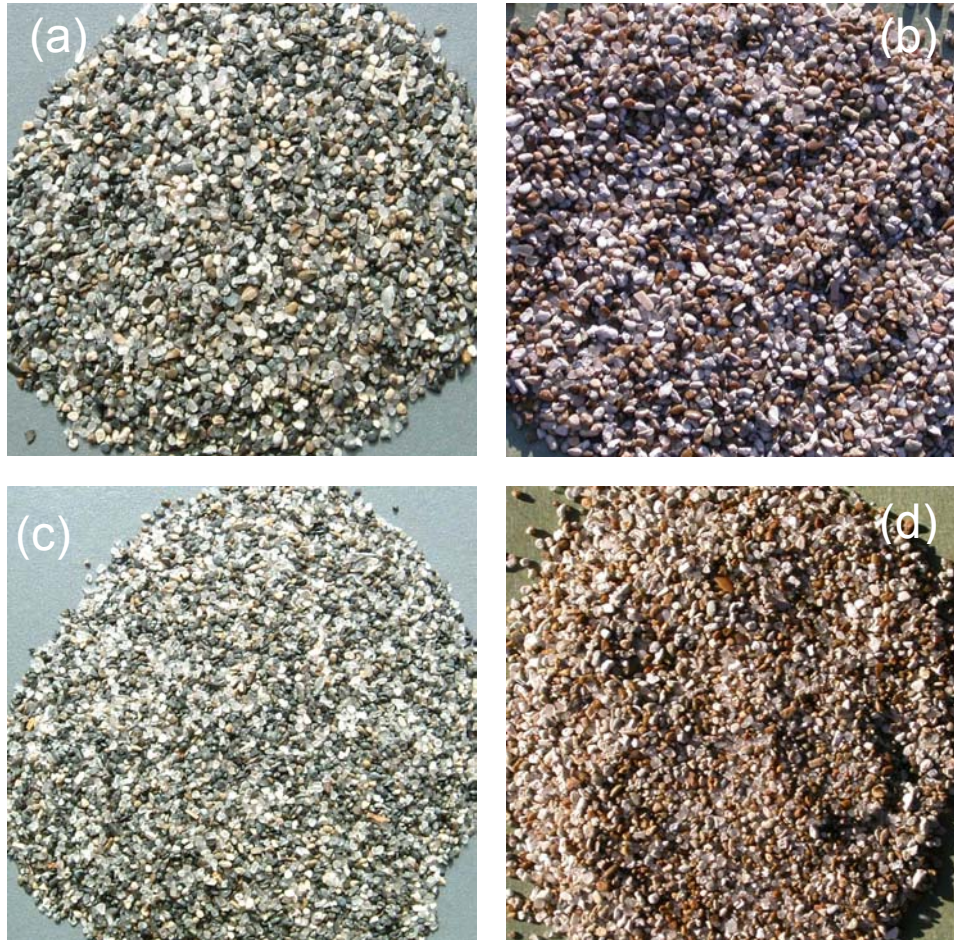


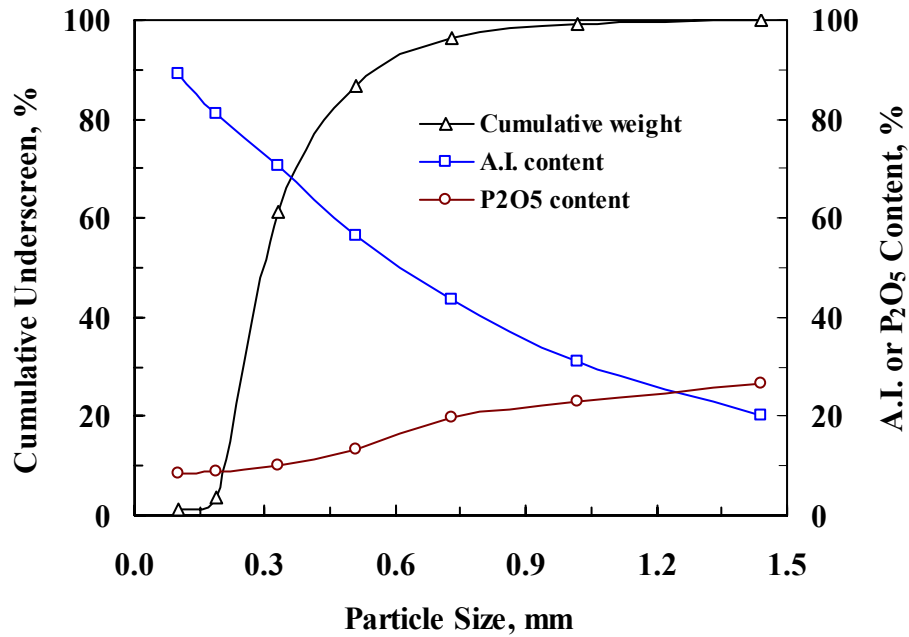
Figure 19. A.I. Contents of Different Particle Size Fractions.





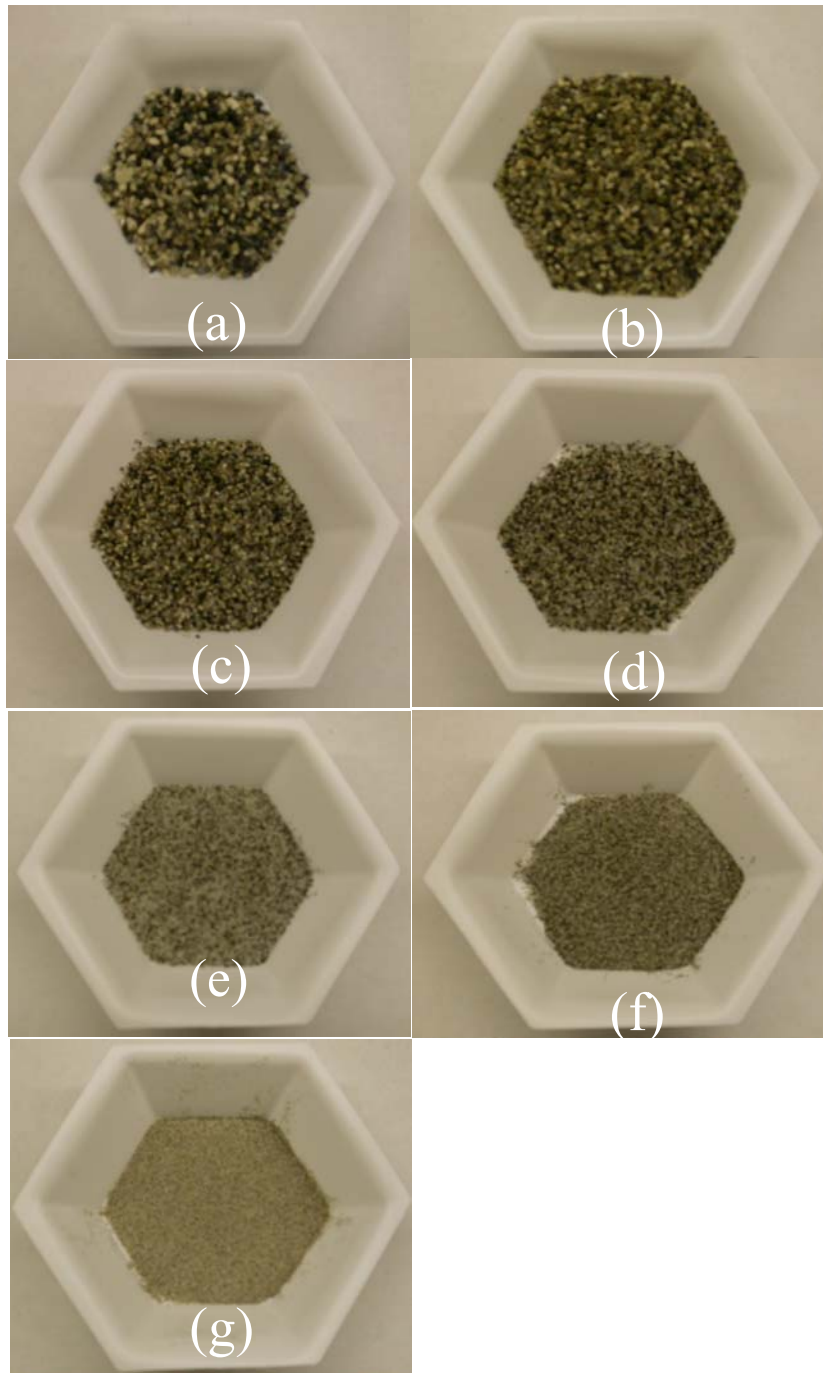
**Figure 20. Color and Appearance of Two Phosphate Samples: (a) 16×20 Mesh (Sample A); (b) 16×20 Mesh (Sample B); (c) 20×30 Mesh (Sample A); (d) 20×30 Mesh (Sample B).**

## Mosaic Phosphate Sample



**Figure 21. Particle Size Distributions, A.I. and P<sub>2</sub>O<sub>5</sub> Content of the Mosaic Sample.**

One flotation feed sample was collected from the Four Corners mineral beneficiation plant of the Mosaic Company. The P<sub>2</sub>O<sub>5</sub> content and A.I. content of the Mosaic phosphate sample were 12.2% and 63.4%, respectively. Figure 21 shows the cumulative weight content, P<sub>2</sub>O<sub>5</sub> content, and A.I. content in seven size fractions. The weight percent of the fraction that was coarser than 1.18 mm was less than 1% and the weight percent of the fraction that was finer than 0.5 mm was 61%. The P<sub>2</sub>O<sub>5</sub> content increased with increasing particle size, while the A.I. content decreased with increasing particle size. The difference in P<sub>2</sub>O<sub>5</sub> content is reflected in the color and appearance of each size fraction, as shown in Figure 22.



**Figure 22. Particle Size Fractions of Mosaic Phosphate Sample: (a) +16 mesh (+ 1.18 mm); (b) 16×20 Mesh (1.18 × 0.85 mm); (c) 20 × 30 Mesh (0.85 × 0.60 mm); (d) 30 × 40 Mesh (0.60 × 0.425 mm); (e) 40 × 65 Mesh (0.425 × 0.23 mm); (f) 65 × 100 Mesh (0.23 × 0.15 mm); (g) -100 Mesh (<0.15 mm).**

## PICOBUBBLE GENERATION

Figure 23 shows the picobubbles ( $<1 \mu\text{m}$ ) generated by the cavitation tube. Because of the higher surface free energy to be satisfied, the picobubble surface is very active. Picobubbles attach more readily to particles due to their lower ascending velocity and they also act as a secondary collector for particles.



**Figure 23. Picobubbles Generated by Cavitation Tube in a 2” Column.**

## COLUMN FLOTATION WITH CF PHOSPHATE SAMPLE A

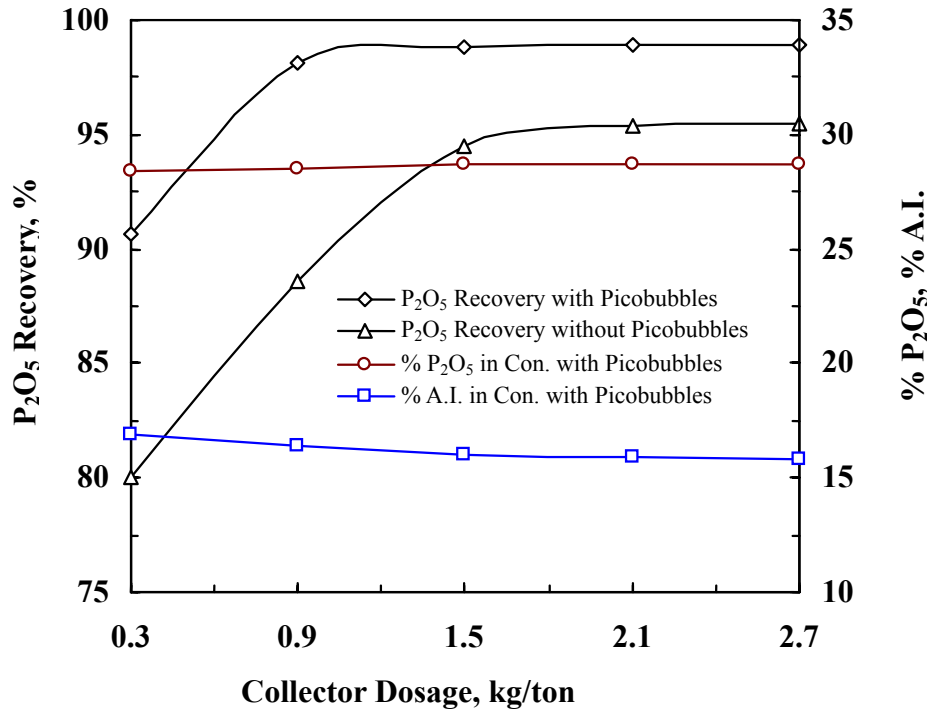
To evaluate the effect of picobubbles on coarse phosphate flotation, a number of flotation experiments were performed at varying collector and frother dosages, superficial air velocities, and solid feed rates using various bubble generators and a specially designed column bottom. A four-factor three-level Box-Behnken experimental design of flotation tests was conducted with CF phosphate sample A.

### Effect of Picobubbles

Figure 24 shows the effect of picobubbles on flotation recovery at varying collector dosages from 0.3 kg/t to 2.7 kg/t. The solid feed rate, superficial air velocity, and frother dosage were fixed constant at 240 g/min, 1.0 cm/s, and 10 ppm, respectively. The curves indicate that the flotation recovery increased significantly as the collector dosage increased from a dosage of 0.3 kg/t to 0.9 kg/t, after which the flotation recovery remained essentially constant. The maximum flotation recovery of more than 98% was achieved at a lower collector dosage of 0.9 kg/t in the presence of picobubbles, producing

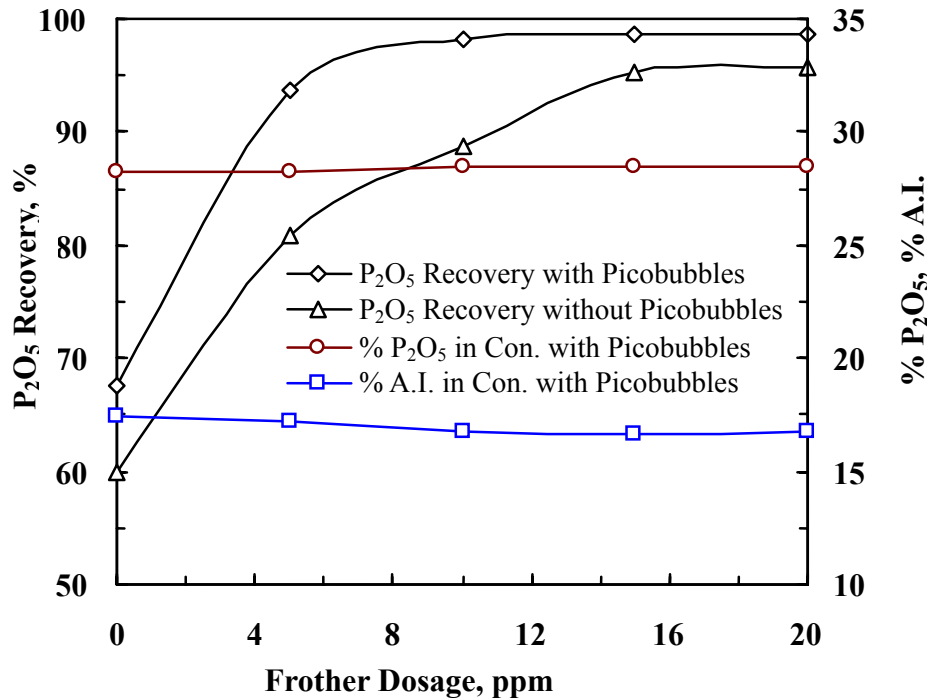


a concentrate of 28.5%  $P_2O_5$ . In contrast, the maximum flotation recovery was only 95%, which was achieved at a collector dosage of 2.1 kg/t in the absence of picobubbles. The improved flotation performance may be attributed to picobubbles that are selectively attached onto the hydrophobic particles, act as the secondary collector on the particle surfaces, and reduce the effective density of the bubble-particle aggregate.



**Figure 24. Effect of Picobubbles on Flotation Recovery at Varying Collector Dosages.**

Figure 25 shows the effect of picobubbles on flotation recovery at varying frother dosage from 0 ppm to 20 ppm. The solid feed rate, superficial air velocity, and collector dosage were fixed constant at 240 g/min, 1.0 cm/s, and 0.9 kg/ton respectively. The flotation recovery increased significantly as the frother dosage increased from a dosage of 0 to 5 ppm; after 10 ppm, the flotation recovery remained essentially constant. The flotation recovery of more than 98% was achieved at a frother dosage of 10 ppm with a concentrate  $P_2O_5$  content of 28.5%. However, in the absence of picobubbles, the flotation recovery was only 88.7% at a frother dosage of 10 ppm and collector dosage of 0.9 kg/t.



**Figure 25. Effect of Picobubbles on Flotation Recovery at Varying Frother Dosages.**

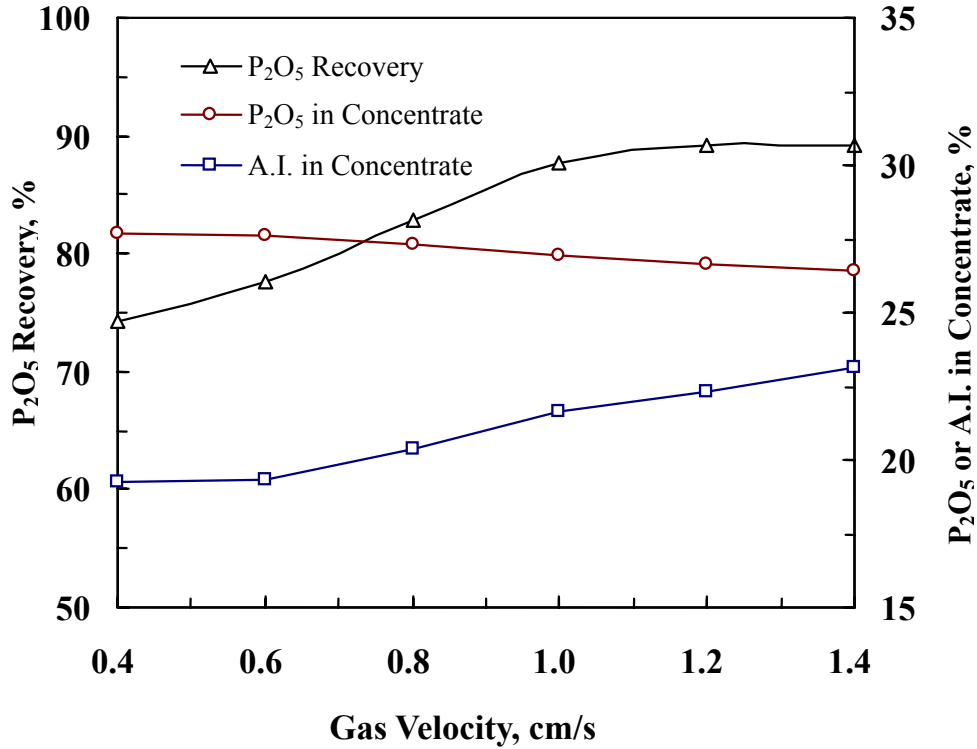
In summary, coarse phosphate flotation with picobubbles yields higher P<sub>2</sub>O<sub>5</sub> recoveries than without picobubbles at the same reagent dosages and aeration rate. The picobubbles enhanced coarse phosphate recovery and reduced flotation reagent consumption, thus reducing the operating cost and improving flotation efficiency.

### Effect of Bubble Generators

To evaluate the effect of various conventional bubble generators on coarse phosphate separation in the presence of picobubbles, flotation experiments were performed at varying superficial air velocities with different bubble generators: (1) sparger only, (2) static mixer only, (3) both static mixer and sparger, (4) both static mixer and cavitation tube, and (5) all three bubble generators combined. The solid feed rate, collector dosage, and frother dosage were fixed constant at 240 g/min, 0.9 kg/t and 10 ppm, respectively.

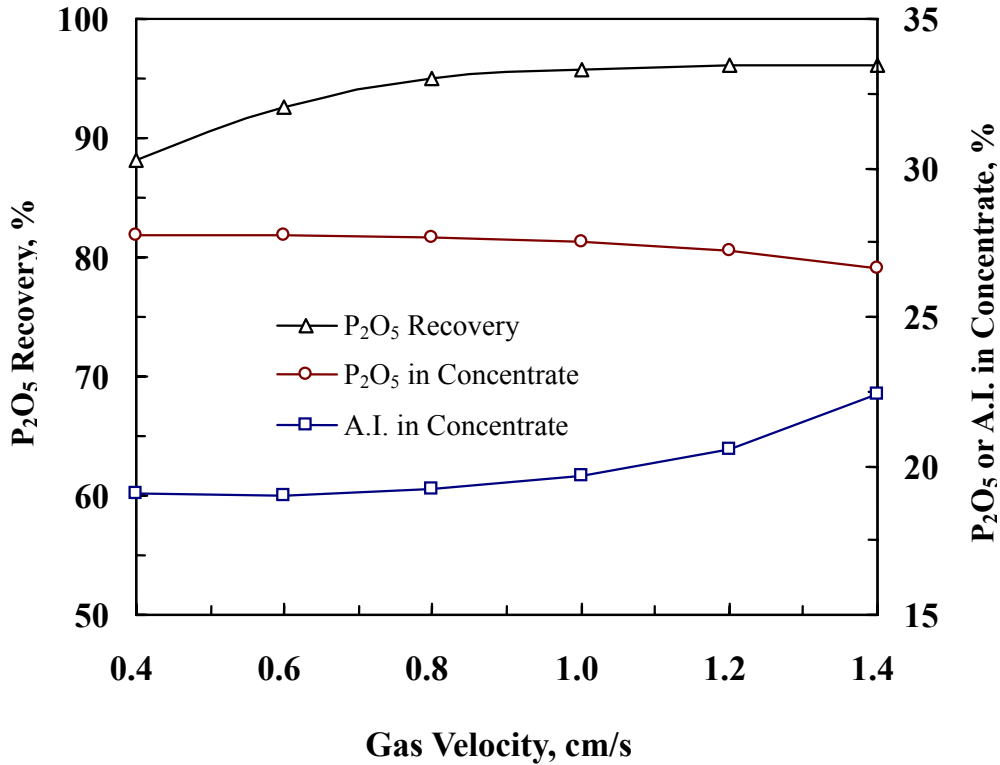
Figure 26 shows the effect of superficial air velocity on concentrate grade and flotation recovery with the sparger only. The flotation recovery increased from 74.2% to 89.1% as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the concentrate was about 27.6% and the A.I. content about 19.3% when the superficial air velocity ranged from 0.4 cm/s to 0.6 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the

concentrate decreased to 26.4% and the A.I. content in the concentrate increased to about 23.1 % as the superficial air velocity increased to 1.4 cm/s.



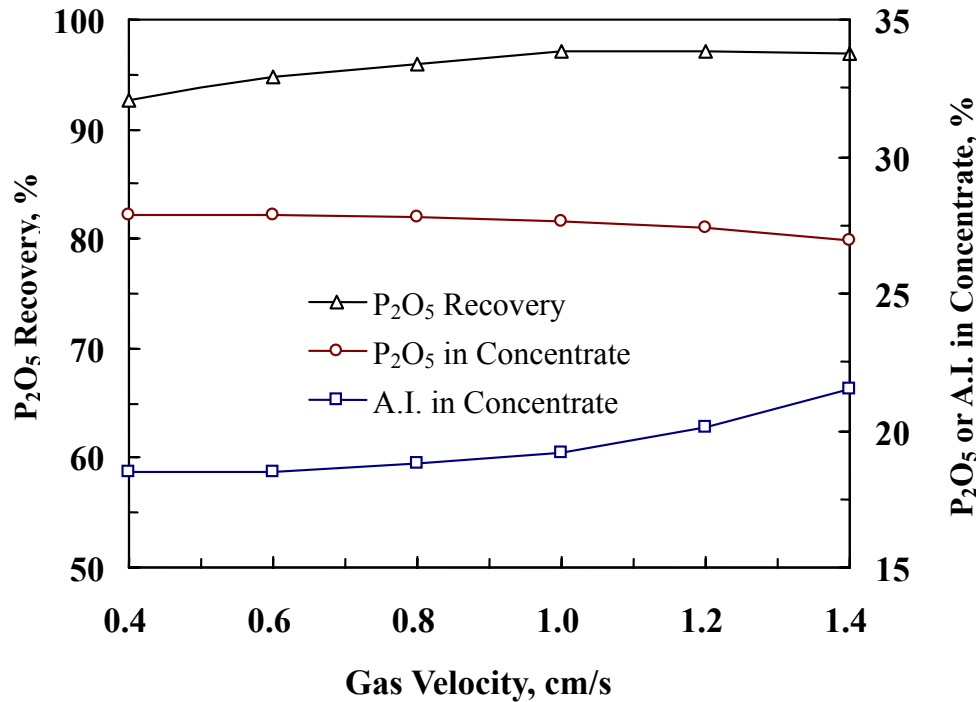
**Figure 26. Effect of Superficial Air Velocity on Concentrate Grade and Flotation Recovery with Sparger Only.**

Figure 27 shows the effect of superficial air velocity on concentrate grade and flotation recovery with the static mixer only. It can be observed from Figure 27 that the flotation recovery increased from 88.1% to 96.1% and the concentrate grade remained nearly constant as the superficial air velocity increased to 1.4 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the concentrate decreased from 27.7% to 26.7% and the A.I. content in the concentrate increased from nearly 19.0% to about 22.4% as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. A comparison of Figure 26 to Figure 27 indicates that the static mixer produced better separation performance.



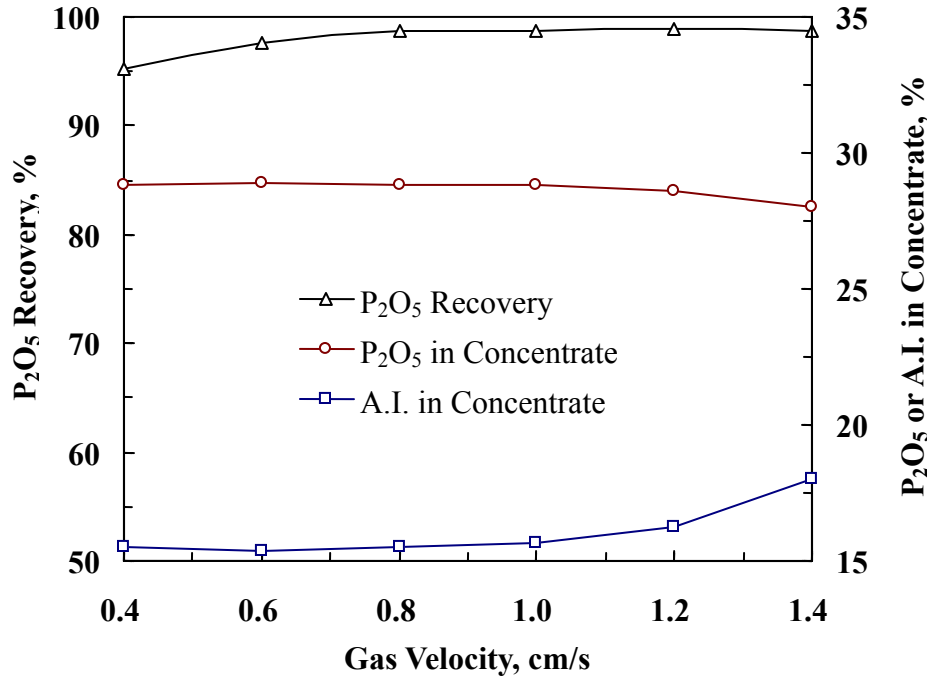
**Figure 27. Effect of Superficial Air Velocity on Concentrate Grade and Flotation Recovery with Static Mixer Only.**

Figure 28 shows the effect of superficial air velocity on concentrate grade and flotation recovery with both the static mixer (20% air flow rate) and sparger (80% air flow rate). Figure 28 shows that the flotation recovery increased from 90.6% to 96.9% and the concentrate grade remained nearly constant as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the concentrate decreased from 27.8% to 26.8% and the A.I. content in the concentrate increased from 18.9% to 21.8% as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. A comparison of Figure 28 to Figure 27 indicates that the sparger did not seem to help. In other words, no sparger was needed when the static mixer was used.



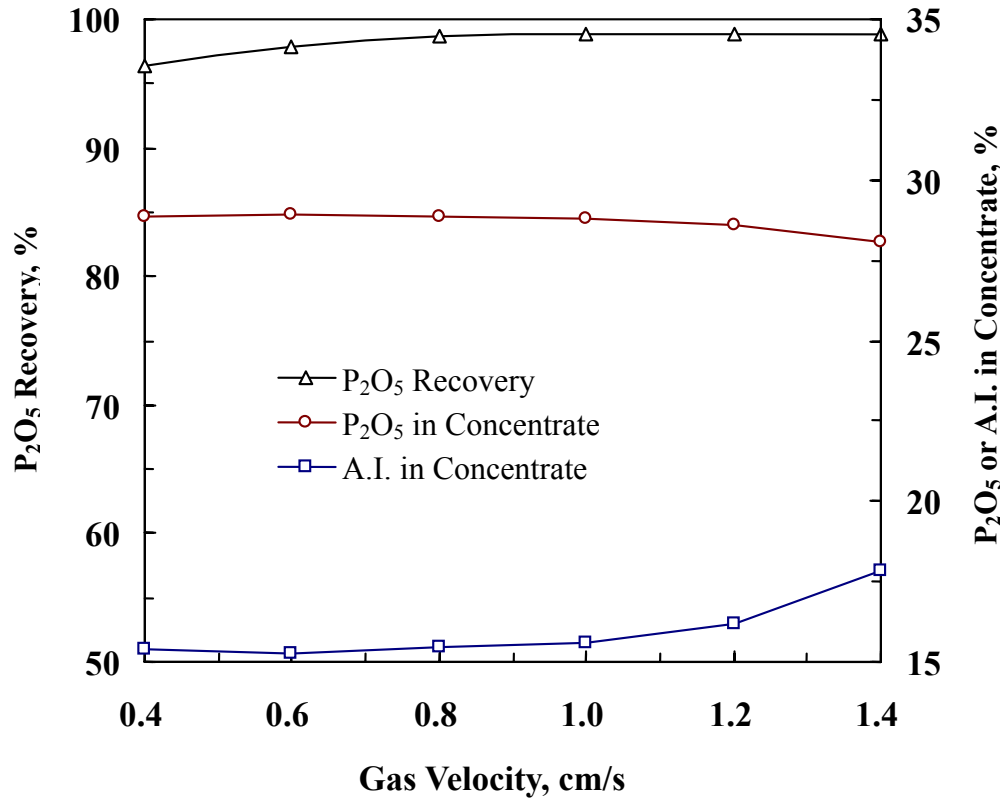
**Figure 28. Effect of Superficial Air Velocity on Concentrate Grade and Flotation Recovery with Both Static Mixer and Sparger.**

Figure 29 shows the effect of superficial air velocity on flotation product grade and flotation recovery at varying superficial air velocity from 0.4 cm/s to 1.4 cm/s in the presence of both the static mixer and cavitation tube. It can be observed from Figure 29 that the flotation recovery increased from 95.3% to 98.8% and the concentrate grade remained nearly constant initially as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the concentrate was 28.9% and the A.I. content was about 15.5% as the superficial air velocity increased from 0.4 cm/s to 0.8 cm/s, after which the P<sub>2</sub>O<sub>5</sub> content in the concentrate decreased to 28.0% and the A.I. in the concentrate increased to 18.0% as the superficial air velocity further increased to 1.4 cm/s. It can be concluded by comparing Figure 29 to Figure 27 that use of the cavitation tube increased P<sub>2</sub>O<sub>5</sub> recovery by 6% and P<sub>2</sub>O<sub>5</sub> grade by 1.2% and reduced A.I. content by about 4%.



**Figure 29. Effect of Superficial Gas Velocity on Concentrate Grade and Flotation Recovery with Both Static Mixer and Cavitation Tube.**

Figure 30 shows the effect of superficial air velocity on concentrate grade and flotation recovery with the combined use of the static mixer (20% air flow rate), sparger (80% air flow rate) and cavitation tube. It can be observed from Figure 30 that the flotation recovery increased from 96.3% to 98.9% and the concentrate grade remained essentially constant as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. The P<sub>2</sub>O<sub>5</sub> content in the concentrate decreased from 28.9% to 28.1% and the A.I. content in the concentrate increased from nearly 15.4% to about 17.9% as the superficial air velocity increased to 1.4 cm/s. The results in Figure 30 are almost identical to those in Figure 29, indicating that the sparger was almost useless in the presence of the static mixer and cavitation tube.



**Figure 30. Effect of Superficial Air Velocity on Concentrate Grade and Flotation Recovery with Combined Use of Static Mixer, Sparger and Cavitation Tube.**

The effect of bubble generators on flotation recovery and product grade at varying superficial gas velocity are summarized in Figures 31 and 32. It can be observed from Figure 31 that the flotation recovery increased steadily as the superficial air velocity increased from 0.4 cm/s to 1.0 or 1.2 cm/s, and remained constant thereafter. Adding the cavitation tube to the column with the static mixer increased coarse phosphate recovery by up to 10%. Figure 32 reveals that the P<sub>2</sub>O<sub>5</sub> content in the concentrate decreased as the superficial air velocity increased from 0.4 cm/s to 1.4 cm/s. Comparing the four curves indicates that the use of picobubbles significantly improves product grade.

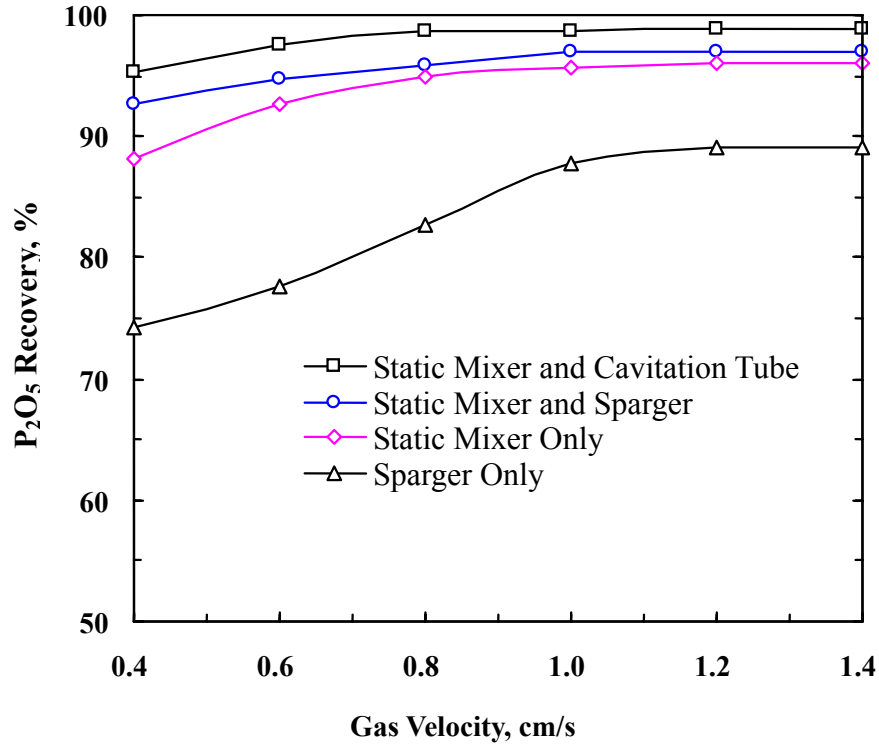


Figure 31. Effect of Bubble Generators on Flotation Recovery at Varying Superficial Gas Velocity.

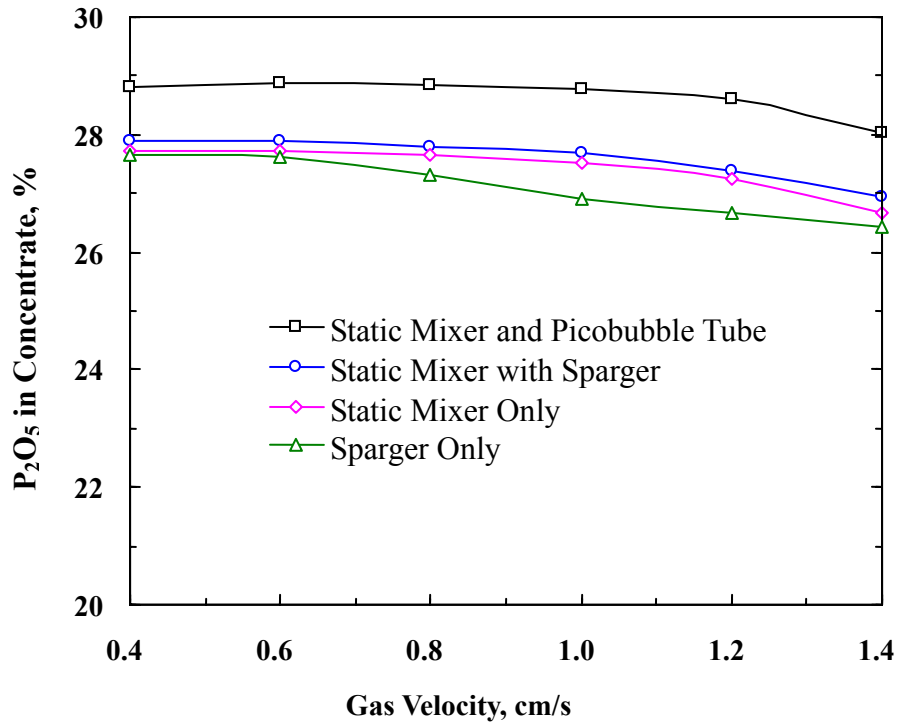
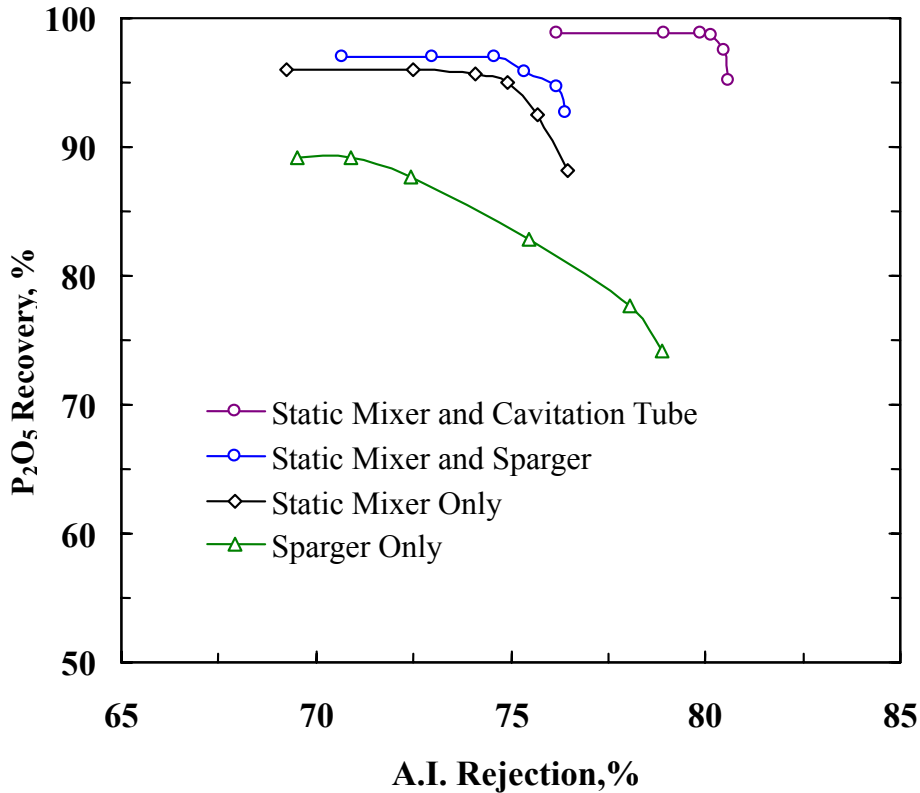


Figure 32. Effect of Bubble Generators on Flotation Product Grade at Varying Superficial Gas Velocity.



Figure 33 shows the relationships between the A.I. rejection and  $P_2O_5$  recovery obtained at varying superficial gas velocity from 0.4 cm/s to 1.4 cm/s. When the cavitation tube and static mixer were used,  $P_2O_5$  recovery was 10%~25% higher than when only the sparger was used at varying A.I. rejection.



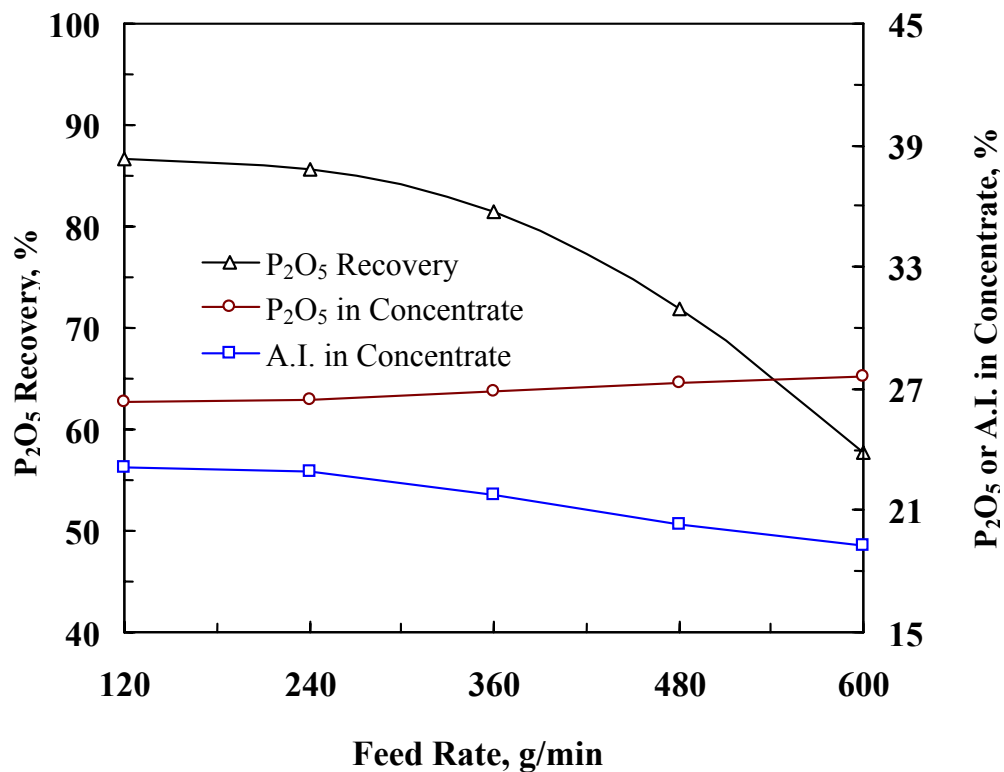
**Figure 33. Relationships Between A.I. Rejection and  $P_2O_5$  Recovery.**

In summary, the flotation performance was optimized by using both the static mixer and cavitation tube. The co-existence of picobubbles and microbubbles considerably increased flotation recovery and reduced the air flow rate required for coarse phosphate flotation. The sparger was useless in the presence of the static mixer and cavitation tube.

## Effect of Specially Designed Bottom

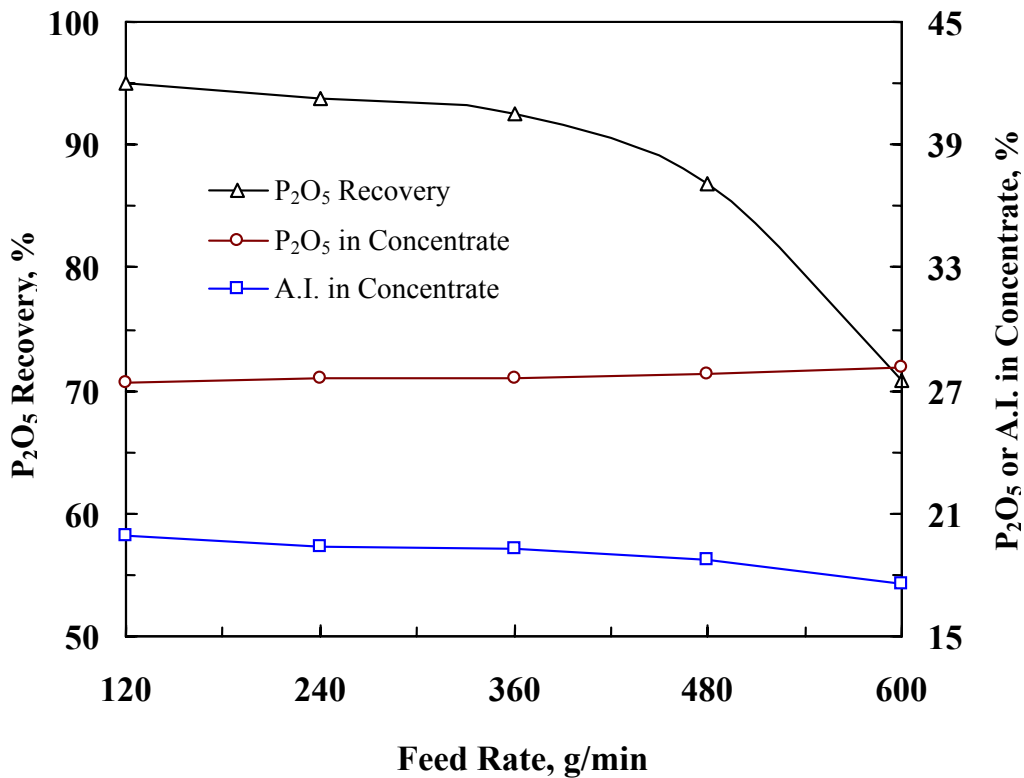
To evaluate the effect of centrifugal separation created by the specially designed bottom on coarse phosphate separation, a number of flotation experiments were performed at varying feed rates under different conditions: (1) without the specially designed column bottom and picobubbles, (2) with the specially designed bottom but without picobubbles, (3) without the specially designed bottom but with picobubbles, and (4) with the specially designed bottom and picobubbles. The collector dosage, frother dosage, and superficial air velocity were fixed at 0.9 kg/t, 10 ppm, and 1.0 cm/s, respectively.

Figure 34 shows the effect of feed rate on concentrate grade and flotation recovery without the specially designed bottom and picobubbles. It can be observed from Figure 34 that the  $P_2O_5$  recovery decreased from about 87% to 57% as the feed rate increased from 120 g/min to 600 g/min. The  $P_2O_5$  in the concentrate increased slightly from about 26.5% to 27.5% as the feed rate increased.



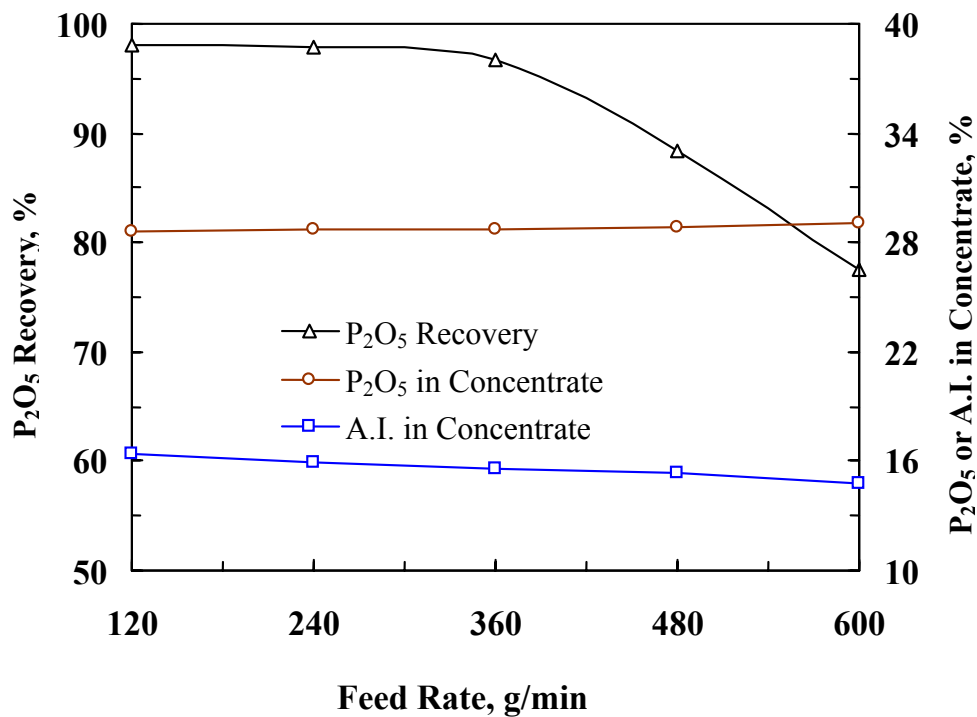
**Figure 34. Effect of Feed Rate on Concentrate Grade and Flotation Recovery without Specially Designed Bottom and Picobubbles.**

Figure 35 shows the effect of feed rate on flotation recovery and concentrate grade with the specially designed column bottom but without picobubbles. It can be observed from Figure 35 that the  $P_2O_5$  recovery decreased slightly from about 95% as the feed rate increased from 120 g/min to 360 g/min. When the feed rate increased from 360 g/min to 600 g/min, the  $P_2O_5$  recovery decreased more significantly. But the lowest recovery of 70% at the highest feed rate was still considerably higher than that achieved without the specially designed column bottom, indicating that the improvement to the column structure had significant benefits. The  $P_2O_5$  in the concentrate increased from 27.5% to 28.0% as the feed rate increased.



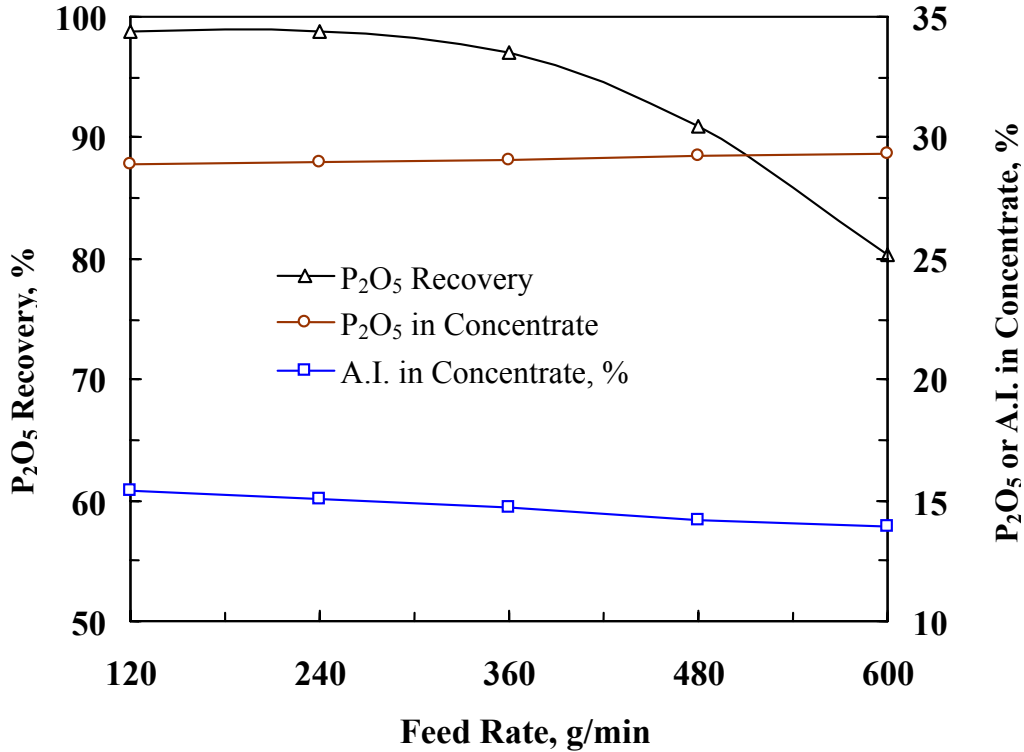
**Figure 35. Effect of Feed Rate on Flotation Recovery and Concentrate Grade with Specially Designed Bottom but without Picobubbles.**

Figure 36 shows the effect of feed rate on flotation recovery and concentrate grade with picobubbles but without the specially designed column bottom. It can be observed that the  $P_2O_5$  recovery decreased from 98% to about 96.5% as the feed rate increased from 120 g/min to 360 g/min. When the feed rate increased from 360 g/min to 600 g/min, the  $P_2O_5$  recovery decreased to 77%. The  $P_2O_5$  in the concentrate increased from 28.5% to 29% as the feed rate increased. Obviously, the flotation performance with picobubbles was even better than that achieved with the use of the specially designed column bottom.



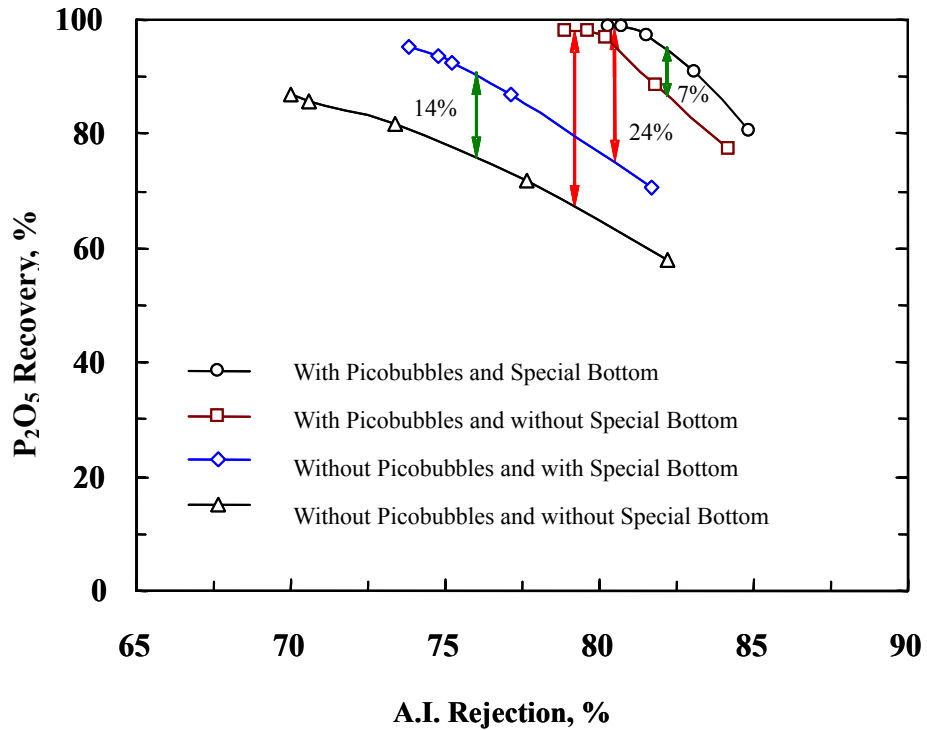
**Figure 36. Effect of Feed Rate on Flotation Recovery and Concentrate Grade with Picobubbles but without Specially Designed Bottom.**

Figure 37 shows the effect of feed rate on flotation recovery and concentrate grade when both the specially designed column bottom and picobubbles were used. The P<sub>2</sub>O<sub>5</sub> recovery decreased from nearly 99% to 97% as the feed rate increased from 120 g/min to 360 g/min. As the feed rate further increased from 360 g/min to 600 g/min, the P<sub>2</sub>O<sub>5</sub> recovery decreased to 80%. The P<sub>2</sub>O<sub>5</sub> in the concentrate was kept essentially constant at 29% as the feed rate increased.



**Figure 37. Effect of Feed Rate on Flotation Recovery and Concentrate Grade with Picobubbles and the Specially Designed Bottom.**

Figure 38 shows the relationships between the A.I. rejection and P<sub>2</sub>O<sub>5</sub> recovery obtained under the conditions examined above. When the specially designed column bottom was not used, the use of picobubbles increased P<sub>2</sub>O<sub>5</sub> recovery by as much as 30%. The improvement in recovery by picobubbles was up to 24% when the specially designed bottom was used. The specially designed column bottom also significantly improved flotation performance, particularly when no picobubbles were introduced. Up to a 14% increase in P<sub>2</sub>O<sub>5</sub> recovery was achieved by the specially designed column bottom, although this increase was reduced to about 7% in the presence of picobubbles.



**Figure 38. A.I. Rejection Versus P<sub>2</sub>O<sub>5</sub> Recovery.**

In summary, both the picobubbles generated by the cavitation tube and the centrifugal gravity separation caused by the specially designed column bottom improved the separation performance and enhanced the P<sub>2</sub>O<sub>5</sub> recovery.

#### **Four-Factor Three-Level Experimental Design**

A four-factor, three-level Box-Behnken experimental design of flotation tests was conducted using Design-Expert 6.8 software acquired from Stat-Ease Inc., Minneapolis, MN. The four process parameters included air flow rate, collector dosage, frother dosage, and slurry flow rate ratio. The levels of process variables were coded as “-”, “0” and “+”, respectively, where “-” represents the low level, “0” represents the middle level and “+” represents the high level of the factors. The specific levels of individual variables are indicated in Table 3. The details of the designed experiments are shown in Table 4. The solid feed rate was fixed constant at 240 g/min.

**Table 3. Levels of Variables.**

Variables	Code	Units	Level		
			Low Level -1	Middle Level 0	High Level +1
Gas flow rate	A	Liter/min.	0.60	1.20	1.60
Collector dosage	B	kg/ton	0.30	0.90	1.50
Frother dosage	C	ppm	5.0	10.0	15.0
Slurry flow rate ratios	D		2:1	3:1	4:1

**Table 4. Experiments Based on Box-Behnken Design.**

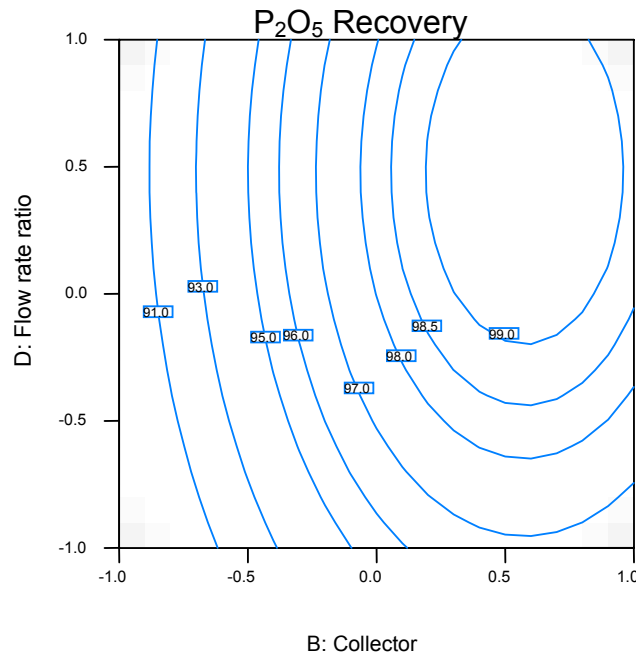
Run	Factor A		Factor B		Factor C		Factor D	
	Gas Flow Rate		Collector Dosage		Frother Dosage		Flow Rate Ratio	
	Level	Liter/min	Level	kg/ton	Level	ppm	Level	
1	1	1.6	-1	0.3	0	10	0	3:1
2	-1	0.6	0	0.9	-1	5	0	3:1
3	0	1.2	0	0.9	-1	5	-1	2:1
4	-1	0.6	-1	0.3	0	10	0	3:1
5	-1	0.6	0	0.9	0	10	-1	2:1
6	0	1.2	0	0.9	1	15	-1	2:1
7	0	1.2	0	0.9	0	10	0	3:1
8	0	1.2	0	0.9	0	10	0	3:1
9	1	1.6	0	0.9	1	15	0	3:1
10	0	1.2	-1	0.3	0	10	-1	2:1
11	-1	0.6	0	0.9	0	10	1	4:1
12	0	1.2	-1	0.3	0	10	1	4:1
13	0	1.2	1	1.5	0	10	1	4:1
14	0	1.2	1	1.5	-1	5	0	3:1
15	0	1.2	-1	0.3	1	15	0	3:1
16	1	1.6	1	1.5	0	10	0	3:1
17	0	1.2	0	0.9	0	10	0	3:1
18	0	1.2	0	0.9	0	10	0	3:1
19	0	1.2	0	0.9	0	10	0	3:1
20	0	1.2	-1	0.3	-1	5	0	3:1
21	0	1.2	0	0.9	1	15	1	4:1
22	1	1.6	0	0.9	0	10	1	4:1
23	1	1.6	0	0.9	0	10	-1	2:1
24	0	1.2	1	1.5	1	15	0	3:1
25	-1	0.6	1	1.5	0	10	0	3:1
26	1	1.6	0	0.9	-1	5	0	3:1
27	-1	0.6	0	0.9	1	15	0	3:1
28	0	1.2	1	1.5	0	10	-1	2:1
29	0	1.2	0	0.9	-1	5	1	4:1

Response surface methodology was used to analyze the above experimental data. Response surface contours were generated for  $P_2O_5$  recovery as a function of the studied variables (i.e., collector dosage, frother dosage, air flow rate, and slurry flow rate ratio). Figures 39, 40, 41, and 42 depict the contours of  $P_2O_5$  recovery between the studied parameters.

The contours of  $P_2O_5$  recovery between collector dosage and slurry flow rate ratio (slurry flow rate in the cavitation tube/slurry flow rate in the static mixer) are shown in Figure 39. All contours were drawn at the midpoint of air flow rate and frother dosage. These contours suggest that the area of the highest  $P_2O_5$  recovery was attained within the present levels of collector dosage and slurry flow rate ratio. The contours of  $P_2O_5$  recovery reveal that, at a given  $P_2O_5$  recovery, increasing flow rate ratio decreased the collector dosage.

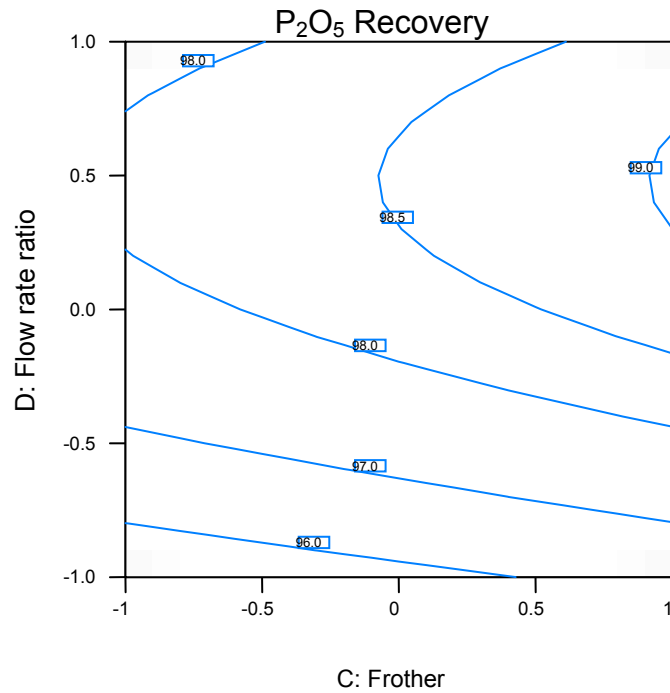
Figure 40 depicts the contours of  $P_2O_5$  recovery between frother dosage and slurry flow rate ratio at the midpoint of air flow rate and collector dosage. The contours of  $P_2O_5$  recovery also reveal that, at a given  $P_2O_5$  recovery, the frother dosage can be considerably reduced by raising the slurry flow rate ratio.

Figure 41 depicts the contours of  $P_2O_5$  recovery between air flow rate and slurry flow rate ratio. All contours were drawn at the midpoint of collector dosage and frother dosage. The contours of  $P_2O_5$  recovery between collector dosage and frother dosage at the midpoint of air flow rate and slurry flow rate ratio are shown in Figure 42, which indicates that, at a given  $P_2O_5$  recovery, the frother dosage can be reduced significantly by slightly increasing the collector dosage.

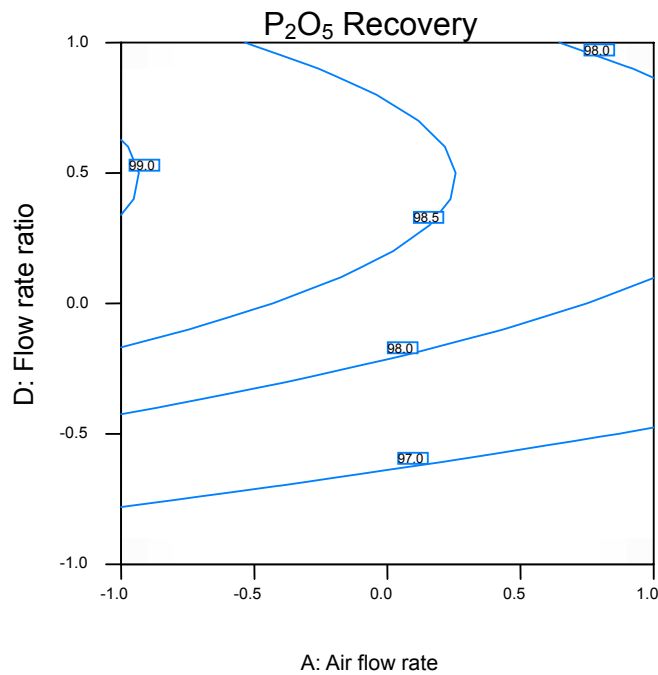


**Figure 39. Contours of  $P_2O_5$  Recovery for Collector Dosage and Slurry Flow Rate Ratio at the Midpoint of Air Flow Rate and Frother Dosage.**

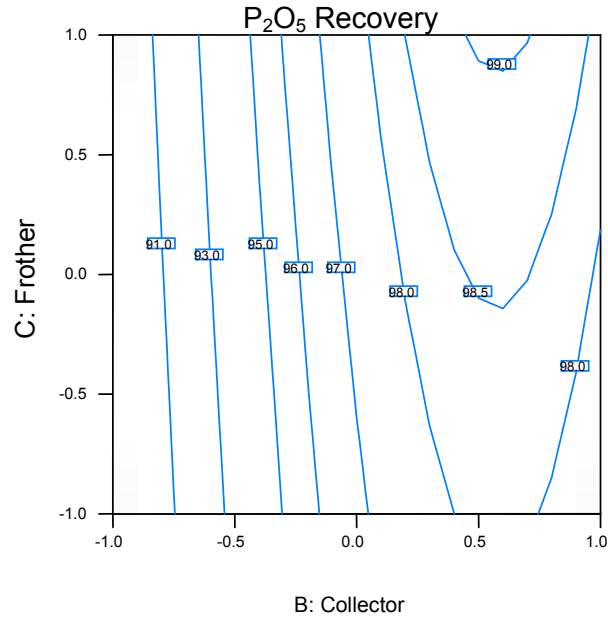




**Figure 40. Contours of P<sub>2</sub>O<sub>5</sub> Recovery for Frother Dosage and Slurry Flow Rate Ratio at the Midpoint of Air Flow Rate and Collector Dosage.**



**Figure 41. Contours of P<sub>2</sub>O<sub>5</sub> Recovery for Air Flow Rate and Slurry Flow Rate Ratio at the Midpoint of Collector Dosage and Frother Dosage.**



**Figure 42. Contours of P<sub>2</sub>O<sub>5</sub> Recovery for Collector Dosage and Frother Dosage at the Midpoint of Air Flow Rate and Slurry Flow Rate Ratio.**

### Summary

The above-mentioned flotation test results with CF phosphate sample A indicate that use of both the cavitation tube and static mixer as bubble generators for the flotation column to produce optimum bubble size distribution was very beneficial to coarse phosphate flotation. The co-existence of picobubbles and microbubbles decreased the collector dosage, frother dosage and air flow rate. Integration of centrifugal gravity separation and picobubble-enhanced flotation further improved separation performance.

### COLUMN FLOTATION WITH CF PHOSPHATE SAMPLE B

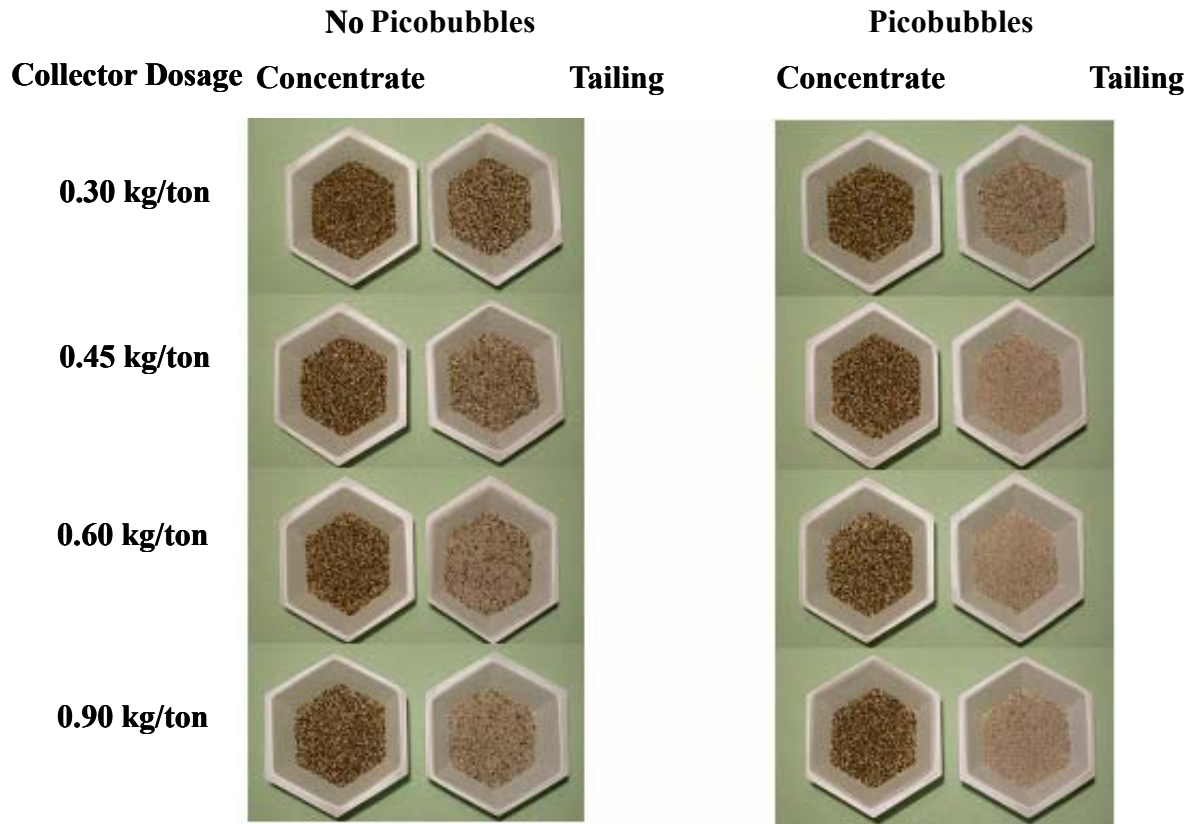
There were significant differences in color, particle size distribution, P<sub>2</sub>O<sub>5</sub> content, A.I., etc., between CF phosphate samples A and B. CF sample A was mainly composed of black phosphate particles, while sample B was composed of brown phosphate particles. The flotation test results of CF sample B are shown in Figures 43, 44, and 45. The solid feed rate, superficial air velocity, and frother dosage were fixed constant at 240 g/min, 1.0 cm/s, and 10 ppm, respectively.



**Tailings without picobubbles**

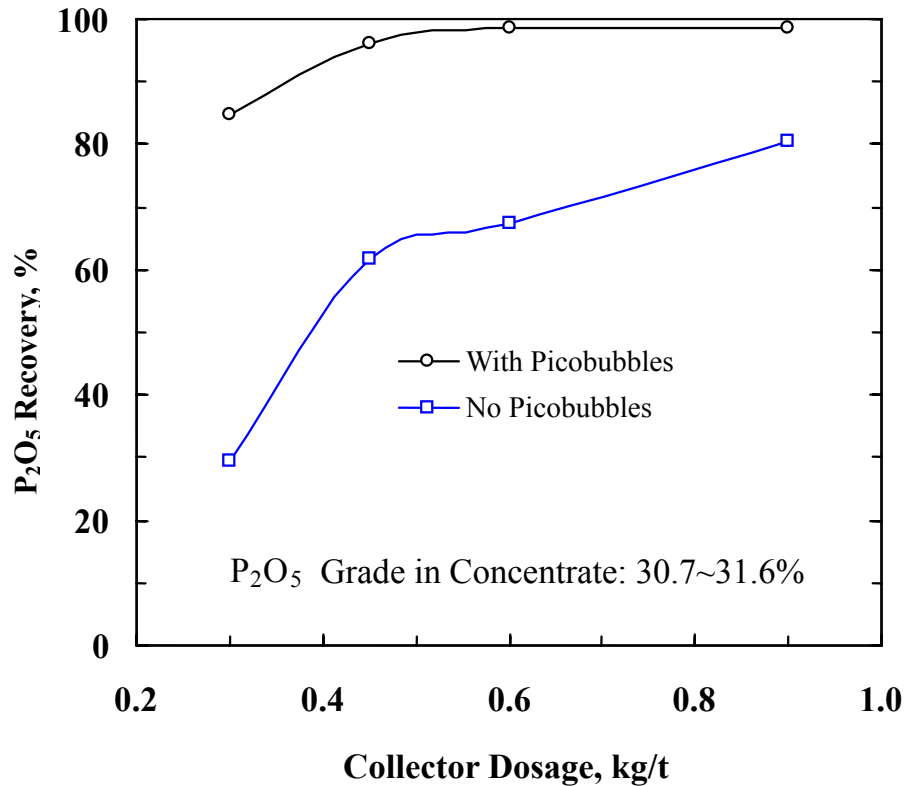
**Tailings with picobubbles**

**Figure 43. Flotation Tailings without and with Picobubbles.**



**Figure 44. Effect of Picobubbles on Flotation Performance at Varying Collector Dosages.**

Figure 44 shows that there was no noticeable difference between the concentrates of flotation obtained without picobubbles and with picobubbles. However, Figures 43 and 44 show that the tailings were much purer when picobubbles were present. As the collector dosage increased from a dosage of 0.3 to 0.9 kg/t, the differences between the flotation tailings produced with and without picobubbles diminished.



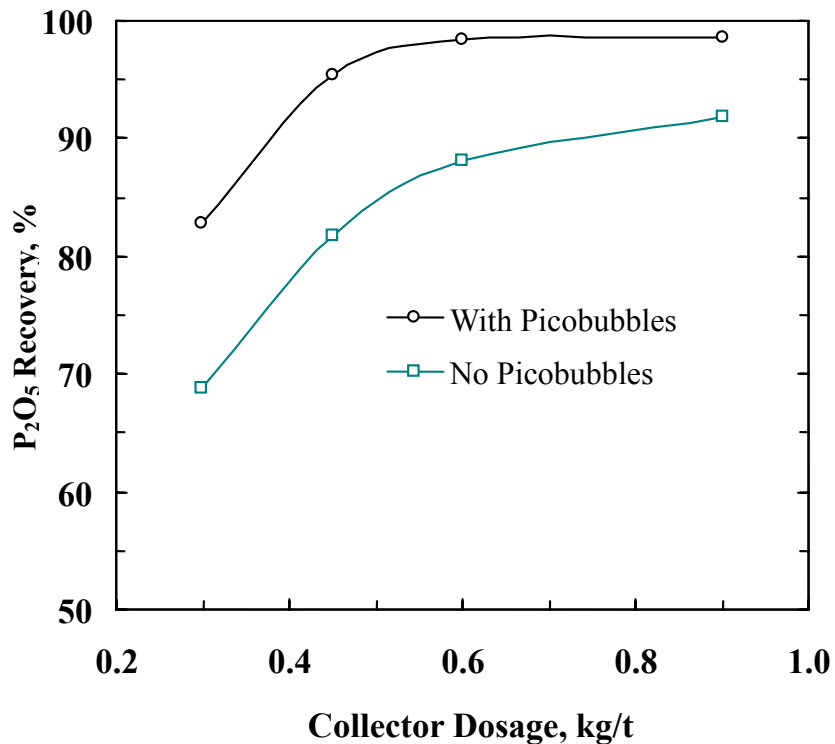
**Figure 45. Effect of Picobubbles on Flotation Recovery at Varying Collector Dosages.**

Figure 45 shows the effect of picobubbles on coarse phosphate flotation recovery at varying collector dosages from 0.3 kg/t to 0.9 kg/t. It can be observed from Figure 45 that flotation recovery increased consistently as collector dosage increased from 0.3 to 0.9 kg/t when no picobubbles were used. However, when picobubbles were used, the flotation recovery remained essentially constant after the collector dosage increased from 0.6 to 0.9 kg/t. Flotation recovery was more sensitive to collector dosage in the absence of picobubbles. The presence of picobubbles significantly increased flotation recovery, especially at lower collector dosages. At a given flotation recovery, the presence of picobubbles reduced the required dosage of collector. For example, to achieve about 80% P<sub>2</sub>O<sub>5</sub> recovery, 0.9 kg/t collector was required in the absence of picobubbles; only 0.3 kg/t collector was needed in the presence of picobubbles.

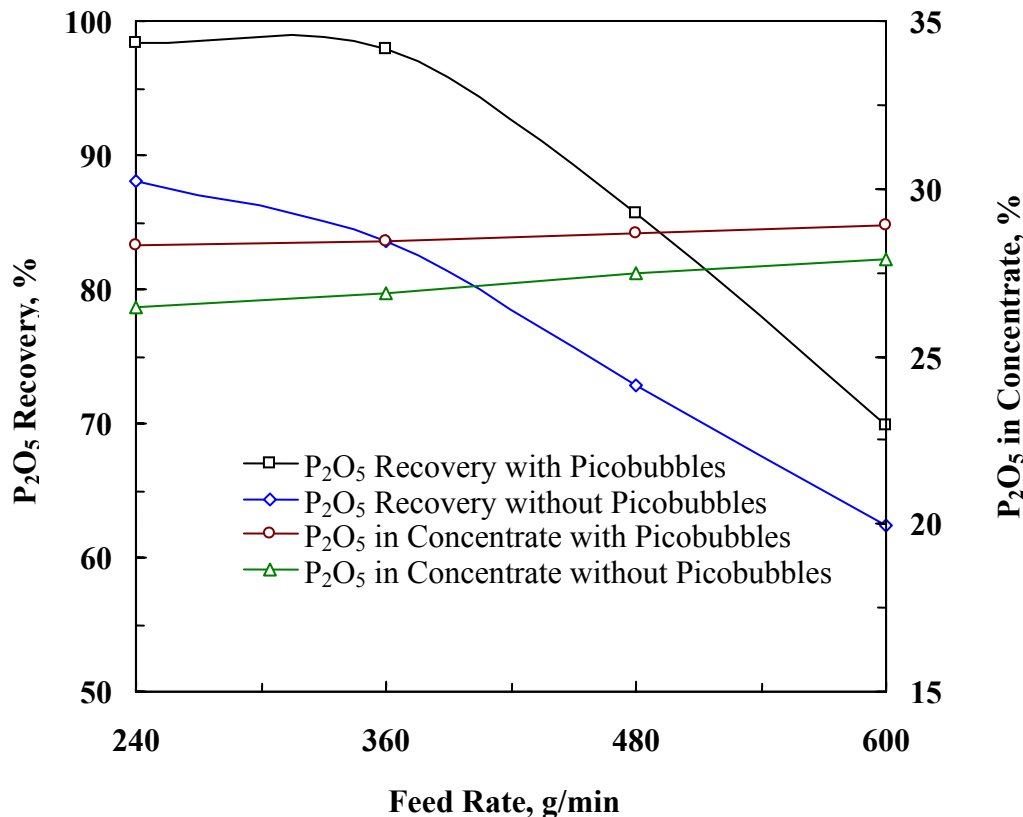
### **COLUMN FLOTATION WITH MOSAIC PHOSPHATE SAMPLE**

Figure 46 shows the effect of collector dosage on product grade and flotation recovery at varying collector dosage from 0.3 kg/t to 0.9 kg/t. The superficial air velocity, frother dosage, and feed rate were fixed constant at 1.0 cm/s, 8 ppm, and 240 g/min, respectively. It can be observed from Figure 46 that the flotation recovery

increased as the collector dosage increased from a dosage of 0.3 to 0.9 kg/t when no picobubbles were used. In the presence of picobubbles, the flotation recovery remained essentially constant after the collector dosage increased to 0.6 kg/t. Similarly, flotation recovery was more sensitive to collector dosage in the absence of picobubbles than in the presence of picobubbles. The presence of picobubbles increased flotation recovery by 14% at lower collector dosages. At a given flotation recovery, the presence of picobubbles reduced the required dosage of collector. For example, to achieve 90%  $P_2O_5$  recovery, about 0.7 kg/t collector was required in the absence of picobubbles; only 0.4 kg/t collector was needed in the presence of picobubbles. The maximum flotation recovery achieved without picobubbles was about 95% when 0.9 kg/t collector was used. In contrast, in the presence of picobubbles, the maximum flotation recovery was more than 98% and was achieved at a lower collector dosage of 0.6 kg/t.

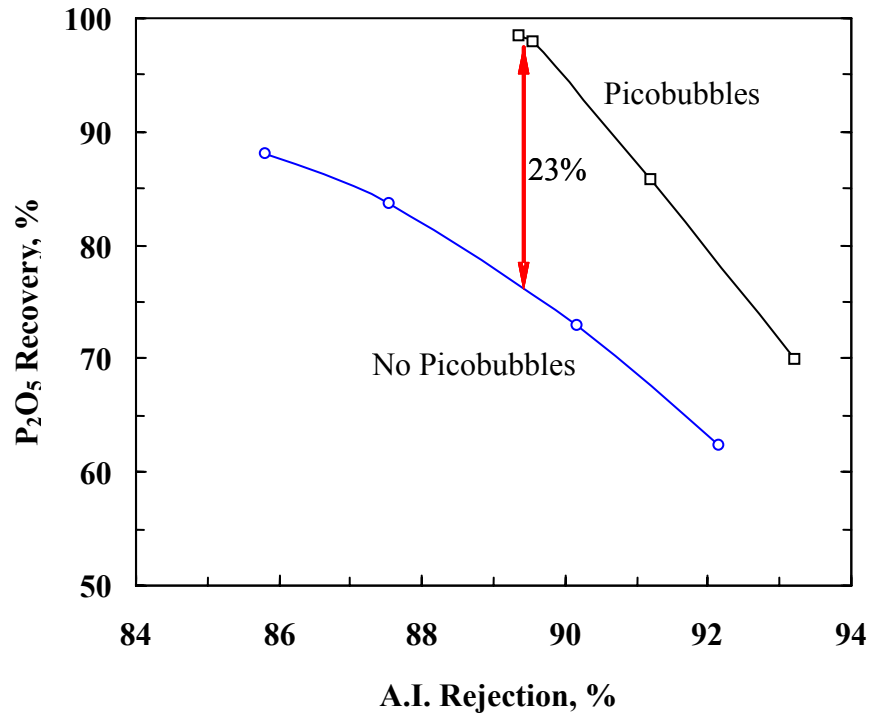


**Figure 46. Effect of Picobubbles on Flotation Recovery at Varying Collector Dosages.**



**Figure 47. Effect of Picobubbles on Flotation Recovery at Varying Feed Rates.**

Figure 47 shows the effect of picobubbles on concentrate grade and flotation recovery at varying feed rates. The superficial air velocity, frother dosage, and collector dosage were fixed constant at 1.0 cm/s, 8 ppm, and 0.6 kg/t, respectively. When picobubbles were not used, it can be observed from Figure 47 that the P<sub>2</sub>O<sub>5</sub> recovery decreased from about 88% to 62%, while the P<sub>2</sub>O<sub>5</sub> in the concentrate increased slightly from about 26.4% to 27.9% as the feed rate increased from 240 g/min to 600 g/min. In the presence of picobubbles, the P<sub>2</sub>O<sub>5</sub> recovery decreased slightly from about 98.4% to 97.9% as the feed rate increased from 240 g/min to 360 g/min. When the feed rate increased from 360 g/min to 600 g/min, the P<sub>2</sub>O<sub>5</sub> recovery decreased more significantly with the feed rate. The lowest recovery of 69.9% at the highest feed rate was still considerably higher than that achieved without picobubbles. The P<sub>2</sub>O<sub>5</sub> in the concentrate increased from 28.3% to 28.9% as the feed rate increased.



**Figure 48. A.I. Rejection Versus P<sub>2</sub>O<sub>5</sub> Recovery.**

Figure 48 shows the relationships between the A.I rejection and P<sub>2</sub>O<sub>5</sub> recovery obtained under the conditions examined above. The use of picobubbles increased P<sub>2</sub>O<sub>5</sub> recovery by 23% at 89% A.I. rejection. At a given P<sub>2</sub>O<sub>5</sub> recovery, for example, 88% flotation recovery, the A.I. rejection of flotation in the presence of picobubbles was about 5% higher than that in the absence of picobubbles.



## CONCLUSIONS

The following conclusions can be drawn based on the above test results and discussion:

(1) Microflotation experimental results showed that bubble size should be reduced to improve flotation rate at a given air flow rate. Within a certain range of particle size, collection efficiency can be increased by increasing particle size. However, when the particle size exceeded a certain limit, the collection efficiency decreased as the particle size increased due to the high detachment rate.

(2) Picobubbles are characterized by an inherently high probability of collision, a high probability of attachment, and a low probability of detachment due to their tiny size, and high free surface energy. They can function as a bridge between the coarse phosphate particles and conventional-sized bubbles, and therefore are very efficient in enhancing flotation recovery of coarse phosphate particles.

(3) The use of picobubbles in flotation significantly enhanced the  $P_2O_5$  recovery of coarse phosphate at the same reagent dosage and aeration rate, based on the test results of two CF Industries phosphate samples and one Mosaic phosphate sample. Picobubbles increased  $P_2O_5$  recovery by up to ~23-30% at a given A.I. rejection, depending on the characteristics of the phosphate samples.

(4) The picobubbles reduced flotation reagent consumption, thus reducing the operating cost and improving floatation efficiency. Picobubbles reduced collector dosage by one-third, or in some cases one-half, since picobubbles are selectively attached onto the hydrophobic particles and act as the secondary collector on the particles' surfaces.

(5) Use of both a cavitation tube and static mixer as bubble generators for the flotation column produced optimum bubble-size distribution for coarse phosphate flotation. The cavitation-generated picobubbles decreased the required aeration rate for the static mixer, further reducing the operating cost of flotation.

(6) Picobubbles greatly increased throughput. Picobubbles have a high surface-area-to-volume ratio and a high bubble density at a fixed flow rate. Picobubbles that selectively generated or attached onto phosphate particle surfaces increased the surface hydrophobicity, and thus increased the flotation kinetics rate and capacity.

(7) The centrifugal gravity separation of phosphate particles caused by the specially designed column bottom improved the separation performance and enhanced the  $P_2O_5$  recovery. Centrifugal gravity-enhanced picobubble flotation technology can be easily implemented in the industry with a minimum retrofit cost.

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