CHAPTER 9

Pilot-Plant Evaluation of a Water Insoluble Hydroxamic Acid Collector for Single Stage Flotation of Florida Phosphate Rock

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ABSTRACT

Recent laboratory results have demonstrated that selective flotation of phosphate rock can be achieved in a single stage with improved separation efficiency when compared to the standard double float process. The new reagent chemistry is based on the use of a water insoluble alcoholic solution of alkyl hydroxamic acid as collector following a conditioning procedure similar to that currently used by the Florida phosphate industry. The effectiveness of the new collector chemistry has been demonstrated by the results from single stage bench scale flotation experiments for feed material from plants in Florida, North Carolina, and Utah. Now pilot plant testing at a feed rate of 700–900 lb/hr has been completed in order to evaluate the hydroxamic acid collector on a continuous basis. Results from the pilot-plant campaign confirm the findings from laboratory experiments. Single stage flotation recovery of 95% was reached with a concentrate grade of 32% P_2O_5 for coarse feed material (16×35 mesh).

Initial economic analysis of the new flotation chemistry with AERO 6493 shows a strong dependence on the reagent price. If the cost of AERO 6493 could be reduced to $1.80/lb, the single stage flotation of coarse phosphate with the alkyl hydroxamic acid/alcohol collector would be cost competitive with the traditional double float process using fatty acid and fuel oil.

INTRODUCTION

Recent research results (Miller et al. 2000; Miller et al. 2002a; Miller et al. 2002b) demonstrate that water-insoluble alcoholic solutions of alkyl hydroxamic acids can be used as selective collectors for phosphate flotation that can increase separation efficiency especially for coarse feed material; in this way the standard double float process can be reduced to a single step. The experimental results indicate that high separation efficiencies can be achieved in single stage flotation with these new collectors (Miller et al. 2000). The effectiveness of the new collector chemistry was demonstrated by single stage bench scale flotation experiments of feed material from plants in Central Florida, North Carolina, and Utah (Miller et al. 2002a). Particular effectiveness was achieved for coarse feed material from these phosphate operations. In some cases, the single stage concentrate grade reached

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31% P_2O_5 with 95% recovery from low grade (5% P_2O_5) coarse feed (16×35 mesh). Such separation efficiency could not be achieved using the traditional fatty acid/fuel oil collector. High solids conditioning (70–75% solids by weight) was found to be necessary to achieve the desired separation efficiency. Significantly, the flotation response is essentially independent of pH for the hydroxamic acid collector, and the natural pH of the system was found to be satisfactory for flotation in most cases.

Subsequently, the new collector has now been evaluated for use by the Florida phosphate industry in pilot-plant studies and the experimental results, which confirm the findings from laboratory experiments, show an improved separation efficiency especially for coarse phosphate flotation feed from the Cargill South Fort Meade (SFM) plant.

PILOT-PLANT TESTING AT JACOBS ENGINEERING

Pilot-plant testing was carried out at the Jacobs Engineering pilot plant facility in Lakeland, Florida. The flowsheet for the pilot flotation system is shown in Figure 1. The feed material was loaded by a front end loader into a screw feeder and pulped by tap water. The slurry was pumped into a screw classifier to dewater to 70–75% solids. Then the slurry was discharged into a vertical conditioning tank with impeller and the new collector (AERO 6493) was added. The conditioning time was about 2–3 minutes. After conditioning, the slurry was diluted to 20% solids and fed to the flotation circuit which consisted of two flotation cells (DECO Flotation machine, total active volume 5 ft^3). Flotation products and feed samples were taken every 20 minutes. Three samples were combined and the composite taken for analysis. Shown in Figure 2 are photographs of operations at the pilot plant.

The flotation variables considered were the collector dosage and percent solids during conditioning. The pilot-plant testing used feed material from the Cargill SFM plant. Two flotation feeds, fine flotation feed and coarse flotation feed, were tested. The particle size distributions for fine feed and coarse feed are shown in Figures 3 and 4 together with the particle size distributions for concentrate and tailing products. The feed rate was about 700–900 lb/hr.

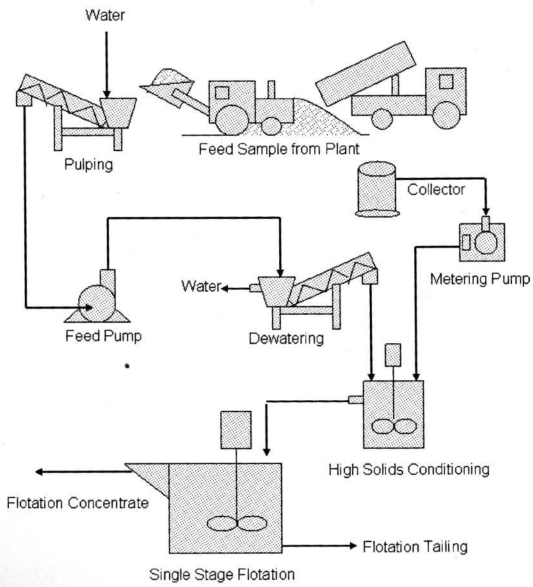
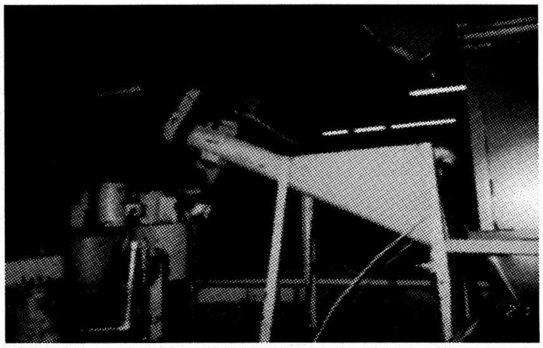
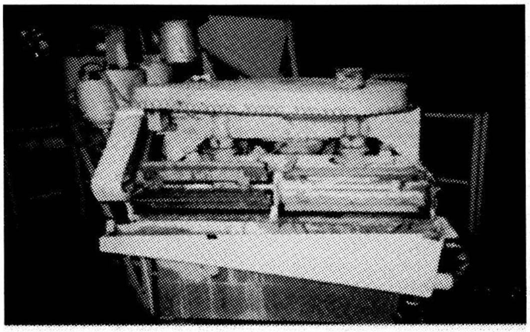


Figure 1 Flowsheet for pilot-plant testing

Loading, pulping, and pumping of feed



Dewatering and high solids conditioning



Single stage flotation

Figure 2 Photographs of pilot-plant operation

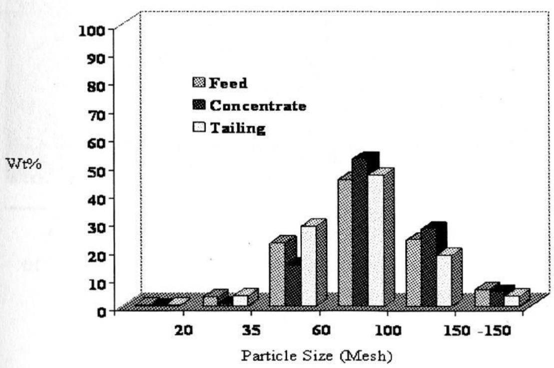


Figure 3 Particle size analysis for fine flotation feed, concentrate, and tailing from pilot testing at a feed rate of 900 lb/hr and conditioning at 74% solids

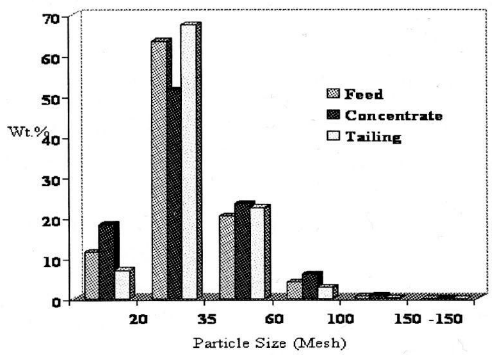


Figure 4 Particle size analysis for coarse flotation feed, concentrate, and tailing from pilot testing at a feed rate of 700 lb/hr and conditioning at 71% solids

RESULTS AND DISCUSSION

Flotation With Cargill SFM Fine Feed

The new collector (AERO 6493) was tested with Cargill SFM fine flotation feed. The results in Figure 5 are from collector addition experiments. Conditioning was at about 74% solids and a natural pH of 7. The feed rate for the pilot plant testing was about 900 lb/hr for fine feed. The results show that a recovery of 86% with a concentrate grade of 30% P_2O_5 was achieved in single stage with an addition of 850 g/t of the new collector.

Flotation with oily, water-insoluble collectors is frequently governed by selective wetting/ spreading phenomena and the formation of aeroflocs, which are complex aggregates of air, water, the liquid collector phase, and mineral particles. In this case, high solids conditioning is preferred to achieve the creation of stable aeroflocs of sufficient buoyancy for flotation. Shown in Figure 6 is the X-ray CT spectroscopy image of a cross-section of aeroflocs formed with francolite particles, air bubbles, and the image of a cross-section of aeroflocs formed with francolite particles, air bubbles, and the new collector. It can be observed that the rate of agglomeration and size of aeroflocs increase as the amount of small air bubbles increases during the flotation experiment. The hydrophobic particles are triggered by the small air bubbles to form large aeroflocs. It is evident that the separation efficiency does not vary significantly for a collector addition.

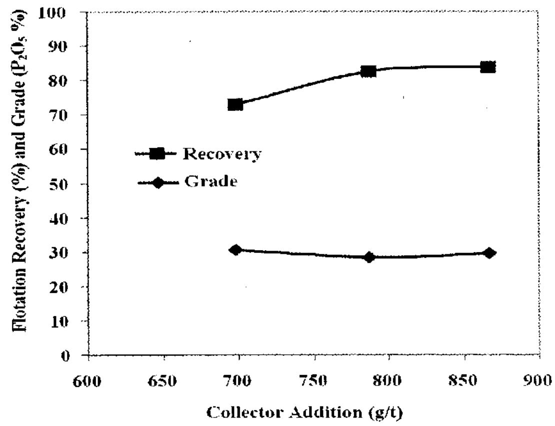


Figure 5 Effect of collector addition on single stage pilot-plant flotation of Cargill fine feed at a feed rate of 900 lb/hr and conditioning at 74% solids

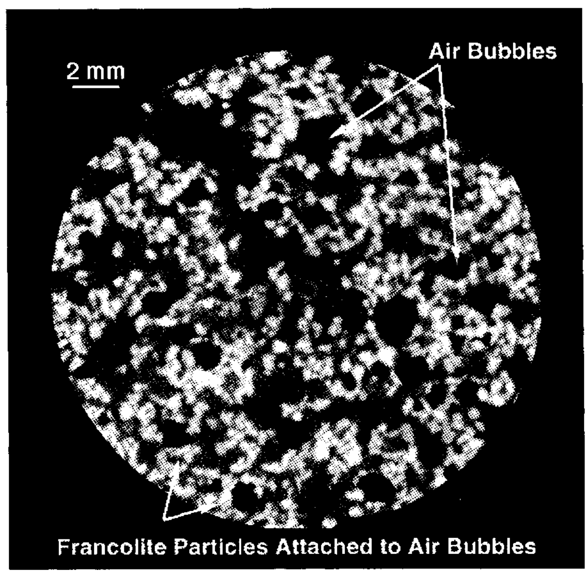


Figure 6 X-ray micro CT image of aeroflocs formed by francolite particles, air bubbles during flotation with the hydroxamic acid collector

Flotation With Cargill SFM Coarse Feed

Pilot-plant flotation results for the coarse feed at different collector additions are shown in Figure 7. The conditioning was done at 71% solids and a natural pH of 7. It can be seen from the results presented in Figure 7 that with 1,200 g/t collector dosage a concentrate with a grade of 32% P_2O_5 AT 95% recovery can be achieved in single stage pilot scale flotation.

During the coarse feed flotation, the feed rate was reduced from 900 lb/hr to 700 lb/hr because the conditioning solids were difficult to control and the flotation time appeared to be insufficient. The results from pilot testing were consistent with the results from bench scale flotation experiments. The best results from the pilot plant campaign are summarized in Table 1.

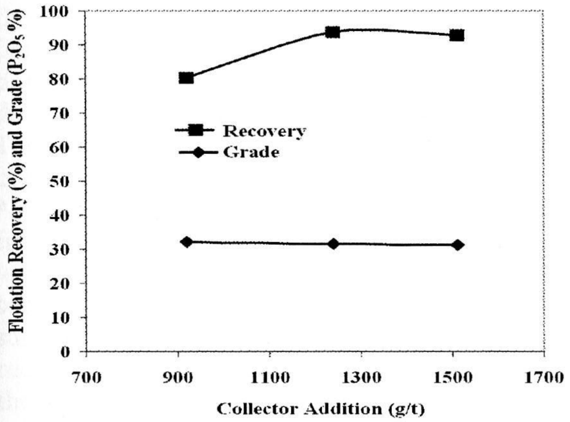


Figure 7 Effect of collector addition on single stage pilot-plant flotation of Cargill coarse feed at a feed rate of 700 lb/hr and conditioning at 71% solids

Flotation Water Quality

Tap water was used in these flotation experiments. The feed was conditioned with collector, AERO 6493, at a dosage of 800 g/t at 75% solids for 3 minutes. Then the slurry was transferred into the flotation cell and diluted to 20% solids with tap water. After flotation the water from filtration of the tailing and concentrate products was collected and analyzed. The Whatman #4 coarse fast filter papers were used for filtration. The flotation results and water analyses are presented in Table 2. These data are used as a baseline. Notice that the TOC content is 6.50 mg/L, of which 35% or 2.28 mg/L would be contributed from the collector if none of the collector adsorbed/attached to the particles.

Figure 8 shows the locked cycle flotation procedure. In this test the tap water was used for

Table 1 Results from single stage pilot-plant flotation of phosphate feed from the Cargill SFM plant using the new hydroxamic acid collector (AERO 6493)

Feed	Condition	Product	Wt %	P_2O_5 %	Recovery %
	Dosage 850 g/t	Concentrate	27.96	29.6	85.94
Fine Feed	Conditioning Solids	Tailing	72.04	1.88	14.06
	74 %	Feed	100.00	9.63	100.00
	Dosage 1200 g/t	Concentrate	38.80	31.55	94.88
Coarse Feed	Conditioning Solids	Tailing	61.20	1.08	5.12
	71%	Feed	100.00	12.9	100.00

Table 2 Analytical results for open cycle flotation of Cargill feed (12×80 mesh) and discharge water quality without water recycle using AERO 6493 as collector; flotation with tap water at pH 7.41

Grade P_2O_5%	Recovery %	pH	Hardness(1) mg/L	TSS(2) mg/L	TDS(3) mg/L	Turbidity(4) NTU
30.98	93.36	8.07	650	140	820	150
TOC(5) mg/L	COD(6) mg/L	P(7) mg/L	Ca(8) mg/L	Mg(9) mg/L	F(10) mg/L	Dissolved Oxygen(11) mg/L
6.5	240	15	170	54	9.1	10.82

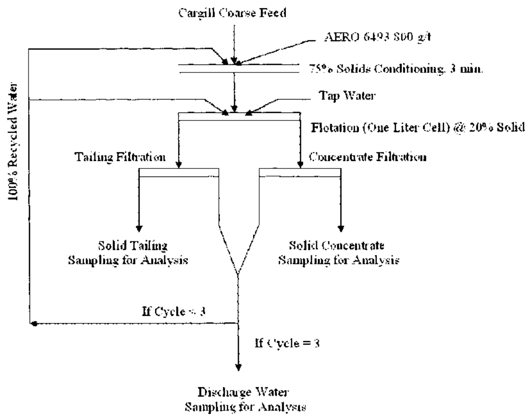


Figure 8 Locked cycle single stage flotation procedure with recycled water

Table 3 Flotation results for locked cycle experiment for Cargill feed (12×80 mesh) with 100% water recycle using AERO 6493 as collector at pH 7.4

Cycle	Products	Wt. %	Grade P_2O_5%	Recovery %
	Concentrate	42.57	32.41	89.36
1	Tailing	57.43	2.86	10.64
	Feed	100.00	15.44	100.00
	Concentrate	45.94	30.07	95.12
2	Tailing	54.06	1.31	4.88
	Feed	100.00	14.52	100.00
	Concentrate	46.13	30.07	95.30
3	Tailing	53.87	1.27	4.70
	Feed	100.00	14.56	100.00

Table 4 Water analyses from cycle 3 locked cycle flotation experiments with Cargill feed (12×80 mesh) water recycled using AERO 6493 as collector at pH 7.4

Grade P_2O_5%	Recovery %	pH	Hardness(1) mg/L	TSS(2) mg/L	TDS(3) mg/L	Turbidity(4) NTU
30.07	95.30	7.97	590	110	820	110
TOC(5) mg/L	COD(6) mg/L	P(7) mg/L	Ca(8) mg/L	Mg(9) mg/L	F(10) mg/L	Dissolved Oxygen(11) mg/L
22	440	13	150	52	16	10.81

the first cycle of flotation. In the first cycle of flotation, a feed sample of 250 grams was conditioned with the new collector, AERO 6493, at a dosage of 800 g/t and 75% solids for 3 minutes. Then the slurry was transferred to the flotation cell and diluted to 20% solids with tap water. After the first cycle of flotation, water from the filtration of tailing and concentrate was collected for the second cycle of flotation. In the second cycle of flotation a second 250 gram feed sample was conditioned and diluted with the recycled water from the first cycle flotation at the same reagent schedule, conditioning time, and flotation conditions. After the second cycle of flotation the water from filtration of tailing and concentrate was collected for the third cycle of flotation. After completing the same procedure as used for the second cycle, the filtration water from the third cycle was collected and analyzed. The Whatman #4 coarse fast filter papers were used for filtration.

Flotation results and the water analyses (essentially the third cycle water) are listed in Tables 3 and 4. The results indicate that the recovery and grade of the phosphate concentrate have stabilized in the third cycle. It also can be seen that there was no significant change in water quality (most analytical results) when the open cycle results are compared to the closed cycle. Notice that the total organic carbon (TOC) in closed cycle increased from 6.50 mg/L to 22.0 mg/L. The chemical oxygen demand (COD) also increased from 240 to 440 mg/L. This change may be due to a build up of the reagent in the closed cycle. Usually in the closed cycle the reagent dosage would be reduced.

Shown in Table 5 is the average analyses of 11 samples of plant water taken from flotation operations in Central Florida, as reported by Jacobs Engineering Group, Inc. (1998) in a survey of phosphate beneficiation plants including the IMC plants and the Cargill plants. Since the individual plant water data is not available, a complete comparison cannot be made. In general, all the analyses listed in Table 2 and Table 5, including total suspended solids (TSS), hardness (as Ca_2CO_3), pH, and P (total P), have higher values for the discharge water from AERO 6493 bench flotation experiments than those for plant water samples, especially for TSS and hardness. Apparently, the difference in water quality is significant. However, the final conclusion on the environmental impact of the new flotation chemistry using AERO 6493 still cannot be made based only on these results since many incomparable variables are involved, such as the time for water sampling after discharge, filtration conditions for concentrate, etc. The analytical results from Table 2 and Table 5 suggest that the hydroxamic acid collector, AERO 6439, addition could be reduced in a locked cycle flotation which would be expected to reduce the TOC content in discharged water without having a negative influence on the separation efficiency.

Further environmental evaluation regarding water quality should be made in plant testing.

ECONOMIC CONSIDERATIONS

It has been documented in a recent workshop (Zhang, 1991) that beneficiation of phosphate is a significant portion of the overall cost of production and at the flotation process is the most costly of all the beneficiation steps including washing, flotation preparation, flotation, in-process storage, and hydraulic station operation. A matter of particular concern in the development of the hydroxamic acid collector

Table 5 Average analyses of 11 plant water samples from central Florida (Jacobs Engineering Group, Inc.)

TSS(1)	Hardness(2)	pH(3)	P(4)
15 ppm	129 ppm	7.6	2.7 ppm

for phosphate flotation is the cost of the new collector chemistry relative to current reagent costs for typical plant operations.

Sources of Data

Since AERO 6493 generally showed significant improvement in flotation efficiency for coarse feed, flotation results used for this preliminary economic evaluation were those from testing of the coarse feed from the Cargill South Fort Meade Plant, Central Florida. Specifically, data for the cost comparison of the new collector chemistry with the traditional collector chemistry were from two sources:

1. The single stage pilot plant flotation results obtained using the hydroxamic acid collector (AERO 6493).
2. The typical flotation results using the traditional double float process with fatty acid/fuel oil (FA/FO) and amine as collectors. Data for the traditional process were obtained from several different references (Wang 1999; Wiegel 1999; Zhang et al. 1997b).

Flotation results and reagent costs are presented in Table 6 for single stage flotation with AERO 6493 and Table 7 for double stage flotation (Crago process) with fatty acid/fuel oil (FA/FO) and amine chemistry.

Economic Analysis

This preliminary economic analysis was carried out considering separation efficiency and, in this regard, includes recovery, grade, reagent cosumption, and the reagent prices. The analysis is based on the economic evaluation model developed by Jacobs Engineering (El-Shall 2001) for phosphate mineral processing.

In this model, a scheme for penalizing lower grade rock has been developed and the economic performance measure is defined as:

$$M = C_pP - C_fF - FC_r$$

Where

M – The economic performance measure, representing dollars earned per year ($/year)

C_p - Sales value of product: C_p = Price of 66% BPL rock x $(B_L/66)^{1.5}$ (B_L = % BPL)

Price of 66% BPL rock (30% P_2O_5): $30/ton (Zhang et al. 1997a)

C_f - Sales value of feed: C_f = Price of 66% BPL rock x $(B_L/66)^{1.5}$

C_r - Total reagent cost: C_r ($/ton feed)

P - Product flowrate: $P = F(\alpha/100)(\varepsilon/100)(100/\beta)$ (ton/year)

F - Feed solid flowrate: F = 4,000,000 ton/year (assumed)

α - Feed P_2O_5 grade (see Tables 6, 7)

β - Concentrate P_2O_5 grade (see Tables 6, 7)

ε - Product recovery (see Tables 6, 7)

The preliminary results comparing the AERO 6493 collector with the traditional double float process using fatty acid/fuel oil (FA/FO) are presented in Table 8 using Jacobs Engineering's model for economic performance. The results indicate that when the price for AERO 6493 is less than $1.80/lb the economic performance for AERO 6493 should be competitive with the traditional double float process.

SUMMARY AND CONCLUSION

It has been found that excellent flotation selectivity is achieved when pure mineral samples are conditioned at high percent solids with water insoluble alcoholic solutions of alkyl hydroxamic acids as collectors. The results from contact angle and high-speed video studies indicate that the hydroxamic acid collector has different spreading characteristics at the surfaces of fluorapatite, dolomite, and quartz. It is evident that colcoposition is an important variable which influences the flotation response. Long branched chain alcohols increase the hydrophobicity and reduce reagent consumption. Understanding of the mechanism of collector attachment and spreading is still unclear and surface chemistry research should be continued to further understand the phenomena involved in the flotation of

Table 6 Pilot-plant flotation results and reagent schedule for single stage flotation with AERO 6493

Process	Feed Grade P_2O_5 % (α)	Concentrate Grade P_2O_5 % (β)	P_2O_5 Recovery % (ε)
Cargill South Fort Meade Fine Feed , Single Stage, pilot Scale Flotation at AERO 6493 Consumption of 1.87 lb/t feed	9.6	29.6	86
Cargill South Fort Meade Coarse Feed, Single Stage, pilot Scale Flotation at AERO 6493 Consumption of 2.65 lb/t feed	12.9	31.55	95

Table 7 Typical flotation results and reagent costs for coarse feed using traditional double float process (FA/FO and amine)

Process	Feed Grade P_2O_5 % (α)	Concentrate Grade P_2O_5 % (β)	P_2O_5 Recovery % (ε)
Typical Double Float Plant Scale Flotation with FA/FO	8.00	31.5	85
Reagents	Reagent (lb/t feed)	Price ($/lb)	Cost ($/t feed)
Na_2SiO_3	0.1-0.4	0.05	0.01~0.02
Na_2CO_3	0.8-1.4 (pH 9)	0.08	0.07~0.11
Fatty Acid	1.4 ~ 2.1	0.15-0.20	0.21 ~ 0.42
Fuel Oil	0.6 ~ 0.9	0.07	0.042 ~ 0.063
H_2SO_4	2 (pH 3.3)	0.03	0.06
Amine	1	0.25-0.30	0.25 - 0.30
Total			0.64~ 0.97

Table 8 Typical results from the economic performance analysis (4 million tons per year of capacity)

Process	Reagent Price $/lb	Reagent Cost $/t feed	Product Flowrate Ton/year	Economic Performance Million $/Year
Single Stage AERO 6493	1.6 ~ 1.8	1.93 ~ 2.17	1,445,324	7.55 ~ 8.51
Double Float FA/FO Amine	0.63 ~ 0.73	0.64 ~ 0.97	1,295,238	7.41 ~ 8.73

phosphate minerals with insoluble alcoholic solutions of hydroxamic acids.

Based on these bench scale flotation results with a water insoluble alcoholic solution of hydroxamic acid (AERO 6493), it seems that a single stage phosphate recovery of 90–95% with a concentrate grade of 31% P_2O_5 is possible for coarse feed from the IMC-Agrico Four Corners Plant. As is the case for the traditional phosphate flotation, high solids conditioning is necessary with the hydroxamic acid collector. Conventional plant practice using traditional fatty acid/fuel oil collector (1,200 g/t) results in only 75–80% recovery at a grade of 31% P_2O_5 after multiple flotation stages in different flotation circuits (double flotation). In the case of coarse feed from the Cargill Plant, the concentrate grade reached 34% P_2O_5 with 93% recovery in single stage bench scale flotation with the new collector. Also significant improvements in flotation were achieved with plant samples from North Carolina and Utah. The results indicate that the hydroxamic acid collector is more effective for the flotation of coarse feed than for the flotation of fine feed. Pilot-plant testing at a feed rate of 700–900 lb/hr was carried out in order to evaluate the new collector in a larger scale continuous flotation experiment. The results from the pilot plant with single stage flotation are summarized in Table 6. For the coarse feed, in the best case a concentrate grade of 31.5% P_2O_5 and 95.0% recovery was achieved. The average concentrate grade is about 31.4% P_2O_5 with 92.8% recovery and 6.96% insol. The results from the pilot-plant testing confirmed the results from bench scale flotation experiments.

The preliminary economic analysis of the new flotation chemistry with the alcoholic solution of the hydroxamic acid collector, AERO 6493, indicates that the economic performance is sensitive to the feed grade and reagent cost. Significant economic effectiveness could be achieved under certain circumstances. For example, at a plant capacity of 4 million tons per year, a marginal economic performance of 7.55~8.51 million dollars per year can be reached for a price of AERO 6493 at $1.6~1.8/lb, in contrast to a price of 0.63~$0.93/lb for the existing traditional double float process with FA/FO and amine. A price lower than $1.60/lb for AERO 6493 would give a much more significant improvement in economic performance. The value of using AERO 6493 would be much more significant if other aspects involved in the entire flotation process were counted, such as energy reduction, water quality, water consumption, equipment investment, the cost of equipment maintenance, etc. Analysis of water from bench scale flotation experiments and review of the literature indicate that there is no significant environmental impact from utilization of the new collector. In fact the AERO 6493 reagent is currently used in the kaolin industry and is not detected in discharged water from these operations.

ACKNOWLEDGMENTS

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