

Spring 3-31-2015

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Recommended Citation

Guoxin Wang and Zhengxing (James) Gu, "Processing Florida Dolomitic Phosphate Pebble with Custofloat[®] Carbonate Collectors" in "Beneficiation of Phosphates VII", P. Zhang, FIPR; J. Miller, Univ. of Utah; L. Leal, Univ. of Sao Paolo; A. Kossir, OCP Group; E. Wingate, Worley-Parsons Services Pty Ltd. Eds, ECI Symposium Series, (2015). http://dc.engconfintl.org/phosphates_vii/11

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Processing Florida Dolomitic Phosphate Pebble with Custofloat® Carbonate Collectors

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ABSTRACT

It was estimated that phosphate reserves associated with high carbonate minerals are greater than those with siliceous gangues worldwide. It has been long recognized that separation of carbonate from phosphate is difficult because those minerals contain same or similar alkaline earth cations which lead them to exhibit similar surface behavior in flotation. With the depletion of easy-to-process phosphate reserves, phosphate deposits with high carbonate impurities must be mined and processed to meet the demand. Crushing, grinding and flotation are considered the most efficient process to recover phosphate from phosphate ores associated with carbonate gangue minerals. Therefore, flotation reagents, especially collectors, are very critical for effective separation of phosphate from carbonate minerals. In recent years, ArrMaz has made great efforts in the development of carbonate flotation collectors with significant success. A series of carbonate flotation collectors have been developed for phosphate ores from various origins. The topic will focus on processing Florida dolomitic phosphate pebble with Custofloat® carbonate collectors.

INTRODUCTION

Phosphate rock is a vital, nonrenewable and non-substitutable mineral resource. The demand must be met through mining, beneficiation and chemical processing of naturally derived materials. Fertilizer industry consumes about 90% of the phosphate concentrate produced. The remaining 10% is used for other applications, such as detergents, water softeners, insecticides, dental products, animal food, etc. To increase agricultural output to meet the need of a continuously growing world population requires long term growth of phosphate production. Florida is one of the largest phosphate producers in the world. However, the output in Florida area is decreasing in recent years due to the depletion of low dolomite, easy-to-process high grade siliceous phosphate reserves. With the phosphate mining moving from central Florida to further south, the phosphate matrix will be leaner in P_2O_5 and higher in dolomite (Zhang, 1993). Dolomite is a worldwide problem in phosphate beneficiation and processing. The MgO in dolomite portion of phosphate rock will create a series of issue in downstream production, such as increasing phosphoric acid viscosity, difficult acid filtration, deposition in transport pipelines, etc (Luo, et al., 2012).

Separation of carbonate from phosphate has long been recognized as a difficult issue because of the similarities of physical and chemical properties, such as (1) oxide minerals with same or similar cationic ions, (2) finely disseminated with phosphate, (3) close specific gravity, (4) similar behavior in conventional fatty acid flotation, etc. Since 1970's, a lot of work has been done for recovering phosphate from Florida dolomitic phosphate pebble. Different reagents including collectors and depressants were developed. Several flotation processes have been innovated or proposed, such as direct flotation, reverse flotation, or cationic process, anionic process, and so on (Gu, et al., 2010).

In general, there is no “universal” reagent or process to separate carbonate from phosphate ores from different sources. Reagents must be developed accordingly for different process to treat different ores. In recent years, ArrMaz has made great effort in developing carbonate flotation reagents based on the characteristics of carbonated phosphate resources from different locations to make the separation of carbonate from phosphate technically and economically more efficient (Gu, et al., 2012). ArrMaz research and development lab has tested the phosphate ores with carbonate impurities from different countries, such as China, Saudi Arabia, Morocco, Tunisia, Israel, Mongolia, Kazakhstan, etc. A series of carbonate flotation collectors have been developed for different phosphate ores from various origins. Some of those reagents have been applied in commercial plant operations. Some of them have been demonstrated through pilot testing.

ArrMaz has also developed several carbonate flotation collectors for recovering phosphate from Florida dolomitic pebble. The detailed results are presented and discussed as following.

RESULTS AND DISCUSSIONS

Pebble Sample and Flotation Feed Preparation

The dolomitic phosphate pebble sample was provided by Mosaic. It contains 24.37% P_2O_5 , 3.3% MgO, 9.67% insol. and other elements. The sample was in size range of about -12+1 mm. In lab, it was crushed to -1.2 mm in a jaw crusher. The mix of 300 gram sample and 200 ml water was ground in a rod mill as flotation feed. Figure 1 shows size distribution of the ground material at various grinding time.

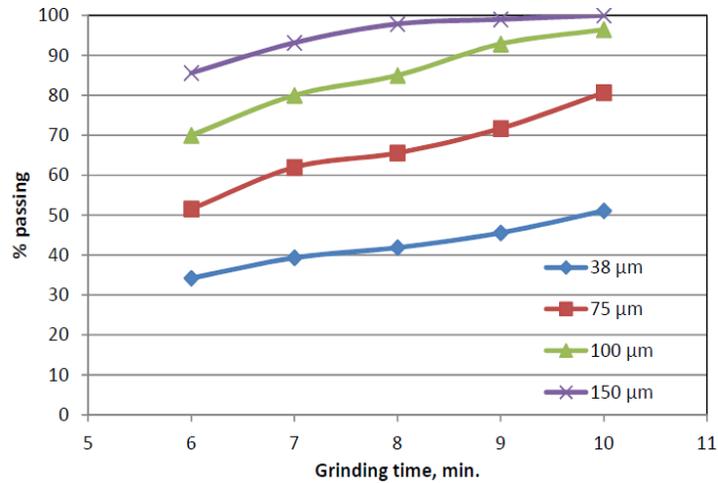


Figure 1. Size distribution at different grinding time

All flotation tests were conducted in one liter Denver D-12 cell at an impeller speed of 1000 rpm. The ground feed was conditioned and floated under same conditions to determine the appropriate grinding time. The flowsheet and reagent conditions are shown in Figure 2. In those tests, phosphoric acid was used as a pH modifier to maintain acidic condition, and Custofloat MP12 was used as a carbonate collector. After grinding, the feed slurry was subjected to one rougher and one cleaner flotation. The underflow of cleaner flotation was collected as phosphate concentrate, and two floats from rougher and cleaner were combined as carbonate tailings. The flotation results of the feed at various grinding time are listed in Table 1.

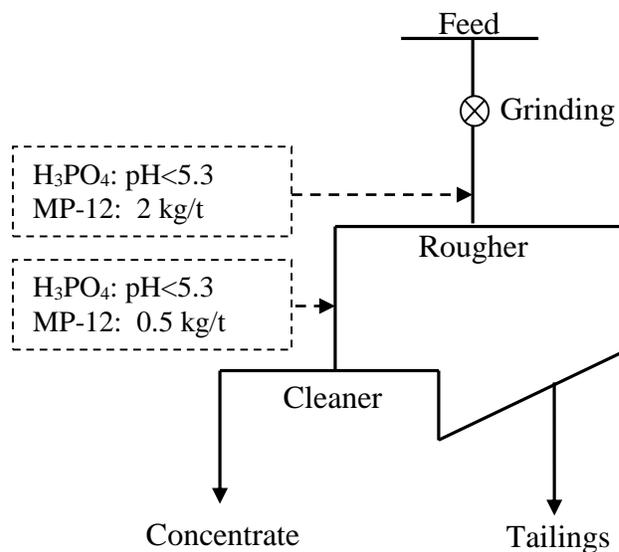


Figure 2. Open circuit for carbonates flotation

Table 1. Flotation concentrate from the feed at various grinding time

Grinding time min.	Concentrate Wt. %	Grade, %		Recovery, %	
		P ₂ O ₅	MgO	P ₂ O ₅	MgO
6	63.07	28.39	0.98	71.49	18.72
7	61.76	28.13	0.75	70.17	15.21
8	61.86	28.56	0.71	70.61	13.21
9	56.42	28.22	0.64	64.40	11.2
10	53.34	28.05	0.60	60.80	10.02

Table 1 shows that short grinding gave higher MgO in concentrate because of not enough liberation, and over grinding lead to lower P₂O₅ recovery. It can be observed that 8' grinding achieved best separation performance. The concentrate with 28.56% P₂O₅ and 0.71% MgO can be obtained at 70.61% recovery. The size distribution and chemical analysis of the feed at 8' grinding is presented in Table 2.

Table 2. Size distribution and chemical analysis of the flotation feed at 8' grinding

Size mesh	Wt. %	Grade, %			Recovery, %		
		P ₂ O ₅	Insol.	MgO	P ₂ O ₅	Insol.	MgO
+100	2.15	26.17	17.54	0.91	2.32	3.87	0.62
+200	32.28	26.14	13.35	1.56	34.73	44.25	15.93
+400	25.71	25.24	11.57	2.32	26.70	30.55	18.87
-400	39.86	22.10	5.21	5.12	36.25	21.33	64.58
Total	100.00	24.30	9.74	3.16	100.0	100.0	100.0

After 8' grinding, about 98% of material passes 100 mesh. The chemical analysis data show that P₂O₅ is quite evenly distributed in all size fractions, but finer fraction contains much higher MgO and coarser size has higher silica impurity.

pH Modifiers and Depressants

H₃PO₄ is a pH modifier. It is also a very effective phosphate depressant for separating carbonate from phosphate. In the study, other options were also tested, such as mixture of H₃PO₄ and H₂SO₄ at 1:1 ratio, and combination of H₂SO₄ as a pH modifier and DPR-1 as phosphate depressant. The tests were conducted with the flowsheet and conditions showing in Figure 2, and H₃PO₄, mixture of H₃PO₄ and H₂SO₄ at 1:1 ratio, and combination of H₂SO₄ and DPR-1 were used as pH modifier and depressant respectively. The flotation results are presented in Table 3.

Table 3. The flotation results with different pH modifiers and/or depressants

pH modifiers and/or depressants	Concentrate Wt. %	Grade, %		Recovery, %	
		P ₂ O ₅	MgO	P ₂ O ₅	MgO
H ₃ PO ₄	61.86	28.56	0.71	70.61	13.21
DPR-1+H ₂ SO ₄	62.95	28.82	0.58	72.93	11.08
H ₃ PO ₄ and H ₂ SO ₄	49.78	28.49	0.63	57.07	9.24

When DPR-1 was used as phosphate depressant and H₂SO₄ as pH modifier, the concentrate contains lowest MgO at best P₂O₅ recovery. It indicates that the application of an effective depressant can improve carbonate flotation selectivity.

Comparison of Carbonate Collector MP-12 and MP-13

Two carbonate collectors, MP-12 and MP-13, were developed for Florida high magnesium phosphate pebble. With 1 kg/t DPR-1 as depressant and H₂SO₄ as pH modifier, the flotation results with carbonate collector dosages at 1.5, 2.0 and 2.5 kg/t for rougher and 0.5 kg/t for cleaner are given in Table 4. The test results show that both collectors are very effective in dolomite flotation, but MP-13 is much stronger than MP-12, and further optimization is needed to find appropriate flotation conditions.

Table 4. Flotation results of collector MP-12 and MP-13

Collector	For rougher kg/t	For cleaner kg/t	Concentrate wt. %	Grade, %		Recovery, %	
				P ₂ O ₅	MgO	P ₂ O ₅	MgO
MP-12	1.5	0.5	65.68	28.53	0.68	75.56	13.50
	2.0	0.5	62.95	28.82	0.58	72.93	11.08
	2.5	0.5	57.59	28.86	0.57	66.62	10.24
MP-13	1.5	0.5	55.58	29.02	0.60	64.66	9.44
	2.0	0.5	51.55	28.42	0.56	59.24	9.04
	2.5	0.5	41.19	28.42	0.49	47.20	6.10

Improving Overall P₂O₅ Recovery by Refloating Rougher and Cleaner Tailings

It can be observed that a phosphate concentrate with less than 0.7% MgO can be easily obtained in an open flotation circuit, but overall P₂O₅ recovery is relatively low, only about 70%. In order to increase overall P₂O₅ recovery, two floats from both rougher and cleaner stages were combined and refloated to produce final carbonate tailing. The sink of re-flotation was combined with the sinks of previous flotation steps as a composite concentrate. Figure 3 presents the flowsheet and reagent conditions, and flotation results are given in Table 5.

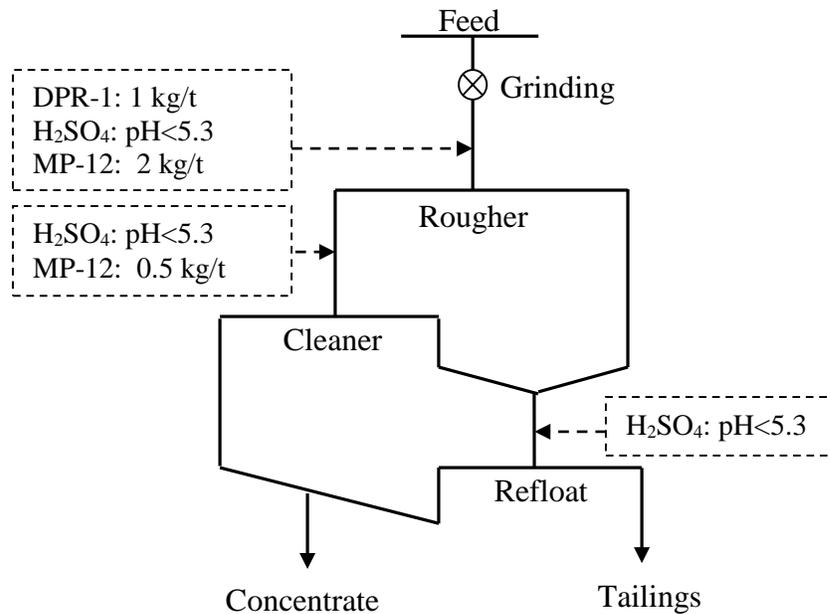


Figure 3. Flowsheet with carbonate re-flotation

Table 5. Flotation results with carbonate re-flotation stage

Reagent	Dosage kg/t	Product	Wt. %	Grade, %			Recovery, %		
				P ₂ O ₅	MgO	Insol.	P ₂ O ₅	MgO	Insol.
DPR-1	1.0	Concentrate	62.95	28.82	0.58	11.69	72.88	11.08	78.85
H ₂ SO ₄	4.5	Middling	14.39	27.95	1.33	8.69	16.20	5.81	13.40
MP-12	2.0+0.5	Carbonate tail	22.66	11.96	12.08	3.19	10.92	83.11	7.75
Feed			100.0	24.87	3.29	9.33	100.0	100.0	100.0
Concentrate + Middling			77.34	28.66	0.72	11.13	89.08	16.89	92.25

By adding a carbonate re-flotation stage, the overall P₂O₅ recovery was increased from 72.93% to 89.10%. The composite concentrate contains 28.66% P₂O₅, 0.72% MgO and 11.13% insol. This phosphate product can be blended with the concentrate from conventional “Crago Process” in the existing plant, and sent to chemical plant for phosphoric acid production. P₂O₅ can also be further upgraded by removing silica impurities. In actual plant operation, the sink of carbonate re-flotation can also be recycled to previous rougher carbonate flotation stage.

Improving P₂O₅ Grade through Removal of Silica Impurities

As seen in the flotation results in Table 5, P₂O₅ grade in the composite concentrate is only 28.66% because it contains 11% insoluble impurities. In order to further increase P₂O₅ grade in the final phosphate concentrate, silica flotation with cationic collector must be employed to remove silica. In general, amine collector is quite sensitive to clays, slimes and various fine particles in the flotation system. For effective silica flotation with an amine collector, the composite concentrate from carbonate flotation circuit was sized at 400 mesh, and plus 400 mesh size fraction was subjected to silica flotation with an amine collector. The float of amine float was discarded as silica tailings. The sink of amine flotation was combined with minus 400 mesh fines to become a final phosphate concentrate. The complete flowsheet with both carbonate and silica flotation is plotted in Figure 4, and the flotation results are given in Table 6.

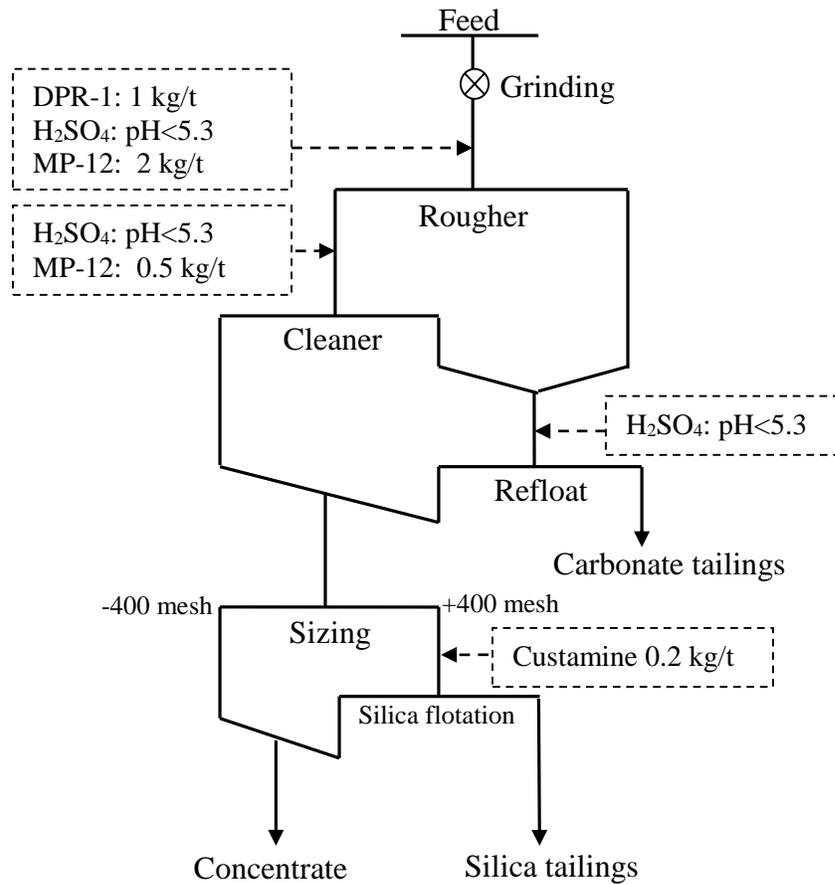


Figure 4. Flowsheet with both carbonate and silica flotation

Table 6. Flotation results with both carbonate and silica flotation

Reagent	Dosage kg/t	Product	Wt. %	Grade, %			Recovery, %		
				P ₂ O ₅	MgO	Insol.	P ₂ O ₅	MgO	Insol.
DPR-1	1	Concentrate	40.51	32.54	0.62	0.79	53.20	7.87	3.39
H ₂ SO ₄	4.5	Fines (-400M)	28.25	29.44	0.99	6.71	33.57	8.76	20.08
MP-12	2+0.5	Silica tail	8.35	6.79	0.17	77.59	2.29	0.45	68.63
Amine	0.2	Carbonate tail	22.89	11.84	11.56	3.26	10.94	82.92	7.90
Feed			100.0	24.77	3.19	9.44	100.0	100.0	100.0
Concentrate + Fines			68.76	31.34	0.77	3.23	86.77	16.44	23.47

The result in Table 6 shows that the sink of silica flotation and minus 400 mesh fines can be combined as final phosphate product. The combined product contains 31.34% P₂O₅ and 0.77% MgO with 86.77% overall recovery.

CONCLUSIONS

ArrMaz carbonate collectors can be successfully used to process Florida dolomitic phosphate pebble. For the feed containing 24.37% P₂O₅, 3.3% MgO and 9.67% insol., a phosphate concentrate with 28.82% P₂O₅ and 0.72% MgO can be obtained at 89% P₂O₅ recovery with carbonate flotation circuit. This product can be further upgraded by sizing and amine flotation. The final composite concentrate contains 31.34% P₂O₅, 0.77% MgO and 3.23% insol. and P₂O₅ recovery is 86%.

REFERENCES

- Gu, Z., Wang, G., and Suldicak, J., 2012, "Improving Dolomite/Francolite Separation Performance Using New Reagents." *Beneficiation of Phosphates, Technology Advance and Adoption*, pp. 329-333.
- Gu, Z., and Peng, F., 2010, "Dolomite Flotation of High MgO Phosphate Pebble Using Different Particle Size Feed." *Beneficiation of Phosphates, Technology Advance and Adoption*, pp. 327-333.
- Luo, L., and Liu, X., 2012, "Relations Between MgO Occurrence in Phosphorite and Its Removal by Flotation Process." *Beneficiation of Phosphates, New Thought, New Technology, New Development*, pp. 53-68.
- Zhang, J., 1993, "Phosphate Beneficiation – Trends of the 90's." *Beneficiation of Phosphate: Theory and Practice*, pp. 399-425.