

Bench Scale Flotation of Sedimentary Phosphate Rock with Hydroxamic Acid Collectors

J.D. Miller*, X. Wang*, and M. Li*

ABSTRACT

It has been discovered that water insoluble alcoholic solutions of alkyl hydroxamic acids serve as selective collectors for the flotation of phosphate mineral resources (Miller et al., 2000). 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. In the best case, from experiments with low grade (5% P_2O_5) coarse feed (16×35 mesh), a single stage phosphate recovery of 95% was achieved with a concentrate grade of 31% P_2O_5 . Such a separation efficiency could not be achieved using the traditional fatty acid/fuel oil collectors as is evident from a comparison of the respective grade/recovery curves.

Keywords: *Flotation, Insoluble collectors, Hydroxamic acid, Alcohol, Phosphate rock, High solids conditioning, Particle size*

INTRODUCTION

Because of the non-selective nature of fatty acid/fuel oil (FA/FO) flotation, generally it is not possible to obtain satisfactory phosphate recoveries with acceptable concentrate grades in single stage flotation of sedimentary phosphate

rock. Thus, the commonly used phosphate flotation process in Florida is the "double float" process, viz. anionic flotation of phosphate minerals at alkaline pH, rougher flotation, followed by acid scrubbing and cationic "reverse" flotation of silica from the rougher phosphate concentrate using an amine collector. Of course with such a double float process the reagent demand is higher and plant capacity must be increased accordingly.

During the past decade much research has been carried out to develop a more efficient flotation technology for the processing of Florida phosphate resources (Lu, 1999; Zhang, 1999, 1994, 1993; El-Shall, 1999; Gu, 1999; Miller, 1999; Wiegel, 1999; Gruber, 1999).

Notwithstanding these contributions, significant improvement in the efficiency of phosphate flotation is still needed in order to reduce requirements for plant space, energy, water, and chemicals and in general, to improve productivity of the phosphate operations. Of particular concern is improved separation efficiency and the ability to treat new dolomitic resources. Phosphate flotation technology needs include (FIPR, 1998):

1. Simplification of the standard flowsheet

*Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah 84112.
Fax: 801-581-4937; E-mail: jdmiller@mines.utah.edu

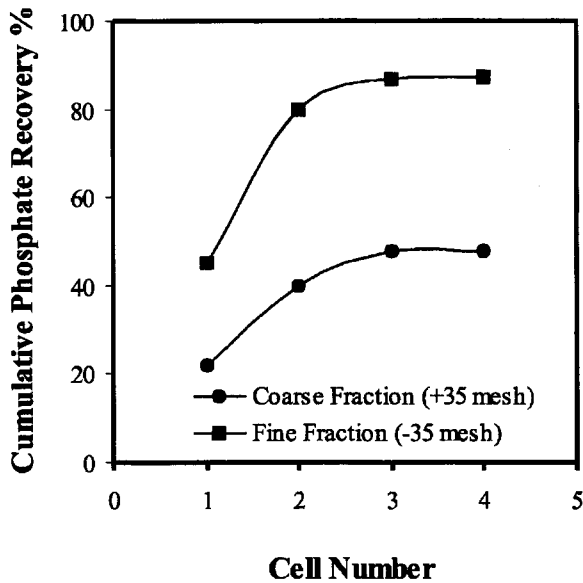


FIGURE 1 Phosphate Flotation Recovery from Plant Operations (Moudgil, 1992)

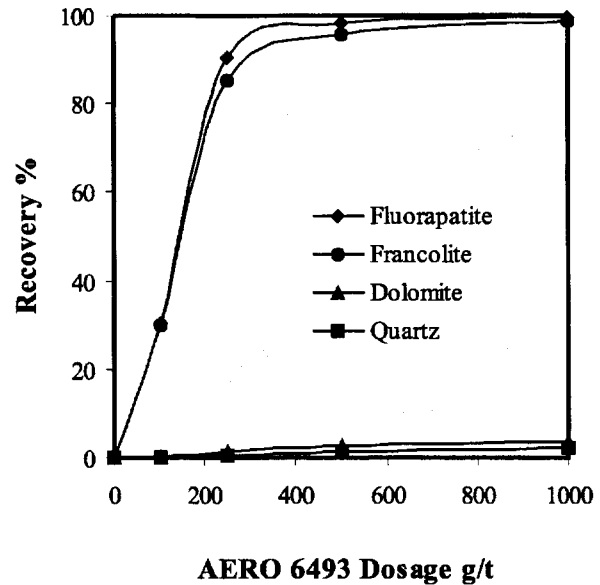


FIGURE 2 Microflotation Recovery of Fluorapatite, Francolite, Dolomite and Quartz as a Function of Collector (AERO 6493) Addition at a Natural pH (pH = 7.5), with Tap Water

2. Improved recovery of coarse phosphate
3. Selective flotation for phosphate recovery from dolomitic resources

For example, the flotation recovery of coarse phosphate has been limited as evidenced by the data presented in Figure 1 (Moudgil, 1992). Recent research results at the University of Utah demonstrate that a selective collector has been discovered which can increase the separation efficiency and simplify the standard flowsheet. This is particularly true for the flotation of coarse feed. The new reagent chemistry is based on the use of water insoluble alcoholic solutions of alkyl hydroxamic acid as collectors following a conditioning procedure similar to that currently used in the industry (Miller et al., 2000). In addition to the selectivity exhibited in microflotation experiments shown by the data presented in Figure 2 (Miller et al., 2001), the effectiveness of the new collector chemistry has been demonstrated by bench scale flotation experiments with plant samples from Florida, North Carolina, and Utah.

Since pioneering research in the 1960s (Fuerstenau et al., 1967, 1970), hydroxamic acids and their salts have been considered for the flotation of minerals containing transition metal elements (Fe, Cu, etc.) as well as for rare earth minerals. In this regard selective flotation chemistry with hydroxamate collectors has been understood to involve chemisorption at cation surface sites with the formation of a chelation compound between the hydroxamate and the surface cation.

Now it has been discovered that selective flotation of phosphate and other minerals can be achieved with alcoholic solutions of hydroxamic acids. This unexpected discovery appears not to involve any specific chelation phenomena at the surface of the phosphate minerals but rather, the selective wetting of the mineral surface by these insoluble hydroxamic acid collectors. Such reagents are available commercially from Cytec and are marketed as AERO 6493 and AERO 6494. These reagents, which are currently being used in the kaolin industry, seem to provide the desired characteristics for improved phosphate flotation technology.

TABLE 1 Other Chemicals Used

Reagent	Formula	Supplier	Purity/Grade
Fatty Acid	$\text{CH}_{15-17}\text{H}_{27-35}\text{COOH}$	Westvaco	Industrial Mixture
Fuel Oil	#5 Fuel Oil	Int. Petroleum	Industrial Mixture
Sodium Carbonate	Na_2CO_3	Mallinckrodt	Analytical Grade
Sodium Hydroxide	NaOH	Aldrich	ACS Reagent
Sodium Silicate	Na_2SiO_3	Fluka	Solution

MATERIAL AND EXPERIMENTS

Flotation Samples

Samples of coarse flotation feed and/or fine flotation feed were taken from IMC-Agrico's Four Corners Plant in Florida, Cargill's Central Florida Plant, PCS's North Carolina Plant, and SF Phosphates Utah Plant. In the case of the IMC-Agrico sample from the Four Corners Plant, approximately 10 gallons of plant water and samples of fatty acid and fuel oil were also collected and shipped to laboratories at the University of Utah. The results from X-ray diffraction indicated that the phosphate minerals in the sample from IMC-Agrico Four Corners Plant were carbonate-fluorapatite, and carbonate-hydroxylapatite. The particle size was determined to be in the range of 12×80 mesh for the coarse feed sample and 20×150 mesh for the fine feed sample.

For the sample from Cargill's Central Florida Plant, the phosphate minerals were found to be similar to the sample from the IMC-Agrico Four Corners Plant containing carbonate-fluorapatite and carbonate-hydroxylapatite. The particle size was determined to be in the range of 12×80 mesh for the coarse feed, 12×150 mesh for intermediate feed and 20×200 mesh for the fine feed.

The X-ray diffraction results show that the phosphate mineral in the sample from the PCS North Carolina Plant was carbonate-hydroxylapatite. The particle size was in the range of 12×150 mesh. The +20 mesh fraction was removed by wet screening and the 20×150 mesh fraction was used as flotation feed.

The sample from the SF Phosphates Utah Plant was taken from rougher flotation feed. The

results from X-ray diffraction analysis indicated that the sample contained dolomite, fluorapatite, calcite and quartz. The phosphate minerals in this feed had been reported to be carbonate-apatite minerals with the chemical formula $\text{Ca}_5(\text{PO}_4\text{CO}_3\text{OH}_3(\text{FOH}))$ (Allen, 1994). The particle size of the sample was determined to be in the range of 20×200 mesh.

Reagents

The collector used was Cytec's AERO 6493, a 30% alcoholic solution of hydroxamic acid, unless otherwise indicated. Other reagents are listed in Table 1.

Bench Scale Flotation

The flotation tests were conducted in 1 liter Denver flotation cells for both the fatty acid/fuel oil collector and the new collector. Unless otherwise indicated, the feed material was conditioned at 70–75% solids for 2 minutes. Then the slurry was transferred into the flotation cell and diluted to about 20% solids with tap water or plant water. The flotation products were filtered, dried, and weighed before digestion and analysis by ICP.

RESULTS AND DISCUSSION

Efficiency of Separation

Single stage flotation efficiency was evaluated for the coarse feed sample (16×35 mesh) from the IMC Four Corners Plant in Central Florida, using the new hydroxamic acid collector. Significant improvement in separation efficiency is clearly evident from the grade/recovery curves comparing the new collector with the

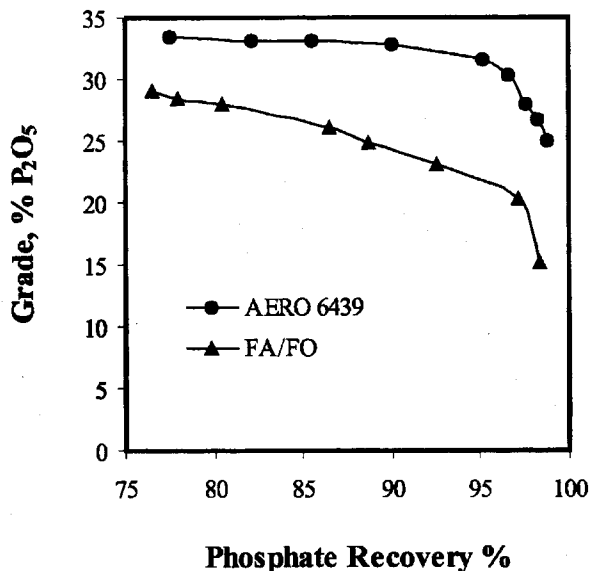


FIGURE 3 Comparison of Grade/Recovery Curves Obtained with Cytec's AERO 6493 Collector and the Traditional FA/FO Collector for Single Stage Flotation of Coarse Feed (16 x 35 Mesh, 5.65% P₂O₅) from the IMC-Agrico Four Corners Plant, Central Florida

traditional fatty acid/fuel oil (FA/FO) collector as presented in Figure 3. The results indicate that a high separation efficiency is obtained with the new collector. Notice the significant difference in concentrate grade. An excellent concentrate product (31% P₂O₅) was achieved at 95% recovery with the new collector in single stage flotation.

Collector Addition

Shown in Figure 4 is the flotation response as a function of collector addition for flotation feeds from Central Florida, North Carolina, and Utah. Typically the recovery increases with an increase in collector addition. Generally the results indicate that flotation recovery and/or concentrate grade have been improved significantly when the new collector AERO 6493 is compared with the traditional FA/FO collector. It seems from these bench scale results that a dosage of 800 to 1200 g/t will be required to achieve satisfactory flotation results. Although recent results from water recycle testing suggest that the collector demand can be reduced.

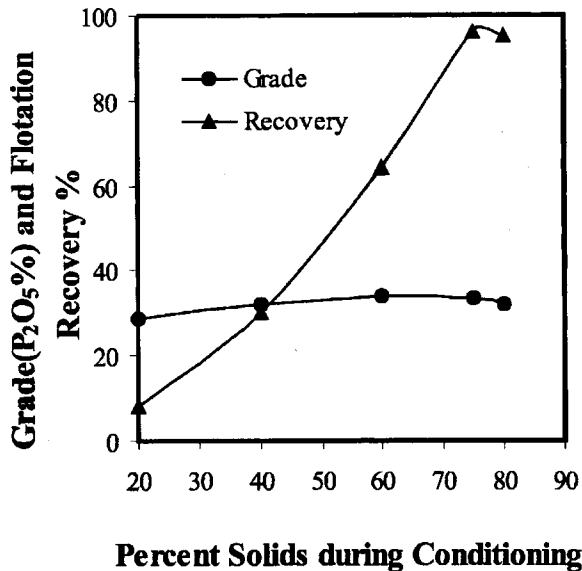


FIGURE 5 Single Stage Flotation Response as a Function of Percent Solids during Conditioning with 1000 g/t AERO 6493 for Coarse Feed from the Cargill Plant

High Solids Conditioning

The critical feature of high solids conditioning is revealed by the data for coarse feed from the Cargill plant presented in Figure 5. Note that the recovery decreases significantly when the percent solids drops below 70% whereas the concentrate grade decreases slightly from 34% to 32%. As discussed in other contributions (Lu, 1999; Miller, 2001) high solids conditioning seems to be necessary for oily, water insoluble collectors in order to achieve adequate distribution and selective spreading at the surface of phosphate minerals.

Particle Size

Typically, the efficient recovery of phosphate from coarse flotation presents a major problem in industrial practice. In this regard the effectiveness of the hydroxamic acid collectors for coarse phosphate flotation is quite impressive as demonstrated by the data presented in Figures 3 and 4. In similar fashion the flotation of fine feed is improved with hydroxamic acid collectors

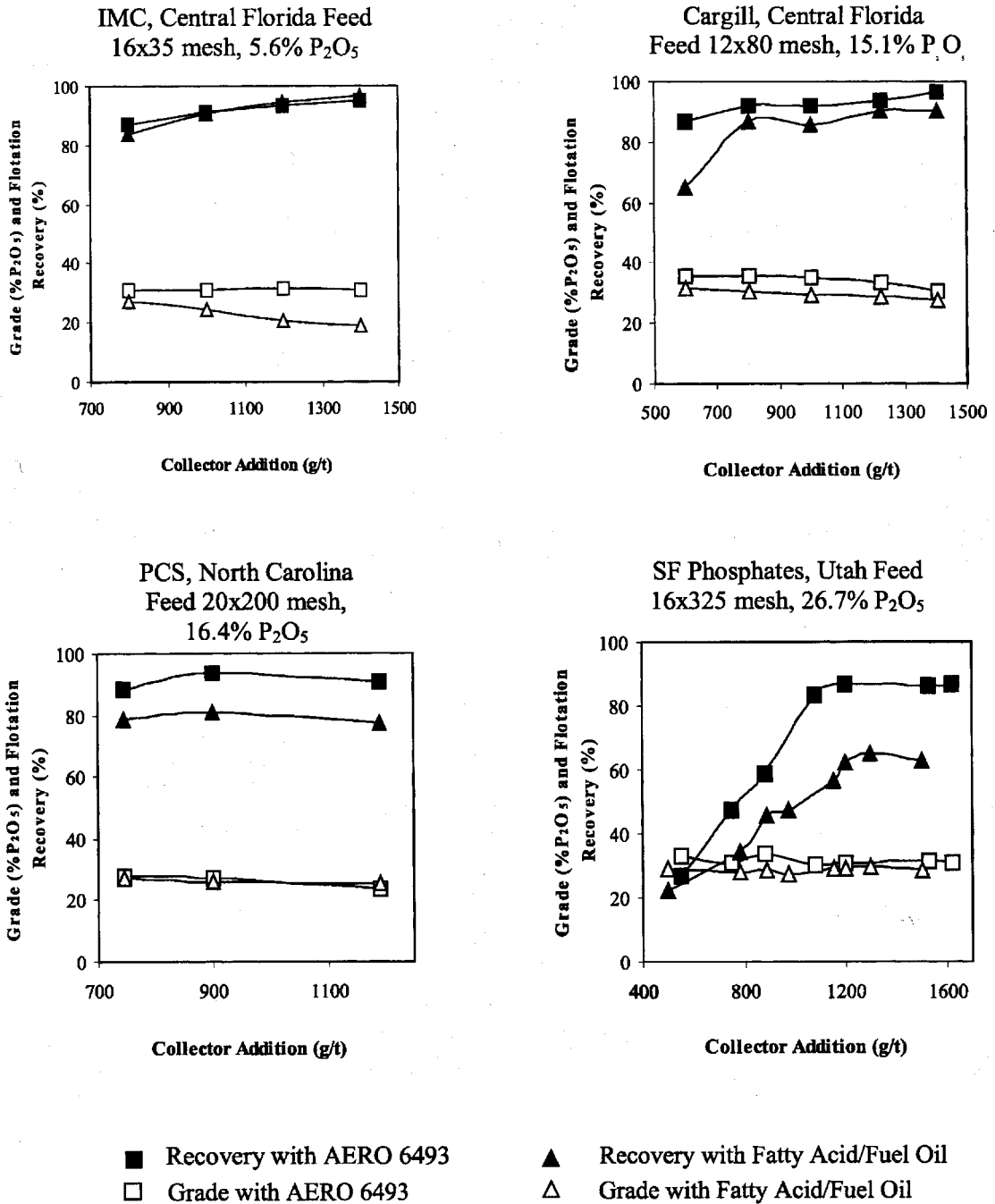


FIGURE 4 Single Stage Flotation Recovery and Concentrate Grade as a Function of Collector Dosage at Natural pH 7.5 for Phosphate Feed Received from Different Plant Operations

TABLE 2 Evaluation of the New Collector (AERO 6493) vs. Fatty Acid/Fuel Oil for Fine Feed from Four Corners, Central Florida (single stage flotation, collector 800 g/t, tap water)

Collector	Product	Wt. %	P ₂ O ₅ %	P ₂ O ₅ Recovery %
FA/FO	Concentrate	19.42	17.68	91.03
	Tailing	80.58	0.42	8.97
	Feed	100.00	3.77	100.00
AERO 6493	Concentrate	10.68	30.14	85.11
	Tailing	89.32	0.63	14.89
	Feed	100.00	3.78	100.00

when compared to the traditional FA/FO collector as shown by the results presented in Table 2 for low grade fine feed from the IMC-Agrico Four Corners Plant. In this case a 30% P₂O₅ grade was achieved in a single stage at 85% recovery with the new collector. The traditional fatty acid/fuel oil collector does not provide for such a high selectivity. However compared with the results from the flotation of coarse feed, the recovery from the flotation of fine feed is lower with the new collector.

Samples of phosphate feed from Cargill were tested in order to evaluate the effect of particle size on flotation efficiency. The results in Figure 6 indicate that an excellent separation was achieved for both the coarse and intermediate size flotation feed and that the separation efficiency decreases with a decrease in particle size. As might be expected the single stage grade and recovery from fine feed with an insoluble collector is less than from coarse feed. This effect is evident from the results obtained for both the IMC and Cargill samples. The reason for this sensitivity to particles size is that fine particles consume collector and are more easily entrapped in the aeroflocs that form during flotation with insoluble collector oils. (Miller et al., 2001).

Effect of Plant Water

The issue of plant water was considered and these results are presented in Table 3 for coarse feed from the IMC-Agrico Four Corners Plant. The influence of plant water on the effectiveness of the new collector does not seem to be significant.

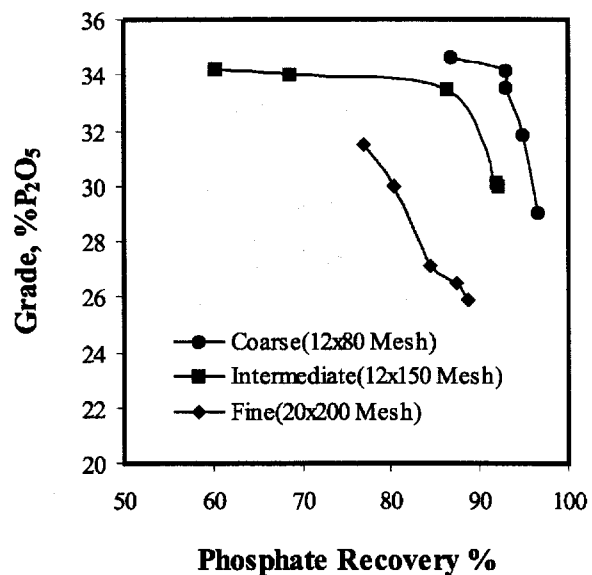


FIGURE 6 Single Stage Flotation Grade/Recovery Curves for Different Sizes of Phosphate Feed from the Cargill Plant

North Carolina Phosphate

The sample from the PCS North Carolina Plant was evaluated with the hydroxamic acid collector and the results are presented in Table 4. Excellent recovery was achieved with the new collector. Compared with the results from the single stage flotation of other samples from Florida and Utah, the concentrate grade is slightly lower in quality. See Figure 4. The significant improvement in recovery is revealed from the results comparing the new collector with the traditional fatty acid/fuel oil collector as presented in Figure 4.

TABLE 3 Test Results for Deslimed Coarse Feed from the IMC-Agrico Four Corners Plant with New Collector (AERO 6493) Using Tap Water and Plant Water (single stage flotation, Na₂CO₃ 400g/t, Na₂SiO₃ 400g/t, pH 8.6)

Collector	Product	Wt. %	P ₂ O ₅ %	P ₂ O ₅ Recovery %
Tap Water	Concentrate	17.32	31.12	95.18
	Tailing	82.68	0.33	4.82
	Feed	100.00	5.66	100.00
Plant Water	Concentrate	17.39	31.02	94.36
	Tailing	82.61	0.39	5.64
	Feed	100.00	5.71	100.00

TABLE 4 Results from Single Stage Phosphate Flotation of Feed from the PCS North Carolina Plant Using the New Hydroxamic Acid Collector (AERO 6493)

Product	Wt. %	P ₂ O ₅ %	Recovery %
Concentrate	57.32	27.52	96.35
Tailing	42.68	1.40	3.65
Feed	100.00	16.37	100.00

TABLE 5 Results from Single Stage Phosphate Flotation of Feed from the SF Phosphates Utah Plant Using the New Hydroxamic Acid Collector (AERO 6493)

Product	Wt. %	P ₂ O ₅ %	MgO%	Recovery%
Concentrate	70.88	32.26	0.28	85.74
Tailing	29.12	13.08	0.94	14.26
Feed	100.00	26.67	0.47	100.00

Utah Phosphate

The sample from the SF Phosphates Plant near Vernal Utah was tested to determine the effectiveness of the new hydroxamic acid collector. The single stage flotation results presented in Table 5 indicate that a high quality phosphate concentrate (32% P₂O₅), containing less than 0.3% MgO, can be made at more than 85% recovery from the rougher flotation feed. The improved flotation recovery is clearly demonstrated by the results comparing the new collector with the traditional fatty acid/fuel oil collector shown in Figure 4.

SUMMARY

In general, 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% P₂O₅ 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% P₂O₅.

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. A pilot plant testing program will be conducted to demonstrate the effectiveness of the hydroxamic acid collector chemistry to industry.

ACKNOWLEDGEMENT

Gratitude is expressed to IMC-Agrico, Cargill, PCS Phosphate and SF Phosphates for providing the plant samples used in this study. Financial support from the University of Utah and the Florida Institute of Phosphate Research is gratefully acknowledged.

REFERENCES

- Allen, M.P. 1994. The Vernal Phosphate Rock Mill: Beneficiation of Phosphates: Theory and Practice, Eds. Hassan El-Shall, B.M. Moudgil, R. Wiegel, SME, Littleton, Colorado, pp. 85-91.
- El-Shall, H., Cheng, Y.H., Abdel-Khalek, N.A., and Gupta, S. 1999. A Parametric Study of Column Flotation of Florida Phosphates: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 75-86.
- Florida Institute of Phosphate Research, 1998. 1998-2003 Strategic Research, Programmatic & Management Priorities, Bartow, Florida.
- Fuerstenau, M.C., Miller, J.D. and Gutierrez, G. 1967. Selective Flotation of Iron Oxide: Transactions SME/AIME, 238, pp. 200-203.
- Fuerstenau, M.C., Harper, R.W. and Miller, J.D. 1970. Hydroxamate vs. Fatty acid Flotation of Iron Oxide: Transactions SME/AIME, 241, pp. 69-73.
- Gruber, G.A. 1999. Anionic Conditioning for Phosphate Flotation: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 303-313.
- Gu, Z., Gao, Z. and Zheng S. 1999. Beneficiation of Florida Dolomitic Phosphate Pebble with a Fine-Particle Flotation Process: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 155-162.
- Lu, Y., Liu, N., Wang, X. and Miller, J.D. 1999. Improved Phosphate Flotation with Nonionic Polymers: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 3-19.
- Miller J.D., Wang, X., Lu, Y., Liu, N. and Yin, D. 1999. Plant-Site Evaluation of Air-Sparged Hydrocyclone Technology for Phosphate Flotation Separation: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 195-209.
- Miller J. D., Wang, X. and Li, M. 2000. Selective Flotation of Phosphate Minerals with Hydroxamate Collectors: US patent pending.
- Miller J. D., Wang, X. and Li, M. 2001. Selective Flotation of Phosphate Minerals with Alcoholic Solutions of Alkyl Hydroxamic Acids: to be published in the Proceedings of the Engineering Foundation Conference, Beneficiation of Phosphates III, St. Pete Beach, Florida, December 2-7, 2001.

- Moudgil, B.M. 1992. Enhanced Recovery of Coarse Particles During Phosphates Flotation: Publication No. 02-067-099, Florida Institute of Phosphate Research, Bartow, Florida.
- Moudgil, B.M. and Somasundaran, P. 1986: Advances in Phosphate Beneficiation: Advances in Mineral Processing, Proceedings of a Symposium Honoring Nathaniel Arbiter March 3-5, 1986, Ed. P. Somasundaran. SME, Littleton, Colorado, pp. 426-441.
- Zhang, P. 1993. Phosphate Beneficiation-Trends of 90's: In Beneficiation of Phosphate: Theory and Practice, Eds. Hassan El-Shall, B.M. Moudgil and R. Wiegel. SME, pp. 399-415.
- Wiegel, R. 1999. Phosphate Rock Beneficiation Practice in Florida: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, Littleton, Colorado, pp. 271-275.
- Zhang, P. 1994. Phosphate Beneficiation - Challenges and Opportunities: Separation Processing: Heavy Metals, Ions and Minerals, Ed. M. Misra, The Minerals, Metals & Materials Society.
- Zhang, P., Yu, Y., Hanson, H. and Snow, R. 1999. Fundamental and Practice Implications of the Role of Polymers in Separating Silica from Phosphate: Beneficiation of Phosphates-Advances in Research and Practice, Eds. Patrick Zhang, Hassan El-Shall, Ronald Wiegel, SME, pp. 41-52.